HIGH-TEMPERATURE ELASTICITY AND ANHARMONICITY IN LAYERED THERMOELECTRIC MATERIALS

By

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ABSTRACT

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The ability to predict materials with desired thermal conductivity from a large material database can significantly improve the efficiency of experimental work. Lattice thermal conductivity is controlled by the velocity and relaxation time of phonons (lattice vibrations). Phonon scattering is closely related to the anharmonic lattice vibrations of a material, while phonon velocity depends on density and, bond stiffness. In this research, the relationship between structure, bonding, and thermal properties is discussed in two classes of layered materials, AM_2X_2 intermetallic compounds and GeTe - Sb₂Te₃ alloys.

First, we study the origin of the anomalously low lattice thermal conductivity of MgMg₂Sb₂ compare to other isostructural AMg_2Pn_2 compounds (A = Mg, Ca, Yb, and Pn = Sb and Bi). By employing high-temperature X-ray diffraction (XRD) and resonant ultrasound spectroscopy (RUS) techniques, we have shown that the low lattice thermal conductivity is due to previouslyunrecognized soft shear modes and highly anharmonic acoustic phonons in layered MgMg₂Sb₂. Combined with the phonon calculations from our collaborators, we attribute the anomalous thermal behavior of MgMg₂Sb₂ to the instability of the vibrational modes that originated from the weak bonding of the Mg, which is too small for the octahedral site. Second, we investigate the phase stability of the AMg₂Pn₂ system with mixed occupancy of Mg, Ca, Sr, or Ba on the cation (A) site. We show that the small ionic radius of Mg²⁺ leads to limited solubility when alloyed with larger cations such as Sr or Ba. Third, by performing in-situ high-pressure synchrotron X-ray diffraction, we showed that a few AM_2X_2 compounds can exhibit phase transitions at high-pressure, most of which are previously unrecognized. In addition, we observed that the compressibility of MgMg₂Sb₂ and MgMg₂Bi₂ is near-isotropic, whereas other isostructural AM_2X_2 compounds show clear signs of anisotropy between the in-plane and out-of-plane compressibility as is typical of layered compounds. We have analyzed the compressibility, transition pressure/temperature, anisotropy, as well as the type of phase transition to develop a deeper understanding of the stability and bond strength of different AM_2X_2 compounds.

Lastly, we observed and explained the lattice stiffening and flattened lattice thermal conductivity curve with increasing temperature in GeTe - Sb_2Te_3 alloys. Unlike most compounds that soften with increasing temperature, the elastic moduli of (GeTe)₁₇ - Sb_2Te_3 stiffen with increasing temperature before the phase transition. We investigate GeTe, Sb_2Te_3 , and (GeTe)₁₇ - Sb_2Te_3 from room temperature up to the phase transitions with high-temperature XRD, high-temperature RUS, and transport property measurements. We attribute the stiffening behavior to the gradual diffusion of layered vacancies to random vacancies on the cation site, which profoundly impact the elastic properties and the transport properties of the material.

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CHAPTER 1

BACKGROUND AND INTRODUCTION

1.1 Thermoelectric materials

Thermoelectric materials can be used to either convert a temperature gradient to an electrical potential or create a temperature difference from a voltage difference [76], which has a wide range of applications from our daily life to space explorations. Portable thermoelectric refrigerators have replaced the traditional refrigeration units with heavy fragile compressors. On a larger scale, thermoelectrics have applications in generating electricity from waste heat in the automotive industry [77]. In recent years, NASA has been developing the radioisotope thermoelectric generators that can be used for more than seventeen years [78, 79]. In addition to the environmental benefit, since thermoelectric devices have no moving parts, they are also less prone to failure compared to traditional powering system.

As powerful as thermoelectric devices may seem, the application of thermoelectric materials is still heavily limited by their low conversion efficiency. The thermoelectric conversion efficiency is correlated to its figure of merit,

$$zT = \frac{\sigma \alpha^2}{\kappa} T,$$
 (1.1)

which requires a material to have a high Seebeck coefficient, α , high electrical conductivity, σ , and low thermal conductivity, κ . This requirement is not easily achieved as these properties are highly interdependent. Successful thermoelectric materials to date generally have a combination of light carrier effective mass, high band degeneracy, and either complex unit cells or strongly anharmonic bonding [16, 23, 80, 81].

1.2 Thermal transport

The figure of merit is related to the Seebeck coefficient, electrical conductivity, and thermal conductivity. A good thermoelectric material almost always benefits from an inherently low lattice thermal conductivity [23, 81]. Therefore, thermal conductivity is the focus of this research. Essentially, all mobile particles that have directional propagation in the presence of a temperature gradient are contributors to the total thermal conductivity of a material [2]. For semiconductors, the dominant thermal components are charged carriers and lattice vibrations, which are referred to as the electrical thermal conductivity and the lattice thermal conductivity, respectively.

As shown in Figure 1.1, lattice vibrations in a material can be classified into two types of motion mechanisms. These periodic quantum excitations in a structure are called phonons, which can be described as quasi-particles that interact with other particles within the rules of classical mechanics. The word "phonon" comes from a Greek word meaning "sound or voice". Opposing vibrations of atoms can form standing waves, known as optical modes. Due to small average group velocity, optical phonons are typically not the subject of study in the field of thermal transport. On the contrary, the waves that propagate in the same directions, known as acoustic phonons, dominate the heat transport of a material due to their large net group velocity [1, 2]. We can obtain direct information of acoustic phonons from elastic moduli, which will be discussed in the next few sections.

Note that even though optical phonons are typically not considered as a primary contributor to lattice thermal conductivity, there are some studies on the participations of optical phonon in thermal conduction in specific materials systems, especially for nanostructures in which the frequencies of the optical phonons is comparable to the size of the lattice. For example, in a study by Tian et al. [82], DFT calculations have shown that optical phonon can contribute over 20% of the nanostructure silicon as compared to less than 5% in the bulk material.



Figure 1.1: A schematic demonstration of acoustic and optical phonon vibrations. Optical phonons form standing waves with negligible net group velocity, whereas acoustic phonons dominate the heat transport of a material due to their large net group velocity [1, 2].

A widely used approximation $\kappa_L = \frac{1}{3}C_v v^2 \tau$ provides a guide to the lattice thermal conductivity, κ_L , of a material, which is the product of heat capacity, C_v , the speed of sound, v, and phonon relaxation time, τ [23]. Compared with the inherent nature of the heat capacity, v and τ can be more readily controlled by materials scientists. Both of these properties are closely related and are therefore the focus of this study, both of which are closely related to the chemical bonding and the structure of the compound.

1.2.1 Speed of sound and elastic moduli

When we compare lattice thermal conductivity across different compounds or classes of materials, it is tempting to jump to conclusions about different sources of external scattering. In particular, scattering from defects, grain boundaries, or nanoparticles. While these are important effects, the impact of speed of sound should always be considered first.

The speed of sound can be represented by the slope of the acoustic branch in a phonon dispersion when frequency approaches zero (Γ -point), which is easily accessible for a lot of materials via DFT calculations. The speed of sound v, is also correlated with the elastic moduli, E, via density, ρ ,



Figure 1.2: An example of the calculated phonon dispersion of the diamond. TA represents the transverse acoustic branch and LA represents the longitudinal acoustic branch. All other modes except the three acoustic modes are optical modes, which are usually of much higher frequency. The slopes of LA and TA branches at the Γ -point are the longitudinal and transverse (shear) speed of the sound, respectively.

by the general relationship of the form $v \propto \sqrt{\frac{E}{\rho}}$. An example of a calculated phonon dispersion of diamond is shown in Figure 1.2. TA represents the transverse acoustic branch and LA represents the longitudinal acoustic branch. All modes except the three acoustic modes are optical modes, which are usually of much higher frequency. The slope of LA and TA at Γ -point are the longitudinal and shear speed of the sound of this material. The transverse speed of sound only depends on a material's shear modulus and density, whereas the longitudinal speed of sound is related to compressibility, shear modulus, and density.

In isotropic materials (i.e. non-directional polycrystals), the speed of sound can be calculated from the elastic moduli via Eq 1.2 and Eq 1.3, in which v_L is the longitudinal (transverse) speed of sound, v_s is the shear speed of sound, *B* is the bulk modulus, and G is the shear modulus of a material. In materials with lower symmetry (i.e. single crystals or textured polycrystals), the relationship is more complex, since the speed of sound is dependent on direction and polarization. The complete single-crystal elastic tensor C_{ij} has up to 21 independent terms in a triclinic single crystal. The details of the tensor notations, the tensor component in various symmetries, and anisotropic tensor properties can be found in ref [83].

$$v_L = \sqrt{\frac{B + 4/3G}{\rho}} \tag{1.2}$$

$$v_s = \sqrt{\frac{G}{\rho}} \tag{1.3}$$

From these two equations above, we can see that high density and soft bonds (i.e. low elastic moduli) typically lead to low group velocity, and vice versa. Bigger atoms are generally related to softer bonds [84]. Materials with soft bonds, low speed of sound, and high anharmonicity are generally favorable for thermoelectric materials. Note that soft bonds do not necessarily mean a mechanically weak sample. In fact, softer bonds are often associated with materials that are less prone to brittle failure, which is more favorable for practical applications [85].

1.2.2 Umklapp scattering



Figure 1.3: A schematic demonstration of normal scattering and Umklapp scattering. The left and right edge of the grey box represent the range of the first Brillouin zone. k_1 and k_2 are the initial wave vectors before the scattering, and k_3 is the resulting wave vector after the scattering.

In a perfect single crystal with no other scattering sources, the phonon relaxation time, τ , is related to the Umklapp scattering rate, which is an anharmonic phonon-phonon interaction process that exists even in a flawless crystal. Phonon-phonon interaction falls into two categories - Normal scattering and Umklapp scattering. A schematic demonstration of normal scattering versus Umklapp scattering can be seen in Figure 1.3. k_1 and k_2 are the initial wave vectors before the scattering, and k_3 is the resulting wave vector after the scattering. Normal scattering refers to a harmonic process in which the resulting wave vector, k_3 , is inside the first Brillouin zone. The momentum is conserved, and this type of phonon-phonon interaction does not directly contribute to lattice thermal resistance [86]. Note that even though normal scattering does not directly contribute to the lattice thermal conductivity, the resulting longer wave vector can increase the possibility of Umklapp scattering during the next stage. Umklapp scattering occurs when the sum of the wavevectors, k'_3 , exceeds the first Brillouin zone. Due to the periodic nature, the point outside the first Brillouin zone can be expressed as a point inside the zone, k_3 , which corresponds to a wave flipping back in the opposite direction [86].

The general temperature dependence of Umklapp scattering, τ_U , is described in Eq. 1.4 [87, 88, 89, 90, 91],

$$\tau_U \propto \frac{\bar{M}v^3}{V^{1/3}\gamma^2\omega^2 T},\tag{1.4}$$

in which \overline{M} is the average mass, T is temperature, v is the speed of sound, V is the unit cell volume per atom, ω is the phonon frequency, and γ is the Grüneisen paramters. Among all the scattering mechanisms, Umklapp scattering is often the dominant mechanism in thermoelectric materials and it becomes increasingly important at high-temperature due to the 1/T temperature dependence of the phonon relaxation time, τ . A schematic demonstration of the temperature dependence of the phonon relaxation time of Umklapp scattering compared to other scattering mechanisms (i.e carrier-carrier scattering and defect scattering) is shown in Figure 1.4.

In contrast to the easy accessibility of the speed of sound, the scattering rate, τ_U is more difficult to be directly measured experimentally, or have a unified approach to be computed. However, the rate of softening, the Poisson's ratio, and thermal expansion are related to anharmonic bonding



Figure 1.4: A schematic demonstration of the temperature dependence of the phonon relaxation time of Umklapp scattering compared to other scattering mechanisms (i.e carrier-carrier scattering and defect scattering). Umklapp scattering becomes increasingly important at high-temperature due to the 1/T temperature dependence of the phonon relaxation time.

potential, and can therefore be used as a rough estimate of the Grüneisen parameter, which is correlated with τ_U . These will be explained in detail in the next few sections.

1.2.3 Softening of elastic moduli with temperature

The Grüneisen parameter, named after Eduard Grüneisen, quantifies the anharmonicity of a material. The Grüneisen parameter describes the vibrational properties of a crystal lattice as a function of unit cell volume (i.e. temperatures) [92]. The vibration of atoms in a solid depends on the potential energy of its chemical bonds as a function of displacement, r. This is given by

$$V(r) = V(0) + a_2(r - r_0)^2 + a_3(r - r_0)^3 \dots,$$
(1.5)

where $r - r_0$ is the relative displacement of an atom from its equilibrium position, r_0 , and a_2 and a_3 are the magnitude of the harmonic and anharmonic terms, respectively. The degree of anharmonicity can be represented by a_3/a_2 (or a_4/a_2 if there is no a_3 terms in certain symmetries), in which the $a_2(r-r_0)^2$ is the symmetric term and $a_3(r-r_0)^3$ is the term that breaks the symmetry. The elastic modulus, *E*, is co-related to the curvature of the vertex of the potential function, $E = \frac{1}{r_0} \left(\frac{\partial^2 V}{\partial r^2}\right)_{r=r_0}$. A larger curvature corresponds to a narrower potential well and thus stiffer



Figure 1.5: A schematic demonstration of interatomic potential and its relationship with thermal expansion and elastic moduli. A larger curvature corresponds to a narrower potential well and thus a smaller thermal expansion and stiffer bond.

bond. The curvature of an anharmonic potential well decreases with increasing potential energy / atomic displacement / temperature. In the classic Taylor expansion model, as given by Eq 1.5, the curvature of potential well is a constant as a function of energy in a harmonic potential well. The elastic modulus is therefore also a constant as a function of temperature. Note that the thermal expansion for a perfectly harmonic crystal might not be zero, as predicted in a calculation study by Matthias et al. [93]. However, in this study, we will use the classic model to explain the observed anharmonic phenomenon. The more anharmonic the potential well is, the more rapidly a solid will soften with increasing temperature. Longer chemical bonds tend to be softer, but this does not necessarily imply that they must also be more anharmonic. However, in general, we associate highly harmonic materials (e.g., diamond) with bonds that are stiff, short, and strong. In contrast, most anharmonic solids often have some degree of instability in the structure leading to bonds that are weak in some respects. Alternatively, we can view this relationship from the perspective of the melting temperatures. Weaker bonds lead to lower melting temperatures, which require the elastic

moduli to soften faster since liquids have elastic moduli close to zero.



Figure 1.6: Three selected materials that range from very soft and anharmonic to very stiff and harmonic. θ_E is related to the Einstein temperature, the slope of the linear region equals the s/θ_E ratio, Y_0 is the Young's modulus at the lowest temperature (~0 K), and $\gamma_{Ledbetter}$ is the Grüneisen parameter [3, 4, 5]. Figure taken from W. Peng et al. [6]

The elastic response is characterized by the stiffness tensor C_{ij} . For bulk, polycrystalline samples, it is more convenient to refer to Young's modulus, shear modulus, and bulk modulus, all of which can be derived from the single-crystal elastic tensor. The general trend of elastic moduli with temperature is shown in Figure 1.6. The elastic moduli stay mostly constant at low temperatures because low energy vibrations only sample the bottom of the potential well, the curvature of which almost always approximates the harmonic ideal. At higher temperatures, they start to soften linearly assuming no phase transition occurs within the measured temperature range. In 1970, Varshni put forward an equation from the Einstein-oscillator model to illustrate the relationship between the stiffness tensor (or any elastic constant), C_{ij} , Einstein temperature, θ_E , and measurement

temperature, T.

$$C_{ij} = C_{ij}^0 - s/(e^{\theta_E/T} - 1), \qquad (1.6)$$

in which C^0 denotes the elastic-stiffness coefficient at 0 K and θ_E is related to the Einstein temperature. This equation has shown to be the best overall demonstration of the trend in the lowand mid-temperature regime. The value of s/2 represents the curvature of the transition region, which also corresponds to the difference between the value of C_{ij} at 0 K and the y-intercept of the linear fit to the higher temperature linear regime. Further, the linear slope of the high-temperature region without a nearby phase transition can be used to calculate the Grüneisen parameter and Einstein temperature of the materials. Note that at temperatures lower than $\theta_E/50$, the elastic modulus is theoretically expected to follow a T⁴ dependence [94], which can not be accurately represented by the Varshni equation.

One of the equations derived from the Varshni equation by Ledbetter et al. [95]

$$dB/dT = -s/\theta_E = -\frac{3k\gamma(\gamma+1)}{V_a}$$
(1.7)

can directly calculate the Grüneisen parameter of a material from the slope of the bulk modulus dB/dT. *B* is the bulk modulus, *k* is the Boltzmann constant, and V_a is the volume per atom. The slope of the linear section, dB/dT, equals the s/θ_E ratio, from which both variables can be determined when plugged in back to the Varshni equation for a least-square fit. Here, we showed the corresponding Varshni fit of three materials with varying stiffness and anharmonicity - ReB₂, Cu, and Mg₃Sb₂. Since Young's modulus, *Y*, is more widely available than the bulk modulus, therefore, we are fitting the trend of the dY/dT instead of dB/dT here. A narrower transition region to the linear trend means a lower Einstein (Debye) temperature, a faster softening rate, and smaller s/2, which agrees well with the data shown in the table inset in Figure 1.6.



Figure 1.7: Temperature-dependence of the Young's modulus, *Y*, of the selected thermoelectric material [7, 8, 9, 10, 11, 12, 13, 14, 12]. Half-heuslers and $Si_{1-x}Ge_x$ come to the top to be the stiffest thermoelectric materials due to their short covalent bonds. The softest crystalline materials are the layered tetradymites with covalent octahedral layers and vdW bonding. At the lower left corner, PEDOT, a conducting polymer, is shown for comparison, which is an extremely soft material. Figure adapted from W. Peng et al. [6]

1.2.4 Literature review of temperature-dependent elastic moduli of thermoelectric materials

Figure 1.7 compiled some selected temperature-dependent elastic moduli data across different classes of thermoelectric materials from the literature to illustrate the range of behavior. All of the data were collected on bulk polycrystalline specimens using resonant ultrasound spectroscopy. Details about the method are described in Chapter 2. We can see the dual roles of structure and composition in determining elastic moduli. Due to the short and stiff covalent bonds, half heuslers with small atoms are the stiffest thermoelectric compounds, even stiffer than Si-Ge alloys. Similarly, the cage structures of clathrates are also dominated by stiff covalent bonds, enabling them to be the second stiffest thermoelectrics with large cations. Within the same structure type, the differences in atomic size are the determining factor of the differences in the stiffness of compounds.

For example, the Ge-based clathrates are generally softer than Si-based clathrates. However, this does not typically strongly impact the slope, dY/dT, which is used for calculating the Ledbetter Grüneisen parameter, $\gamma_{Ledbetter}$. The clathrates in particular are an example of a large range in Young's modulus, but not much variation in slope. The difference in Young's modulus explains much of the difference in lattice thermal conductivity across materials. For example, half heuslers' lattice thermal conductivities are inherently high due to their high bond stiffness. In particular, ZrNiSn has a lattice thermal conductivity of 17.2 W/mK at room temperature, which is on the high end of TE materials. PEDOT, on the other hand, is a class of electrical conducting polymers with ultra-low thermal conductivities (~ 0.4 - 0.9 W/mK) [96]. The Young's modulus of PEDOT thin films at ambient temperature is typically around 1 GPa [12, 13, 14].



Figure 1.8: The change of the normalized Young's modulus with temperature of various compounds [7, 8, 9, 10, 11, 15]. Figure adapted from W. Peng et al. [6]

Generally, materials with lower melting temperatures soften faster. Figure 1.8 shows the fractional change in Young's modulus with temperature. While SiGe only softens by 3% up to 800 K, traditional thermoelectrics, such as PbTe and SnTe, are typical low melting temperature materials which have a much faster rate of 20%.

1.2.5 Grüneisen parameters

From a microscopic perspective, the mode Grüneisen parameter, γ_i , can be expressed as

$$\gamma_i = -\frac{\partial ln\omega_i}{\partial lnV},\tag{1.8}$$

in which ω_i is the corresponding vibrational frequency of an individual phonon mode *i*, and V is the unit cell volume [92]. Each vibrational mode has its unique response to volume change, which cannot be measured in an experiment without a neutron scattering facility. This makes the experimental data of anharmonicity prohibitively difficult to obtain.

Being able to accurately estimate the Grüneisen parameters is important to understand the Umklapp scattering rate, but unfortunately, there is no single, widely used approach to estimating from experimental data. The reported experimental Grüneisen parameter value is usually a weighted average of all modes. In this regard, different approximations are incorporated into the original equation, making the Grüneisen parameters a more attainable property. There are many different expressions for the thermodynamic Grüneisen parameter that are equally valid, and make use of different measurable quantities.

1.2.5.1 Thermal expansion Grüneisen parameter

Traditionally, experimentalists only have access to the thermodynamic, or "average" Grüneisen parameter. This can be obtained by taking a weighted average of the mode Grüneisen parameters via the specific heat per particle,

$$\gamma = \frac{\sum_{i} \gamma_{i} c_{V,i}}{c_{V,i}},\tag{1.9}$$

in which $c_{V,i}$ is the heat capacity of an individual vibrational mode. When the Einstein heat capacity and the quasi-harmonic approximation (ω is the only term that is affected by volume) is applied, combined with Maxwell relations, the equation

$$\gamma = \frac{\alpha B}{C_V \rho} \tag{1.10}$$

can be derived. C_V is specific heat, α is volumetric thermal expansion, B is the bulk modulus, and ρ is the density of a material. The major downside is that, in the case of a material with very high positive and negative mode Grüneisen parameters, the weighted average might be a small positive value, which lead one to be unaware of the large anharmonicity of that material.

1.2.5.2 Poisson's ratio Grüneisen parameter

Because phonon frequencies are a function of elastic constants, the Grüneisen parameter can also be obtained through various thermodynamic expressions from elastic moduli. Recently, the relationship between the bulk modulus, B, speed of sound, v, and Grüneisen parameters got a lot of attention due to its simplicity for both the experimental and DFT calculations [97, 98, 99, 100]. The equation

$$\gamma = \frac{B}{\rho \overline{\nu}^2} \tag{1.11}$$

was initially derived from the Debye model in a cubic system, but it has been shown to work for other symmetry conditions as well. From an elastic tensors' perspective, it is well-known that

$$\overline{v}^2 = \frac{C_{11} + 2C_{44}}{3\rho} \tag{1.12}$$

and

$$B = \frac{C_{11} + 2C_{12}}{3} \tag{1.13}$$

According to Eq. 1.12 and Eq. 1.13, we can see that $\rho \overline{v}^2$ only equals *B* when $C_{12} = C_{44}$. Therefore, the value of the Grüneisen parameter in Eq. 1.11 can be interpreted as the difference between C_{12} and C_{44} (i.e. $(C_{11}+2C_{12})/(C_{11}+2C_{44})$), or in other words, how uniformly the material reacts to a given strain. By doing transformations using the relationship between the speed of sound, *v*, bulk modulus, *B*, and the Poisson's ratio, μ , one can obtain a single-variable equation

$$\gamma = \frac{3}{2} \left(\frac{1+\mu}{2-3\mu} \right),\tag{1.14}$$

which is a monotonically increasing function in the range of the Poisson's ratio values (0-0.5). A large Poisson's ratio is a hallmark of lattice instability, which corresponds with a large Grüneisen parameter in this expression.

So far, we have introduced three equations for calculating the Grüneisen parameters: Eq.1.6, Eq.1.10, and Eq. 1.14. Although all these equations for Grüneisen parameters are derived from the same origin, they have different scaling and give different values, which can be misleading when one is trying to compare the Grüneisen parameter of a material with other materials using values calculated from a different equation. However, a general trend and conclusion of the Grüneisen parameters can still be made if a variety of equations are used for the selected compounds.

1.3 AM_2X_2 Zintl phases

 AM_2X_2 Zintl phases have attracted plenty of interest in thermoelectric applications due to their chemical diversity and tunability. The highest *zT* of 1.6 has been achieved in *n*-type MgMg₂(Sb,Bi)₂ compounds. Much of the research to date has been focused on optimizing the electronic properties, explaining the band degeneracy, and exploring the dopability of these compounds. In contrast, little research has been done on their phonon behaviors and lattice thermal conductivity. However, even though there is not much tunability for these intrinsic properties, there are some interesting and unanswered questions that can enhance the understanding of the fundamental questions of the relationship between structure and phonons.

In AM_2X_2 compounds with CaAl₂Si₂ ($P\bar{3}m1$) structure type, A is an alkali or alkaline earth or rare earth metal, M is Mg, Al, or a transition metal, and X belongs to a IVA-VIA group element. CaAl₂Si₂ can be characterized by covalently bonded [Al₂Si₂]²⁻ bilayer slabs formed by alternatively oriented AlSi₄ tetrahedra sandwiched by monolayers of Ca²⁺ (see Figure 1.9 a) [101, 102, 35].

1.3.1 The formation rule of Zintl phases

The name "Zintl" comes from the German chemist Eduard Zintl, who discovered and defined a subset of intermetallic compounds that consist of covalently-bonded polyanions surrounded by cations which provide the overall charge balance. Complete charge transfer from the cation to the

anion is assumed for the Zintl phases [103, 104]. Zintl phases were first discovered in 1933 [105, 53] and they have been widely studied on the stability of the structure [38, 39, 36, 37, 45, 46, 47, 56, 50] as well as the electronic structures [106, 107].

The Zintl-Klemm concept (8-N rule) is frequently used to rationalize the relationship between the formula and chemical bonding in Zintl phases, in which N refers to the number of valence electrons available per unit cell per anion [103]. Take AM_2X_2 compounds with the CaAl₂Si₂ structure type as an example. The valence electrons for Ca, Al, and Si are 2, 3, and 4, leading to a total number of 16 valence electrons per formula unit. The number of valence electrons available per unit cell per anion is N = 16 / 4 = 4, if we consider both Al and Si as anions. And therefore, 8 - N = 4. This means that both Al and Si have four-fold coordination, which is consistent with the observed structure (see Figure 1.9 a).

1.3.2 Chemistry of AM_2X_2 compounds in CaAl₂Si₂ structure type



Figure 1.9: a) The CaAl₂Si₂ structure type is formed from $[M_2X_2]^{2-}$ polyanion slabs separated by monolayers of six-fold coordinated cation A. b) Possible element-combinations to achieve the CaAl₂Si₂ structure type according to the 8 - N rule. Figure taken from W. Peng et al. 1.9.

From the electron count in the previous section, we know that the CaAl₂Si₂ structure has 16 nominal

valence electrons per unit cell. In fact, as long as the 16 valence electron rule can be satisfied, the ternary AM_2X_2 compounds will form the CaAl₂Si₂ structure type. This includes mixed occupancies and interstitials. All the elements that can form the CaAl₂Si₂ are shown in Figure 1.9 b). By combining the listed elements on each site, there are more than 100 compounds reported to crystallize in this structure type. This brings a great deal of flexibility in forming and tuning the composition, which has attracted plenty of interest for AM_2X_2 compounds as thermoelectrics.

Note that some of the metallic AM_2X_2 Zintl phases are exceptions for the 8 - N rule, such as $REAl_2Si_2$ and $REAl_2Ge_2$ ((RE= lanthanide rare earth metal). These have 17 valence electrons [59] due to the reduced anti-bonding state filling energy. However, since these compounds do not have a bandgap, they are not typically within the scope of thermoelectrics.

1.3.3 AM_2X_2 compounds as thermoelectrics

Although CaAl₂Si₂ itself is metallic, the majority of the antimonides and some of the bismides in this structure type are narrow band gap semiconductors. The interest in the thermoelectric research of AM_2X_2 compounds started in 2005, when the thermoelectric properties in Ca_xYb_{1-x}Zn₂Sb₂ solid solution were first reported by Gascoin et al. [31]. Compared with other classes of Zintl phases, one of the prominent advantages of CaAl₂Si₂-type compounds is their large variety and unprecedented tunability, providing many opportunities for controlling the transport properties. Since then, large amount of efforts on optimizing and understanding the electronic structure, including band engineering [108, 109, 110, 111], control of defect concentrations [112, 113], aliovalent doping [114], and point defect phonon scattering [31, 115, 116, 27, 33, 28, 32, 117] have emerged. Recently, excellent thermoelectric performance was reported by several independent groups in *n*-type Mg₃(Sb,Bi)₂ alloys, with *zT* up to 1.6 [118, 108, 119, 113, 120]. This record-high *zT* surpasses all previous results for isostructural compounds, which have been exclusively *p*-type.

To date, experimental and theoretical investigations of Mg₃Sb₂ have focused on the electronic



Figure 1.10: The zT of selected *n*-type (dashed curves) and *p*-type (solid curves) of AM_2X_2 compounds. Figure taken from W. Peng et al. [16].

properties [118, 121], the multi-valley conduction band [108, 113, 109, 111], and increasing mobility [120, 122]. In contrast, the anomalously low κ_L of both *n*- and *p*-type Mg₃Sb₂ has not been investigated, though it plays an equally important role in leading to the high *zT*. Here, we will discuss the origins of low lattice thermal conductivity from the perspective of thermal expansion, lattice softening, compressibility, and phase transitions, shedding light on the rarely discussed topic of anharmonicity in AM_2X_2 compounds.

1.4 Summary of research

In this research, we will discuss the origins of low lattice thermal conductivity in two different classes of layered thermoelectric materials from the perspective of thermal expansion, lattice softening, solubility, speed of sound, compressibility, and phase transitions. The main focus of the thesis is on the AM_2X_2 compounds described above, shedding light on the rarely discussed topic

of anharmonicity in AM_2X_2 compounds.

 AM_2X_2 compounds are a particularly attractive class of Zintls for thermoelectrics due to large variety and unprecedented tunability. By employing high-temperature X-ray diffraction (XRD) and resonant ultrasound spectroscopy (RUS) techniques, we have shown that the low lattice thermal conductivity is due to previously-unrecognized soft shear modes and highly anharmonic acoustic phonons in layered MgMg₂Sb₂. Even though different Grüneisen parameter equations give different values, the results repetitively show higher anharmonicity for Mg₃Sb₂ and Mg₃Bi₂ compared to isostructural AM_2X_2 compounds. Combined with the phonon calculations from our collaborators, we attribute the anomalous thermal behavior of MgMg₂Sb₂ to the instability of the vibrational modes that originated from the weak bonding of the Mg, which is too small for the octahedral site. The limited solubility of Sr and Ba on the Mg cation site (i.e. *A*-site) further confirmed the small ionic radius of Mg²⁺.

High-pressure characterizations are not widely used in studying thermoelectric materials, as their application is usually at high temperature, not pressure. However, in - situ high-pressure structural characterization can provide another dimension of variables to observe the stiffness and stability of a material, which can help to understand relationship between structure and phonons of the lattice thermal conductivity. By performing in-situ high-pressure synchrotron X-ray diffraction, we showed that a few AM_2X_2 compounds can exhibit phase transitions at high-pressure, most of which are previously unrecognized. In addition, we observed that the compressibility of MgMg₂Sb₂ and MgMg₂Bi₂ is near-isotropic, whereas other isostructural AM_2X_2 compounds show clear signs of anisotropy between the in-plane and out-of-plane compressibility as is typical of layered compounds. We have analyzed the compressibility, transition pressure/temperature, anisotropy, as well as the type of phase transition to develop a deeper understanding of the stability and bond strength of different AM_2X_2 compounds.

Lastly, to extend our understanding of the structure - property relationships in layered materials, we investigate the GeTe - Sb_2Te_3 homologous series, which is characterized by van der Waals gaps with tunable layer thickness. Unlike most compounds that soften with increasing temperature, the elastic moduli of $(GeTe)_{17}$ - Sb_2Te_3 stiffen with increasing temperature before the phase transition. We attribute the stiffening behavior to the gradual diffusion of layered vacancies to random vacancies on the cation site, which correspondingly leads to a flattened temperature dependence of the elastic moduli.
CHAPTER 2

METHODS

2.1 Overview

For this work, polycrystalline samples of CaMg₂Sb₂, YbMg₂Sb₂, CaMg₂Bi₂, YbMg₂Bi₂, MgMg₂Sb₂ (alternatively written as Mg₃Sb₂), MgMg₂Bi₂ (alternatively written as Mg₃Bi₂), EuAl₂Si₂, SrAl₂Si₂, GeTe, Sb₂Te₃, Bi₂Te₃ were synthesized via ball milling followed by spark plasma sintering. Due to the geometry of the die used for sintering, all the as-synthesized samples are bulk samples with cylindrical geometry. All sintered samples have densities above 97% of the theoretical density, and less than 5% of the impurities were observed based on the relative peak intensity of X-ray diffraction. (GeTe)₁₇Sb₂Te₃ was made by our collaborator, Jared Williams, via a slightly different processing method, which will be described separately in the following sections.

The primary characterization techniques used in this work include high-temperature X-ray diffraction with finely ground powder samples, room-temperature X-ray diffraction with bulk samples, high-temperature resonant ultrasound spectroscopy with bulk cylindrical samples, and in - situ X-ray diffraction in diamond anvil cells with powder or single-crystalline samples. The synthesis, X-ray diffraction, and resonant ultrasound spectroscopy were performed at Michigan State University, whereas *in-situ* X-ray diffractions in diamond anvil cells were performed at Advanced Photon Source in Argonne National Laboratory. The details are demonstrated below.

2.2 Synthesis

All AM_2X_2 compounds, GeTe, Sb₂Te₃, and Bi₂Te₃ discussed in this paper were synthesized by direct ball-milling of stoichiometric elements followed by spark plasma sintering (SPS). The corresponding stoichiometric elements were cut into small pieces in an argon filled glovebox, loaded into stainless steel vials with two 10 mm diameter stainless balls, and milled for one hour using a SPEX mill. Ball-milling was performed under argon atmosphere for 1-hour using a stainless steel SPEX mill. The powder was then loaded into graphite dies with 10 mm bores and sintered under a pressure of 31 MPa using a Dr. Sinter SPS-211LX. The samples were heated to a target temperature in 5 minutes, and then held at the target temperature for 10 minutes. The sintering temperatures and times were customized for each compound depending on their phase diagrams. Details for the specific compounds can be found within each chapter. A heating rate of $50-80^{\circ}C/\text{min}$ was used to reach the target temperature, typically $550-850^{\circ}C$, followed by a 10-minute hold. The densities of all the samples were obtained from direct measurements of mass and geometry. The pressure was removed immediately when cooling started. The phase purity of the samples was confirmed using a Rigaku Smartlab X-ray diffraction system with Cu K α radiation. All sintered samples have densities above 97% of the theoretical density, and less than 5% of the impurities were observed based on the relative peak intensity of X-ray diffraction. The details of each sample will be described in the corresponding chapters.



Seal elements in Ar



Sintered sample



Ball-milling



Seal samples in quartz tubes



SPS



Samples after annealing

Figure 2.1: A demonstration of the synthesis approach in this work. Samples were synthesized by direct ball-milling (under argon) followed by spark plasma sintering (SPS). The as-synthesized samples have a cylindrical geometry. For the annealing process, the samples were wrapped in graphite foils and sealed in glass ampoules under vacuum, which were then held at $500^{\circ}C$ for ten days.

In some cases, an annealing process would be done if the equilibrium state of the material is a major concern. All the samples used for solubility study in section 3.2 were annealed after sintering. The samples were wrapped in graphite foils and sealed in glass ampoules under vacuum, which then held at $500^{\circ}C$ for ten days. Quenching is preferred for high-temperature phase observation.

 $(GeTe)_{17}Sb_2Te_3$ were made by our collaborator, Jared Williams. Samples were prepared using stoichiometric amounts of elemental germanium ingot (99.9999%), antimony shot (99.999%), and tellurium lump (99.999%) from Alfa Aesar. The elements were sealed in quartz ampoules under vacuum, which were then heated to 1173 K and held for 12 hours and water quenched. The material was then ball-milled for 5 minutes and densified using Spark Plasma Sintering (SPS) at a temperature of 673 K and a pressure of 40 MPa for 15 minutes. The structure was identified using a Rigaku X-ray diffractometer. After consolidating in the SPS, the $(GeTe)_{17}Sb_2Te_3$ sample was initially in a metastable cubic structure due to the rapid cooling rate, as described in ref [123]. A single heating cycle to 673 K was sufficient to regain the thermodynamically stable rhombohedral structure, as verified by X-ray diffraction. The densities of the samples yield at least 96% of the theoretical densities.

2.3 Characterization

2.3.1 Resonant ultrasound spectroscopy (RUS)

Traditionally, the measurements of elastic moduli rely on pulse-echo (Figure 2.2 a), in which a large piece of sample was required, and multiple measurements need to be done to obtain longitudinal and transverse velocities [124]. The plane wave approximation, as well as the signal from undesired sources, lowers the reliability of the result.

Resonant ultrasound spectroscopy (RUS) provides the most accurate, efficient, yet non-destructive characterization of elastic moduli in solids [125, 24, 126], which has advantage to extract a complete set of elastic tensor from a single measurement. As shown in Figure 2.2 b), the driving force is a

wide range of vibrational frequencies generated from a piezoelectric transducer, and the response is the resonances from the sample collected by another transducer [125, 24]. Peaks can be observed when the excitation frequency matches the Eigen-frequency of the sample. The spectrum from a single measurement contains sufficient Eigen-modes to extract the complete elastic tensor, assuming size, shape, and density of the sample are known parameters [126]. The mounting in RUS only requires a very light touch between the sample and the transducers, which avoids the problem of thermal expansion mismatch, offering a significant advantage in high-temperature measurement [24, 126].

Elastic moduli are obtained by matching the calculated resonances with observed peaks, which can be computationally more accessible by using samples of well-defined geometries such as parallelepipeds, cylinders, and spheres [127]. The calculated resonances are for perfect geometries with free oscillations. In a real experimental setup, however, deviation from perfect geometry is inevitable, and the sample is not entirely free from external forces. Take a cylinder sample as an example, the modes from a perfect geometry should belong to either torsional, extensional or flexural mode. The first two types are single modes, and the third type of mode occurs in pairs, which appear to be doublets in a spectrum. When a small defect, such as a crack, appears in the sample, the resonant frequencies will be perturbed. For doublets, the two components of the pair modes might not have the same amount of shifts. Therefore, splits of doublets and slight shifts of singlets and would be observed in an imperfect sample.

All the elastic modulus investigations in this paper were done using polycrystalline samples. Polycrystalline samples are isotropic, which means it only requires two independent elastic constants C_{11} and C_{44} for the complete description of the elastic behavior regardless of the space group. The elastic moduli, longitudinal and transverse speed of sound of polycrystalline samples can be calculated applying the isotropic equations:

$$C_{12} = C_{11} - 2C_{44} \tag{2.1}$$



Figure 2.2: a) In pulse-echo ultrasound measurements, the time required for an acoustic wave to travel across the sample is measured. b) In resonant ultrasound, the drive transducer emits acoustic waves over a frequency spectrum. Peaks correspond to the resonant frequencies of the sample. The black dots under the spectrum are calculated peak locations with the predicted elastic constants. The inset is an example of the temperature dependence of the peak positions. This Figure is reproduced from Ref. [17]

$$\mu = \frac{C_{12}}{C_{11} + C_{12}} \tag{2.2}$$

$$Y = 2(\mu + 1)C_{44} \tag{2.3}$$

$$G = C_{44} \tag{2.4}$$

$$B = \frac{YC_{44}}{2C_{44} + 3Y} \tag{2.5}$$

$$v_L = \sqrt{\frac{B + \frac{4}{3}G}{\rho}} \tag{2.6}$$

$$v_s = \sqrt{\frac{G}{\rho}},\tag{2.7}$$

in which Y is Young's modulus, G is shear modulus, μ is the Poisson's ratio, B is bulk modulus, v_L is the longitudinal speed of sound, and v_s is the transverse speed of sound.

Room temperature RUS Cylindrical samples were mounted on a tripod transducer setup (Figure 2.3 a)). One transducer induced vibrations and the remaining two detected the specimen resonances. The sinusoidal driving frequency was swept from 0 to 500 kHz. Each scan was typically completed within a minute.



Figure 2.3: a) Room temperature RUS with a tripod set-up. b) High-temperature RUS set-up.

High-temperature RUS The temperature-dependent elastic moduli were measured by resonant ultrasound spectroscopy using a custom modification of a Magaflux-RUS quasar 4000 system in a furnace with a flowing Ar atmosphere (Figure 2.3 b)). Buffer-rods are glued to the transducer that extended into the furnace for sample mounting. After mounting the sample onto the buffer-rods, the

system would stay in vacuum overnight before backfilled with argon. The maximum temperature of this set-up is $500^{\circ}C$ due to the melting point of the glue on the buffer-rods.

RUS data analysis The RUS data was analyzed using commercial Quasar2000 CylModel software to match the predicted resonant frequencies with observed peaks.

2.3.2 X-ray diffraction (XRD)

Room temperature XRD Room temperature X-ray diffraction is done using a Rigaku Smartlab X-ray diffraction system with copper K α radiation to identify the compositions. Phase purity of the samples was confirmed via peak matching within the ICSD database, and lattice parameters were obtained using Rietveld refinement using PDXL2 [128, 129]. Rietveld refinement uses the least square approach to refine line profile with the peak shape, eak shape parameters, preferred orientation, and the structure factor to match the measured spectrum [130], which has a significant advantage over other methods, such as peak indexing, especially in cases of peak overlapping.

High-temperature XRD Thermal expansion was measured using a Rigaku Smartlab XRD system equipped with a high-temperature stage. The samples were ground into fine powders that were then placed on a graphite foil on top of a platinum tray. The measurements were performed under vacuum to prevent oxidation. The thermocouple goes into the inner part of the platinum tray to increase the accuracy of the temperature measurement (shown in Figure 2.4). The heating rate is 10 K/min with a 1-minute hold, and sample height alignments were performed before each measurement to account for the combined thermal expansion of the holder and sample. Lattice parameters were refined at each temperature using PDXL2. The volume thermal expansion coefficients α_V can be calculated from the refined unit cell volume *V* using equation

$$\alpha_V = \frac{1}{V} \frac{\partial V}{\partial T} \tag{2.8}$$

Similarly, linear thermal expansions along different crystallographic directions can be obtained with

$$\alpha_L = \frac{1}{L} \frac{\partial L}{\partial T} \tag{2.9}$$



Figure 2.4: The high-temperature X-ray diffraction was performed using a Rigaku 1400HT stage. The thermocouple goes into the inner part of the platinum tray to increase the accuracy of the temperature measurement.

2.3.3 In-situ high-pressure synchrotron diffraction in diamond anvil cells (DACs)

A diamond anvil cell (DAC) is a hand-size device that can generate pressures up to a few megabars depending on the size of the anvil. DACs are specialized at *in-situ* measurements of micron-size samples with high-focus beams. This gives the advantage of measuring anisotropic compressibility, observing phase transitions, study the properties of non-quenchable phases, and synthesize novel materials.

2.3.3.1 Loading samples in diamond anvil cells

A schematic picture of a symmetric diamond anvil cell is shown in Figure 2.5. The figure is taken from Dong et al. [18]. The anvils consist of two opposing diamonds. The diamonds are usually cut into 16 facets of with a hexadecagonal surface on the top, which refers to as the culet. The culet size typically ranges from 30 μ m to 800 μ m. Smaller culets are used for high pressure, whereas bigger culets are used for finer pressure steps. The maximum pressures for 200, 300 and 800-micron anvils are approximately 80 GPa, 60 GPa, and 15 GPa respectively.



Figure 2.5: A schematic picture of a symmetric diamond anvil cell. Figure taken from Dong et al. [18].

A gasket made of a hard material is sandwiched between the two anvils to protect the diamonds as well as creating a sample chamber. Rhenium or tungsten gaskets are the most common non-X-ray transparent choices, whereas lighter materials, such as beryllium, are chosen when X-ray transparency is required.

For experiments that require hydrostatic pressure, a liquid pressure transmitting medium is required

to avoid strain variation across the sample. Gas-loading is one of the most common ways to fill the gasket chamber with pressure medium, typical choices are noble gases and nitrogen. Lighter gases such as He and Ne have lower peak intensities and higher solidification pressures, but due to their small atomic sizes, they are hard to be compressed at high pressures. In addition, smaller molecules diffuse into the diamond surface easier than bigger ones, which means they have higher chances to damage the anvils. Larger molecules such as Ar and Kr are softer and easier to compress, but they solidify at a lower pressures and can generate high-intensity peaks. Therefore, these heavy gases have issues of reduced-transparency and less hydrostatic pressure.

2.3.3.2 High-pressure X-ray diffraction experiment details

Our experiments rely on *in-situ* X-ray diffraction to obtain compressibility and detect possible new phases while increasing pressure and temperature. *In-situ* high-pressure X-ray diffraction experiments were conducted at the Advanced Photon Source (APS) in Argonne National Laboratory, beamlines 13-BM-C (GSECARS) and 16-BM-D (HPCAT). The samples were synthesized via ballmilling and SPS as described above. The as-synthesized bulk samples were ground into powder with grain sizes smaller than 1-micron, which was then pressed into flakes before loading into the DACs. The benefit of using flakes rather than powder is for the convenience of sample-loading, which is typically done with the static electrical force from the tip of a tungsten needle. Loading a compressed piece of sample can also prevent the situation in which all the powders move towards the edge of the gasket during gas-loading. Ruby or gold was placed next to each sample for pressure readings. Diamond anvils with culet sizes of 300 and 800 μ m culets and ~130 μ m for 800 μ m culets, respectively. The pre-indented gaskets were drilled in the center to form a hole about half of the corresponding anvil size using an electrical discharge machine (EDM) at Michigan State University or the laser micro-machining system at HPCAT [131].

Neon was loaded as the hydrostatic pressure medium using the COMPRES/GSECARS gas-loading



Figure 2.6: The X-ray transmission image of Mg_3Sb_2 and Mg_3Bi_2 in this study. The low transmission regions are the positions of the samples.

system for all samples. For all the measurements, a gas membrane setup was used to remotely increase or decrease pressure as needed and the pressure was read via the *in-situ* ruby fluorescence system before and after each data collection [132].

The distance and orientation of the detector was calibrated using a CeO₂ standard. The beam size was 12 μ m (horizontal) x 18 μ m (vertical) FWHM at GSECARS and 4 μ m x 4 μ m FWHM at HPCAT. The detector was an online Pilatus 1M at GSECARS and a Mar345 image plate at HPCAT. The position of the samples can be identified from the difference of the X-ray transmission between the sample and diamond (as shown in Figure 2.6). The low transmission regions are the positions of the samples. The pressure was controlled remotely by an inflatable steel membrane during all the measurements.

For the high-temperature high-pressure measurements, a heating unit was set up inside the cell. The heating unit consists of heating wires wrapping around a customized alumina ring with insulation layers on top and bottom of the heating units to create a heating chamber with minimal heat loss (see Figure 2.7). The heating was done under vacuum. K-type thermocouples were glued as close



Wrap heating wire on the ring



Insulate the wires with cement



Glue thermocouple onto the anvil



Tape the heating wire



Put insulation on the both anvils



Close the DAC

Figure 2.7: The HT-DAC set up. Photo taken from the set-up manual written by Dr. Bin Chen and his group members in University of Hawaii.

to the anvil as possible for accurate temperature reading. The rest of the set up is the same as room-temperature ones.

Data analysis for high-pressure X-ray diffraction Dioptas was used for raw data processes. Rietveld refinements for all diffraction patterns were performed using the PDXL2 software [128, 129]. Equation of state fits were performed with the EosFit7 software [133].

The first principles calculations were performed by our collaborators Guido Petretto, Gian-Marco Rignanese, and Geoffroy Hautier. The ABINIT software package [134, 135, 136] was used to perform density functional theory (DFT) and density functional perturbation theory (DFPT) simulations to obtain phonon properties and elastic constants [137, 138, 139, 140]. The exchange-correlation energy was approximated using the PBEsol [141] functional, that has proven to provide

accurate phonon frequencies compared to experimental data [142]. Norm-conserving pseudopotentials [143] extracted from the PSEUDODOJO pseudopotentials table version 0.3 [144] were used for all the elements. The Brillouin zone was sampled with $8 \times 8 \times 5$ Monkhorst-Pack grids [145, 146, 147]. Due to the well-known underestimation of the band gap by standard DFT, we limit our analysis to Mg₃Sb₂, CaMg₂Sb₂ and CaMg₂Bi₂, which are correctly predicted to be insulating within the adopted approximations. The temperature-dependent thermodynamical properties were obtained in the framework of the quasiharmonic approximation from the phonon dispersion curves calculated at different fixed volumes *V* (while still relaxing the position of the atoms and the shape of the unit cell). Mode Grüneisen parameters were obtained as the logarithmic derivative of the phonon frequencies with respect to the volume:

$$\gamma_i = -\frac{V}{\omega_i} \frac{\delta \omega_i}{\delta V},\tag{2.10}$$

where V is volume and ω_i is the mode frequency. The averaged Grüneisen parameter γ has been calculated as the square root of the mode-averaged-squared Grüneisen parameter[148]

$$\gamma = \sqrt{\frac{\sum_{i,q} \gamma_{i,q}^2 C_{i,q}}{\sum_{i,q} C_{i,q}}},$$
(2.11)

where the summation is over all the modes and all the *q*-points in the Brillouin zone. $C_{i,q}$ is the mode contribution to the heat capacity calculated at the Debye temperature θ_D

$$\theta_{\rm D} = n^{-1/3} \sqrt{\frac{5\hbar}{3k_b^2} \frac{\int_0^\infty \omega^2 g(\omega) d\omega}{\int_0^\infty \omega^2 g(\omega) d\omega}},$$
(2.12)

where n is the number of atoms per units cell and $g(\omega)$ is the phonon density of states.

CHAPTER 3

EFFECT OF CATION SIZE ON THE LATTICE DYNAMICS IN AM₂X₂ COMPOUNDS

(Adapted from W. Peng et al. [20]. An unlikely route to low lattice thermal conductivity: Small atoms in a simple layered structure. 2018. Joule, 2(9), 1879-1893.)

3.1 Introduction

 AM_2X_2 compounds with CaAl₂Si₂ ($P\bar{3}m1$) structure type have attracted plenty of interest as thermoelectric materials because of their chemical diversity and tunability. *A* is an alkali or alkaline earth or rare earth metal, *M* is Mg, Al, or a transition metal, and *X* belongs to a group 14 - 16 element. CaAl₂Si₂ can be characterized by covalently bonded [Al₂Si₂]²⁻ bilayer slabs formed by alternatively oriented AlSi₄ tetrahedra sandwiched by monolayers of Ca²⁺ (see Figure 3.1). Mg₃Pn₂ (Pn = Sb, Bi) has the same structure type as the ternary AM_2X_2 , thus, there are two distinct bonding environments for Mg. The Mg on the *A*-site, defined as Mg(1) here, is octahedrally coordinated by six Sb or Bi. In contrast, Mg(2) on the *M*-site is tetrahedrally coordinated by four anions (Sb or Bi).

With only five atoms in a unit cell and strong ionic bonding between the slabs, the lattice thermal conductivity of AM_2X_2 compounds is not exceptionally low compared to other Zintl phases. In the past decades, much research has been done in tuning electronic properties with compositions [149, 114, 31, 115, 116, 27, 33, 28, 32, 117]. Due to the intrinsic cation vacancies of AM_2X_2 compounds, as demonstrated in ref. [149], all the compounds have been *p*-type until the discovery of the first *n*-type MgMg₂Sb₂, which has the highest thermoelectric figure of merit zT = 1.6 [118, 108, 119, 113, 120]. Since then, discussions around the explanations of band degeneracy [108, 109, 110, 111] and *n*-type origin [118, 121, 113] have been the main focus of this compound. In contrast, little research has been done on MgMg₂Sb₂'s thermal conductivity.



Figure 3.1: MgMg₂Sb₂ crystallizes in the CaAl₂Si₂ structure (space group $P\bar{3}m1$), characterized by anionic M_2X_2 slabs separated by A cations. In MgMg₂Sb₂ and MgMg₂Bi₂, Mg(1) occupies the highly distorted octahedrally-coordinated A-site and Mg(2) the tetrahedrally-coordinated M-site [19]. The Mg-Sb bond lengths differ significantly in the two sites. Figure taken from W. Peng et al. [20].

There are some interesting and unanswered questions around the low lattice thermal conductivity of MgMg₂Sb₂ (alternatively written as Mg₃Sb₂). As shown in Figure 3.2 a), the experimental lattice thermal conductivity of MgMg₂Sb₂ is one of the lowest compared to isostructural AM_2X_2 compounds despite its low density [16]. A single-crystal study by Song et al. [150] has confirmed that the low lattice thermal conductivity is an inherent property rather than a result of defect scattering. However, the origin of the low lattice thermal conductivity of MgMg₂Sb₂ has not been investigated, and a detailed study of the phonon density of states is also lacking.

The purpose of this study is to explore the origins of the anomalously low lattice thermal conductivity in MgMg₂Sb₂. By employing high-temperature XRD and RUS studies of AMg_2Pn_2 compounds (A = Mg, Ca, Yb, and Pn = As, Sb and Bi), the temperature dependence of elastic moduli and thermal expansion can be obtained. Combined with the phonon calculation results from our collaborators, one possible origin of the unrecognized soft shearing modes and highly anharmonic acoustic phonons in MgMg₂Sb₂ and MgMg₂Bi₂ are revealed.



Figure 3.2: The experimental lattice thermal conductivity, κ_L , of MgMg₂Sb₂ is significantly lower than isostructural AM_2X_2 compounds with similar a) density and b) predicted speed of sound. κ_L data can be found in Ref. [16]. The average speed of sound, v_s , was estimated using the calculated elastic moduli from MaterialsProject.org and experimental densities [21, 22]. The dashed line is shown as a guide to the eye representing the cube dependence of v_s and lattice thermal conductivity, κ_L , if all else remains constant [23]. Compounds shown in color are the primary focus of the current study. Figure taken from W. Peng et al. [20].

3.2 Synthesis

 AMg_2Pn_2 compounds with A=Mg, Ca, Yb and Pn=Sb, Bi were synthesized by direct ball-milling of the elements followed by spark plasma sintering. The corresponding stoichiometric elements (99.8% Mg shot, 99.5% Ca shot, 99.9% Yb chunk, 99.99% Sb from Alfa Aesar and 99.99% Rotometal Bi) were used. The details of balling and sintering can be found in Chapter 2. The maximum temperature and hold time used during spark plasma sintering are shown in Table 3.1. All samples were at least 97% of the theoretical density. Phase purity was confirmed using a Rigaku X-ray Diffraction system, showing that samples contained less than 3% of secondary phases.

Table 3.1: Maximum temperature and hold time used during spark plasma sintering of AMg_2Pn_2 (*A*=Mg, Ca, Yb and *Pn*=Sb, Bi) samples.

	Mg ₃ Sb ₂	CaMg ₂ Sb ₂	YbMg ₂ Sb ₂	Mg ₃ Bi ₂	CaMg ₂ Bi ₂	YbMg ₂ Bi ₂
Temp. ($^{\circ}C$)	850	650	650	600	700	700
Time (min)	15	10	10	10	10	15

3.3 Experimental temperature dependence of elastic moduli and speed of sound



Figure 3.3: Experimental (asterisk) and computed (circles) elastic moduli of AMg_2Pn_2 compounds tend to decrease as a function of increasing unit cell volume and bond length. The anomalously low shear moduli of Mg_3Sb_2 and Mg_3Bi_2 are significant, suggesting soft bonding are unique to these two binary compounds [22].

The elastic moduli of solids tend to become softer with increasing bond length [151]. Within compounds in the same structural pattern, if the unit cell volume increases, the elastic moduli are therefore expected to decrease. As shown in Figure 3.3, this trend is observed in ternary AMg_2Pn_2 compounds in both the experimental (A=Mg, Ca, Yb and Pn=Sb, Bi) and computational elastic moduli (A=Mg, Ca, Sr, Ba and Pn=P, As, Sb, Bi) obtained from the MaterialsProject.org [21]. Note that we omitted the computed elastic moduli of rare-earth-containing compounds due to poor agreement with experiment. Mg₃Sb₂ and Mg₃Bi₂, however, are outliers in Figure 3.3. The bulk and shear modulus of Mg₃Sb₂ and Mg₃Bi₂ are much softer compared to compounds with similar unit cell volume. The weak bonding in Mg₃Sb₂ was reported in an earlier study of the elastic moduli of AM_2X_2 compounds [152], but the impact on κ_L was not previously recognized.



Figure 3.4: Temperature-dependent a) Young's modulus, b) shear modulus, and c) longitudinal and d) transverse speed of sound measured using resonant ultrasound spectroscopy. Quantities were normalized to the room temperature value. Data for $Si_{0.8}Ge_{0.2}$, PbTe, and SnTe are from Ref. [9, 10, 24]. Figure taken from W. Peng et al. [20].

High-temperature resonant ultrasound spectroscopy was used to obtain the elastic moduli of polycrystalline AMg_2Pn_2 samples with A=Mg, Ca, Yb and Pn=Sb, Bi at different temperatures. Polycrystalline samples are isotropic, which means it only requires two independent elastic constants C_{11} and C_{44} for the complete description of the elastic behavior. The elastic moduli, longitudinal and transverse speed of sound of polycrystalline samples can be calculated applying the isotropic equations in the experimental section.

Figure 3.4 shows the normalized temperature dependence of the Young's and shear moduli of AMg_2Pn_2 (A=Mg, Ca, Yb and Pn = Sb, Bi) along with a few well-known compounds Si_{0.8}Ge_{0.2}

[24], PbTe [9] and SnTe [10] as a comparison. $Si_{0.8}Ge_{0.2}$ is known to be more harmonic and stiffer, whereas PbTe and SnTe are typical anharmonic and soft materials.

Over the measured temperature range, the elastic moduli of MgMg₂Sb₂ and MgMg₂Bi₂ soften by an impressive amount of ~25% in contrast to a ~5% decrease for CaMg₂Pn₂ and YbMg₂Pn₂ samples. The softening rate of the elastic moduli with temperature, as explained in Chapter 1, can be directly correlated with anharmonicity. The results are an indication that MgMg₂Sb₂ and MgMg₂Bi₂ are significantly more anharmonic compared to other AM_2X_2 compounds. Additional evidence can be seen from thermal expansion (see Figure 3.5). MgMg₂Bi₂ and MgMg₂Sb₂ has a higher thermal expansion coefficient compared to other AMg_2Pn_2 compounds, which again shows their anharmonic bonding nature.



Figure 3.5: Experimental thermal expansion of YbMg₂Bi₂, CaMg₂Sb₂, CaMg₂Bi₂, MgMg₂Sb₂, and MgMg₂Bi₂. As we can see, MgMg₂Bi₂ and MgMg₂Sb₂ has the highest thermal expansion coefficient compared to other AMg_2Pn_2 compounds. Figure taken from W. Peng et al. [20].

3.4 Lattice dynamics and Grüneisen parameters of AMg₂Pn₂

To better understand the origin of anharmonic behavior in MgMg₂Sb₂ as well the discrepancies of thermal expansion and elastic moduli, a computational investigation of lattice dynamics is necessary. The calculation results shown below are done in collaborations with Guido Petretto, Gian-Marco Rignanese, Geoffroy Hautier at Université catholique de Louvain. The phonon properties and elastic constants were obtained from density functional theory (DFT) and density functional perturbation theory (DFPT) simulations using the ABINIT software package [134, 135, 136].

As shown in the stacked partial phonon density of states (PDOS) of MgMg₂Sb₂, CaMg₂Sb₂, and CaMg₂Bi₂ in Figure 3.6, the anion is responsible for the low frequency modes whereas the cation (*A*) and metal site (M=Mg(1)) vibrations are distributed in the mid- and high-frequency regime, respectively. Given that low-frequency acoustic vibrations dominate the lattice thermal transport, it is natural for one to expect that the cation species does not have much impact on the anharmonicity of these compounds, which is clearly not the case for AMg_2Pn_2 compounds.



Figure 3.6: The partial phonon density of states of $MgMg_2Sb_2$, $CaMg_2Sb_2$ and $CaMg_2Bi_2$ shows that the low-, mid-, and high-frequency regimes are dominated by displacements of the anions, *Pn*, cations, *A*, and metal site, M=Mg(1), respectively. Figure taken from W. Peng et al. [20].

The interactions between the cation and anion site are somehow having a major impact on the acoustic modes in MgMg₂Sb₂. A comparison of the phonon dispersions of MgMg₂Sb₂, CaMg₂Sb₂, and CaMg₂Bi₂ can demonstrate this point. The slopes of the transverse and the longitudinal acoustic branches represent the transverse and longitudinal phonon velocities, respectively. As shown from the black lines in Figure 3.7, a smaller slope as well as the "dips" around the *A*-, *L*-, and *M*-point on the transverse acoustic branch of MgMg₂Sb₂ set this compound as an outlier.



Figure 3.7: The black lines are the phonon dispersion of MgMg₂Sb₂, CaMg₂Sb₂, and CaMg₂Bi₂ at 0 K. The volume dependence of the phonon dispersions are shown through the thickness of the bands, with red and blue representing positive and negative values of mode Grüneisen parameters, respectively. Figure taken from W. Peng et al. [20].

As mentioned in Chapter 1, the frequency shift with the unit cell volume is defined as the mode Grüneisen parameter, representing local anharmonicity of a certain vibration mode.

$$\gamma_i = -\frac{V}{\omega_i} \frac{\delta \omega_i}{\delta V},\tag{3.1}$$

where V is volume and ω_i is the mode frequency. To quantify the degree of anharmonicity of each acoustic vibrational mode, the volume dependence of the frequency are also shown Figure 3.7 via the colored bands. The thickness of the bands represent the normalized mode Grüneisen parameters, from which *A*-, *L*-, and the *M*-point of the transverse phonons in MgMg₂Sb₂ are identified as modes with large Grüneisen parameters and therefore most unstable.

The red and blue color bands in Figure 3.7 represent the positive and negative values of mode Grüneisen parameters, respectively. A locally negative thermal expansion in a material with a

positive average thermal expansion coefficient is usually a result of a local metastable mode. This can be seen in Figure 3.8, the absolute values of the mode Grüneisen parameters of $MgMg_2Sb_2$ can reach as high as ~5 at the low-frequency regime, but the similar amount of positive and negative distribution of the value lead to a low average mode Grüneisen parameter. As a comparison, the acoustic mode Grüneisen parameters of $CaMg_2Sb_2$ only contain densely distributed positive values. A negative thermal expansion corresponds to a negative Grüneisen parameter value from definition, but it is contributing to the overall anharmonic phonon-phonon scattering. The large mode Grüneisen parameters of $MgMg_2Sb_2$ lead to high anharmonic phonon-phonon scattering rate, leading to its anomalously low lattice thermal conductivity.



Figure 3.8: The mode Grüneisen parameters as a function of frequency. Figure taken from W. Peng et al. [20].

One might notice that the thermal expansions of Mg₃Sb₂ and Mg₃Bi₂, in contrast to the drastic difference in elastic moduli, are only slightly higher compared to other AM_2X_2 compounds (Figure 3.5. While elastic moduli and speed of sound is related solely to the slope of acoustic branches upon Γ -point, the thermal expansion is an effect from the average of all the vibrational modes in both the acoustic and optics regimes. The negative mode Grüneisen parameters in the acoustic branches, for example, can lead to a lower average Grüneisen parameter and therefore reduced thermal expansion.

3.5 Breaking of Pauling's radii rule

Given the results above, it comes to the question of the fundamental reasons behind the unusual phonon properties of MgMg₂Sb₂. The cation size plays an important role in the stability of CaAl₂Si₂ structure type relative to other AM_2X_2 structures (i.e. BaCu₂S₂ and ThCr₂Si₂ structure types) [16, 153, 45]. In the sphere packing model proposed by Pauling for ionic solids, the smallest stable cation to anion radius for octahedral coordination is given by r_{cation} : $r_{anion} = 0.414$ [154].

Figure 3.9 shows the estimated r_{cation} : r_{anion} for AMg_2Pn_2 compounds, in which compounds with A=Mg have r_{cation} : r_{anion} below the stability limit, while compounds with larger cations are predicted to be stable in a six-fold coordinated environment. If the radii ratio is less than the minimum, the polyhedron is more likely to get distorted in order to depart the anions from touching. This distortion is featured in both MgMg_2Sb_2 and MgMg_2Bi_2, in which large octahedral bond angle variances of 26.53° and 36.01° can be observed. As a comparison, the octahedral bond angle variance in CaMg_2Sb_2 and CaMg_2Bi_2 is only 1.77° and 5.04°. The cation radii were from ref [155, 156] using the values for 2+ valence and 6-fold coordination. The anionic radii were estimated by taking the average A-Pn bond length and subtracting the corresponding cation radii, yielding $r_P = 1.93$ Å, $r_{As} = 2.07$ Å, $r_{Sb} = 2.23$ Å, and $r_{Bi} = 2.29$ Å.

3.6 Conclusion

Inherently low lattice thermal conductivity is typically associated with dense materials or compounds with lattice complexity. The unusually low lattice thermal conductivity of Mg_3Sb_2 , in contrast, shows that it is possible for a simple structure with low density to have high phonon scattering rates and low lattice thermal conductivity when structural instability is presented.

This was shown experimentally by the rapid decrease of the speed of sound and elastic moduli in Mg_3Sb_2 and Mg_3Bi_2 with increasing temperature, which is a direct consequence of the softening of the acoustic modes. By combining ab initio phonon calculations and high-temperature elasticity



Figure 3.9: For octahedral coordination (CN=6), Pauling's radius ratio rules predict a minimum stability limit of r_{cation} : $r_{anion} = 0.414$. For Ca, Sr, Eu, and Yb, this rule is satisfied. In contrast, the Mg cation is too small, which leads to a distorted octahedral environment and may be responsible for weak, anharmonic interlayer bonding. Figure taken from W. Peng et al. [20].

measurements, we showed that Mg_3Sb_2 and Mg_3Bi_2 are highly anharmonic, in contrast to the Caand Yb-containing AMg_2Pn_2 compounds investigated here. Large mode Grüneisen parameters, both negative and positive, were predicted in the acoustic branches of Mg_3Sb_2 and Mg_3Bi_2 , which are expected to have a large contribution to thermal transport.

We attribute this unique behavior to the small radii of Mg, which is undersized for the octahedrallycoordinated cation site. The poor fit of the Mg cation is suspected to lead to weak interlayer bonding, which was observed as the soft shear modes both experimentally and computationally. This behavior ultimately results in the highly anharmonic behavior of the acoustic branches and thus low thermal conductivity. These results suggest more broadly that soft shear modes resulting from undersized cations provide a potential path to low lattice thermal conductivity in ionic layered structures.

CHAPTER 4

LIMITS OF CATION SOLUBILITY IN AMg₂Sb₂ (A=Mg, Ca, Sr, Ba) ALLOYS

(Adapted from W. Peng et al. [25]. 2019. Limits of cation solubility in *AMg*₂Sb₂ (*A*= Mg, Ca, Sr, Ba) alloys. Materials (Basel, Switzerland), 12(4).)

4.1 Introduction

Given that the small cation size is the origin of anharmonicity in MgMg₂Sb₂ and the smallest cation that can occupy the octahedral site (*A*) of AMg_2Pn_2 is Mg, the next question is what is the impact of the cation size on solubility. Complete solubility has been reported in most AM_2X_2 isotructural alloys with the CaAl₂Si₂ structure type regardless of the substitution site [30, 31, 32, 28, 27, 28, 29, 28, 33, 34].

Thus far, much of the *zT* optimization of *n*-type MgMg₂Sb₂ has focused on alloying or doping on the anion site.(e.g. alloying Bi and doping Te on the Sb site of MgMg₂Sb₂). In contrast, for most of the previous work on the isostructural *p*-type AM_2X_2 compounds, alloying on the cation site (A = Mg, Ca, Sr, Ba, Sm, Eu, Yb) was a frequent approach to improve and optimize thermoelectric performance. For example, the mixed occupancy of A = Ca, Yb, and Eu in the AZn_2Sb_2 [27, 28, 31] and ACd_2Sb_2 systems [32, 28, 33, 29], and more recently in the AMg_2Pn_2 system, have been investigated of their effect on enhancing the thermoelectric performance [34, 111, 30].

Alloying on the cation site is appealing in two major perspectives. Recall $zT = \frac{\sigma^2 \alpha}{\kappa}T$. Previous evidence has shown that the site disorder often increases the ratio of electronic mobility to lattice thermal conductivity [30, 31, 32], which is beneficial to a higher *zT*. Equally importantly, alloying subtly affect the defect formation energy for cation vacancies, which is the dominant intrinsic defect in this structure type [157, 149]. This allows for optimization of the carrier concentration without introducing additional dopants.

Although isovalent alloying on the cation site in *n*-type $MgMg_2Pn_2$ has not yet been reported, one would expect that similar *zT* enhancements could be achieved through this strategy (assuming that *n*-type doping can still be achieved for $A \neq Mg$.)

In the present study, we reported the solubility limits of larger cations (e.g., Ca, Sr, Ba) alloyed with Mg on the *A* cation site in AMg_2Sb_2 compounds. Even though alloying on the *A* site seems to be an applicable approach to further optimize the thermoelectric properties of *n*-type MgMg_2Sb_2, the present study shows that the small ionic radius of Mg²⁺ leads to limited solubility of any cation larger than Ca.

4.2 Experimental

Table 4.1: The SPS temperatures of $(Ca_xMg_{1-x})Mg_2Sb_2$, $(Sr_xMg_{1-x})Mg_2Sb_2$, $(Ba_xMg_{1-x})Mg_2Sb_2$, (Mg_2Sb_2) , and $(Ba_xCa_{1-x})Mg_2Sb_2$.

$(Ca_xMg_{1-x})Mg_2Sb_2$	x=0	x=0.1	x=0.2	x=0.3	x=0.4	x=0.5	x=0.6	x=0.7	x=0.8	x=1
Temp (° C)	850	810	790	770	750	730	710	690	670	650
$(Sr_xMg_{1-x})Mg_2Sb_2$	x=0	x=0.1	x=0.2	x=0.4	x=0.6	x=0.7	x=0.8	x=0.9	x=1	-
Temp ($^{\circ}C$)	850	800	750	750	750	750	750	750	700	-
$(Ba_xMg_{1-x})Mg_2Sb_2$	x=0	x=0.3	x=0.5	x=0.8	x=0.9	x=1	-	-	-	-
Temp ($^{\circ}C$)	850	750	700	700	700	700	-	-	-	-
$(Ba_xCa_{1-x})Mg_2Sb_2$	x=0	x=0.1	x=0.3	x=0.5	x=0.7	x=0.9	x=1	-	-	-
Temp (° C)	650	700	700	700	700	700	700	-	-	-

Samples of $(Ca_x Mg_{1-x})Mg_2Sb_2$ (*x*=0, 0.1, 0.2, 0.3, 0.4, 0.5, 0.6, 0.7, 0.8, 1), $(Sr_x Mg_{1-x})Mg_2Sb_2$ (*x*=0, 0.1, 0.2, 0.4, 0.6, 0.7, 0.8, 0.9, 1), $(Ba_x Mg_{1-x})Mg_2Sb_2$ (*x*=0, 0.3, 0.5, 0.8, 0.9, 1), and $(Ba_x Ca_{1-x})Mg_2Sb_2$ (*x*=0, 0.1, 0.3, 0.5, 0.7, 0.9, 1) were synthesized via direct ball-milling of elements followed by spark plasma sintering (SPS). The corresponding stoichiometric elements (99.8% Mg shot, 99.5% Ca shot, 99% Sr chunk and 99%+ Ba rod, and 99.99% Sb from Alfa Aesar) were used. The details of balling and sintering can be found in Chapter 2. The maximum temperature and hold time used during spark plasma sintering are shown in Table 4.1. The densities of all the samples were obtained by measurement of mass and geometry, yielding at least 97% of the theoretical density. All of the alloyed samples were annealed after sintering to ensure homogeneity. The samples were wrapped in graphite foils and sealed in glass ampules under vacuum, which were then held at $500^{\circ}C$ for ten days. The samples were quenched to room temperature in air. X-ray diffraction was performed before and after annealing. The lattice parameters and $R_w p$ values from refinements of powder XRD patterns can be seen in the Appendix.

4.3 **Results and discussion**

Among AMg_2Sb_2 and AMg_2Bi_2 compounds, Mg is the smallest cation that can occupy the octahedral site (*A*). The ionic radius of Mg²⁺ in an octahedral environment is 0.72 Å, which is significantly smaller than that of Ca²⁺ (1.00 Å), Sr²⁺ (1.18 Å) or Ba²⁺ (1.35 Å) [155, 156]. The divalent rare-earth metals Sm, Eu, and Yb can also occupy the cation site, having ionic radii in between that of Ca and Sr. In the present study, alloyed samples in the series (Ca_xMg_{1-x})Mg₂Sb₂ (*x*=0, 0.1, 0.2, 0.3, 0.4, 0.5, 0.6, 0.7, 0.8, 1), (Sr_xMg_{1-x})Mg₂Sb₂ (*x*=0, 0.1, 0.2, 0.4, 0.6, 0.7, 0.8, 1), (Sr_xMg_{1-x})Mg₂Sb₂ (*x*=0, 0.1, 0.2, 0.4, 0.6, 0.7, 0.8, 0.9, 1), (Ba_xMg_{1-x})Mg₂Sb₂ (*x*=0, 0.3, 0.5, 0.8, 0.9, 1) were synthesized to investigate the phase stability when cations of increasingly divergent ionic radii occupy the *A* site in AMg_2Sb_2 . Note that Ca, Sr, and Ba are too large to occupy the tetrahedrally-coordinated *M* site of the AM_2X_2 compounds. Therefore, with increasing amount of Ca, Sr, or Ba, the observed mixed occupancy is solely presented on the *A* = Mg site, not on the *M* = Mg site.

For the $(Ca_xMg_{1-x})Mg_2Sb_2$ series, we find that the lattice parameters undergo a linear change with calcium alloying for *x*=0-1 (Figure 4.1a) and b)), showing that $(Ca_xMg_{1-x})Mg_2Sb_2$ forms a complete solid solution according to Vegard's rule [158]. In contrast, alloying Mg with larger cations (Sr or Ba) leads to phase separation into a Mg-rich phase and Mg-poor phase, indicating a eutectic-like phase diagram.

The lattice parameters of $(Sr_xMg_{1-x})Mg_2Sb_2$ and $(Ba_xMg_{1-x})Mg_2Sb_2$ are shown in Figure 4.1c)f). For the Sr-Mg alloy, a slight decrease in the lattice parameters *a* and *c* indicates a small (roughly 10%) solubility for Mg on the Sr site, but no solubility of Sr on the Mg site. In the Ba-Mg alloy,



Figure 4.1: a-b) For the $(Ca_xMg_{1-x})Mg_2Sb_2$ series, the lattice parameters *a* and *c* underwent a linear change with calcium alloying ratio. c-d) For the $(Sr_xMg_{1-x})Mg_2Sb_2$ series, the lattice parameters indicate a 10% solubility for Sr on Mg site, and no solubility for Mg on Sr site. e-f) For $(Ba_xMg_{1-x})Mg_2Sb_2$ series, the lattice parameters show no solubility between Ba and Mg on the cation site. Note that the MgMg_2Sb_2 phase can be observed from X-ray diffraction pattern when *x* = 0.8 in the Sr-Mg series and for *x* = 0.8 and 0.9 in the Ba-Mg series, but the peak intensities are too low for reliable refinement of lattice parameters. Figure taken from W. Peng et al. [25].

no solubility of Ba on the Mg site, or of Mg on the Ba site was observed. Note that the lattice parameters shown in Figure 4.1 were measured after annealing at $500^{\circ}C$ for ten days.



Figure 4.2: The linearly varying lattice parameters in the $(Ba_xCa_{1-x})Mg_2Sb_2$ alloy indicate complete solid solubility of this system. Figure taken from W. Peng et al. [25].

In the ionic metal model proposed by Hume-Rothery for substitutional solid solutions, differences in ionic radius, polarizability, structure, valence, and electronegativity are the key factors affecting the solubility [159, 160, 161]. Here, the atomic size difference is expected to play a dominant role in the stability [161, 162]. To estimate an upper limit for size mismatch on the cation site in the AMg_2Sb_2 compounds discussed here, we use the limit established by the partial solubility of the Sr-Mg system. For substitutions of a small cation by a larger one, the upper limit size mismatch is estimated by $(r_{Sr}-r_{Mg})/r_{Mg} = 64\%$. For substitutions of a larger cation by a smaller one (e.g., Mg on the Sr site) the limit is given by $(r_{Sr}-r_{Mg})/r_{Sr}=39\%$. To test these limits, the Ba_xCa_{1-x}Mg₂Sb₂ series was synthesized. The radii difference of Ba to Ca is 35% and Ba to Ca is 25.9%, both of which are smaller than the critical size difference. As shown by the linearly increasing lattice parameters in Figure 4.2, the Ba_xCa_{1-x}Mg₂Sb₂ alloy is found to be a complete solid solution, as predicted.

A survey of prior alloying studies of isotructural AM_2Pn_2 compounds suggests that the limit proposed here is likely to be generic to the cation-site alloying. As shown in Figure 4.3, the ionic radius ratio, $(r_1-r_2)/r_2$, for all possible combinations of cations where $r_1 > r_2$ are summarized here. The ionic radii were obtained from ref [155, 156] using the values for 2+ valence and 6-fold coordination. Square symbols indicate cation combinations that have been experimentally attempted, while circles represent our predictions. Indeed, this figure illustrates that it is only possible to exceed the predicted size mismatch limit by alloying with Mg on the cation site. All other combinations have sufficiently similar ionic radii (e.g., Ca-Yb [30, 31, 32, 28], Ca-Eu [27, 28, 29], Yb-Eu [28, 33], Mg-Yb [34].) to form complete solid solutions.



Figure 4.3: The cation radii difference of AM_2X_2 calculated from $(r_1-r_2)/r_2$ for all possible combinations of cations where $r_1 > r_2$. In each combination, the smaller species is listed first. Square symbols represent experimental observations, while circles represent predictions. The limited solubility in Sr/Mg (present study) and Sm/Mg (Ref [26]) alloys provide an approximate upper limit for cation radii mismatch. The complete solubility of Ca/Eu [27, 28, 29], Ca/Yb [30, 31, 32, 28], and Yb/Eu [28, 33] Mg/Yb [34] have been confirmed by prior studies. Figure taken from W. Peng et al. [25].

One notable exception in the literature is the $(Sm,Mg)Mg_2Sb_2$ system, investigated in 2006 by Gupta et al. [26]. Depending on synthesis conditions, alloying with Sm on the Mg site was shown to lead to either phase separation or to the formation of a superstructure in which Mg and Sm occupy alternating cation monolayers. The ionic radii of Sm^{2+} is similar to that of Sr^{2+} , which appears to be around the upper limit for ionic radius on the A = Mg site. However, no superstructure formation was observed after quenching from high temperature for any of our alloyed samples. The upper size limit established here may provide guidance for doping on the Mg site in MgMg_Sb_2. Recently,

La³⁺ and Y³⁺ on the Mg site were successfully used as an *n*-type dopants [163, 164]. The ionic radii of La³⁺ are similar to that of Yb²⁺, as are the radii of the majority of trivalent lanthanides, and Y^{3+} has a even smaller radii between Yb²⁺ and Mg²⁺. This suggests that the radii of these *n*-type dopants will not be a primary factor limiting their solubility. We note, however, that complete solid solubility would never be expected for alio-valent dopants in Zintl phases. Further, in alio-valent doping, the size of the dopant is only a minor factor. Other factors controlling solubility such as the valence of the dopant and the impact that the dopant has on the chemical potential of other types of defects.

4.4 Conclusion

In AM_2X_2 alloys, the existence of complete solid solubility is found to depend strongly on the difference between the ionic radii of the alloyed species. For mixed occupancy on the cation site, the partial solubility of Mg on the Sr site in the $(Mg_xSr_{1-x})Mg_2Sb_2$ series indicates that the size mismatch of Sr and Mg can be used as an approximate upper limit to guide future alloying and doping studies. Indeed, among all cations that are known to occupy the *A* site in AM_2X_2 compounds, we find that only Mg is sufficiently small to lead to phase separation, and only when alloyed with cations with radii equal to or larger than Sr (e.g., Ba, Eu, or Sm).

CHAPTER 5

HIGH-PRESSURE COMPRESSIBILITY, ANISOTROPY AND PHASE TRANSITIONS OF AM_2X_2 COMPOUNDS

(Adapted from M. Calderon and W. Peng et al. [165] and W. Peng et al. [6].

[165] Anisotropic structural collapse of Mg_3Sb_2 and Mg_3Bi_2 at high pressure. 2020. Chemistry of Materials (submitted).

[6] High-pressure behavior of layered AM_2X_2 compounds. 2020. (in preparation))

5.1 Introduction

High-pressure is an effective tool for the discovery of novel phases of known materials, synthesis of new compounds, as well as studying structure-property relationships. The most fascinating aspect of pressure is that it allows the variation of bonding environment without varying chemical compositions, which can avoid introducing new variables to the system and provides an opportunity for *in-situ* observations without disturbance [166].

In the past few years, the alloys between Mg_3Sb_2 and Mg_3Bi_2 have become increasingly interesting as *n*-type thermoelectric materials, with a thermoelectric figure of merit higher than any other isostructural Zintl phases as well as the traditional thermoelectric materials such as Bi_2Te_3 [167, 168, 120, 118]. One of the major reasons for such a high figure of merit of *n*-type Mg_3Sb_2 is because of their exceptionally low lattice thermal conductivity [169, 170, 171, 118, 67, 172]. The results described in Chapter 3 [20] have explained the anomalously low lattice thermal conductivity of Mg_3Sb_2 using a combination of resonant ultrasound spectroscopy and DFT phonon calculations, giving insights into the rapid softening of the speed of sound, soft shear acoustic modes, and large Grüneisen parameters originated from the loosely-bonded Mg-Sb octahedron [20].

As described in the previous sections, Mg₃Sb₂ and Mg₃Bi₂ are binary members of the CaAl₂Si₂

structure type ($P\bar{3}m1$), making them part of a broader family of AM_2X_2 Zintl compounds. Traditionally, AM_2X_2 compounds are described as layered structures [106, 102, 35], which consists of the covalent $[M_2X_2]^{2-}$ slabs and the ionically-bonded interlayer A^{2+} cations to provide the overall charge balance [115]. However, as suggested by the first-principles study by Zhang et al., this layered structure description is not suitable in the case of Mg₃Sb₂ and Mg₃Bi₂ [67] even though they share the same structural description, since the Mg(1)-Sb and Mg(2)-Sb bonds in Mg₃Sb₂ are quite similar with respect to the degree of charge transfer from Mg to Sb. The study further showed the calculated near-isotropic compressibility of Mg₃Sb₂ under pressure to prove this quasi-isotropic bonding prediction [67].

Thus far, much of the experimental studies related to the elastic behavior of the AM_2X_2 compounds were focused on the temperature-dependence. However, equally importantly, the pressuredependence of the same set of material can provide a different aspect of insights - but the data on this relationship is generally lacking. In fact, there have been only a handful of high-pressure studies of compounds in the CaAl₂Si₂ structure type, despite their long history and technological importance [173, 174, 175]. The understanding of lattice stability and bonding environment can benefit the understanding of fundamental thermoelectric properties such as lattice thermal conductivity, which can be studied with high-pressure experiments.

In addition to the ability to obtain anisotropic compressibility, for a given composition, pressure can simulate different bonding and atomic size conditions, which can be a leading factor for phase transitions. Specifically, the structure type of AM_2X_2 compounds is controlled partially by the cation to anion size ratio [16]. This generates an even higher tendency for the ambient phase to transform to other competing structures types when pressure is applied. In a study by Zevalkink et al. [174], SrAl₂Si₂ transformed from the CaAl₂Si₂-type to the ThCr₂Si₂-type structure at 3 GPa / 700 K. In a more recent study, pressure-induced polymorphism between the trigonal structure ($P\bar{3}m1$) and monoclinic structure was reported by Gui et.al [176], in which single-crystal CaMn₂Bi₂



Figure 5.1: Structure types formed by AM_2X_2 compounds with VEC = 16 include a) the trigonal CaAl₂Si₂ structure type ($P\bar{3}m1$), b) the orthorhombic BaCu₂S₂ structure type (Pnma), and c) the tetragonal ThCr₂Si₂ structure type (I4/mmm). d) The stability range of each structure can be delineated as a function of the atomic radii, $f = r_A/(r_M + 0.2r_X)$, while the polarity of the M-X bond is clearly not a deciding factor [35, 36, 37, 38, 39, 40, 41, 42, 43, 44, 45, 46, 47, 48, 49, 50, 51, 52, 53, 19, 54, 55, 56, 57, 58, 59, 60, 61, 62, 63, 64, 65, 66]. Figure taken from W. Peng et al. [16].

exhibits a displacive structural transition to a monoclinic structure $(P2_1/m)$ between 2-3 GPa at room temperature. Therefore, it is likely that the AM_2X_2 phases being selected for this elastic moduli study can also transform into polymorphic forms at high-pressure/temperature.

In the present study, we investigate the high-pressure behaviors experimentally using *in-situ* synchrotron X-ray diffraction of Mg₃Sb₂, Mg₃Bi₂, YbMg₂Bi₂, CaMg₂Sb₂, and EuAl₂Si₂ under different pressure and temperature conditions at pressures up to ~50 GPa, and temperatures up to 900 K, revealing disparities in the anisotropic compressibility of the ambient and high-pressure structures in Mg₃Sb₂, and the relative elastic anisotropy of the selected AM_2X_2 compounds. Phase transitions have also been observed for the first time in several compounds at different pressures and temperatures. This work provides direct experimental evidence of the bond strength and relative phase stability of AM_2X_2 compounds,

5.2 Phase transition of Mg₃Sb₂ and Mg₃Bi₂ at high-pressure

High-pressure powder diffraction experiments were performed to investigate the compressibility and possible high-pressure phase transitions of the Mg₃Sb₂ and Mg₃Bi₂. As shown in Figure 5.2, the ambient structure pattern shifted consistently with pressure up to \sim 7.8 GPa for Mg₃Sb₂ and \sim 4.0 GPa for Mg₃Bi₂. Above these two pressures, new peaks as well as abrupt changes of compressibility can be observed, indicating a pressure-induced phase transition.

To determine whether or not the phase transition is reversible, we performed a decompression experiment on Mg₃Bi₂. The ambient-pressure $P\bar{3}m1$ structure was completely recovered when the pressure was reduced (see Figure 5.3), indicating the non-quenchability of the high-pressure phase and confirming that the new peaks at high-pressure are not a result of decomposition.

The high-pressure structure was solved on a Mg₃Sb₂ single crystal. The synthesis of the single crystal and structural solution were done by our group member, Mario Calderon. The details of the single crystal diffraction and crystallographic data can be found in ref [165]. A structure solution for Mg₃Sb₂ at 7.8 GPa was reached in the monoclinic C2/m space group. As shown in Figure 5.4, the high-pressure monoclinic structure of Mg₃Sb₂ can be viewed as a distorted variant of the original trigonal structure at low pressure. The tetrahedrally coordinated Mg(2)₂Sb₂ slab in the ambient phase transforms into a layer with alternating tetrahedral and square pyramidal coordination environments at high pressure. The same C2/m structure solution provides a satisfactory fit for Mg₃Sb₂ and Mg₃Bi₂ powder data at high pressure, suggesting that both phases undergo the same high-pressure phase transition.

5.3 Compressibility and anisotropy of Mg₃Sb₂ and Mg₃Bi₂

To investigate the impact of cation size on the pressure response of AM_2X_2 structures, we first study the binary members of the AM_2X_2 family: the ambient- and high-pressure structures of Mg₃Sb₂ and Mg₃Bi₂. The pressure-dependence of the volume per formula unit for Mg₃Bi₂



Figure 5.2: Powder diffraction patterns of a) Mg_3Sb_2 and b) Mg_3Bi_2 at ambient temperature reveal the emergence of new peaks belonging to a high-pressure phase above 7.8 and 4.0 GPa respectively. Peak bars in blue correspond to the trigonal ambient and newly-discovered high-pressure phase. The X-ray wavelength for Mg_3Sb_2 and Mg_3Bi_2 is 0.4133 Å and 0.4340 Å, respectively. Figure taken from W. Peng et al. [6]

and Mg_3Sb_2 from powder and single crystal samples is shown in Figure 5.5, represented by circles and asterisks, respectively. The pressure-dependence of the powder and single crystal data


Figure 5.3: The reversibility of the phase transition was confirmed by decompressing the powder Mg₃Bi₂ sample. All of the original $P\bar{3}m1$ peaks re-emerged below 4.0 GPa. Figure taken from W. Peng et al. [6].



Figure 5.4: Comparison of the a) ambient $(P\bar{3}m1)$ and b) high-pressure (C2/m) structure of Mg₃Sb₂. The high-pressure monoclinic structure of Mg₃Sb₂ can be viewed as a distorted variant of the original trigonal structure at low pressure. c) The four Mg coordination environments in the high-pressure structure. Figure taken from W. Peng et al. [6].

 Mg_3Sb_2 agree well within the measured temperature range. The unit cell volume obtained from the powder data decreases abruptly above approximately 7.8 GPa and 4.0 GPa for Mg_3Sb_2 and Mg_3Bi_2 , respectively. Note that even though the the pattern at 7.8 GPa is shown in Figure 5.2, is not included here. The on-going phase transition made the pattern hard to be accurately refined.



Figure 5.5: The pressure-dependence of the volume per formula unit for Mg_3Sb_2 and Mg_3Bi_2 from powder and single crystal samples are represented by circles and asterisks, respectively. The zero-pressure bulk modulus, K_0 , of both the ambient- and high-pressure phases were obtained from a 2nd-order Birch-Murnaghan equation of state fit, represented by the solid lines. Figure taken from W. Peng et al. [6].

The bulk modulus at zero-pressure, K_0 , of the ambient- and high-pressure phase of each compound was fitted using the powder diffraction data with the 2nd-order Birch-Murnaghan equation of state, which are displayed as the solid curves in Figure 5.5. The V_0 for the ambient structures ($P\bar{3}m1$) were obtained via Rietveld refinement of the corresponding room temperature XRD pattern. For the high-pressure phases (C2/m), since V_0 is unknown, they were treated as an open fitting parameter in the Birch–Murnaghan EOS fit. The zero-pressure bulk modulus of AP- and HP-Mg₃Sb₂ is 38 GPa and 46 GPa, respectively, while the zero-pressure bulk modulus of AP- and HP-Mg₃Bi₂ is 37 GPa and 49 GPa respectively. The zero-pressure bulk moduli of AP-Mg₃Sb₂ and AP-Mg₃Bi₂ obtained in this study is comparable to the results of resonant ultrasound spectroscopy (36 GPa and 38 GPa, respectively) [20] and DFT (42 GPa and 37 GPa, respectively) [22]. The HP structures of both compounds are slightly stiffer than the AP structures, similar to the behavior reported for $CaMn_2Bi_2$ [176]. The exact fitted parameters from the 2nd-order Birch–Murnaghan EOS fit for all four phases are shown in Table A5 in the Appendix. The uncertainties of the pressure and lattice parameters is shown in Tables A6-A9 in the Appendix and the parameters of the 2nd-order and 3rd order Birch-Murnaghan fit can be found in Table A5 in the in the Appendix.



Figure 5.6: a) - b) A comparison of the unit cell of the $P\bar{3}m1$ (ambient) and C2/m (high-pressure) structures. The blue and grey lines are used to outline the ambient-pressure cell in both structure types, while the cyan lines represent the interatomic distance, x, which is equal to a and b in the $P\bar{3}m1$ symmetry. Here, we define a'=b' and c', and a' and g' to represent the primitive unit cell after it has lost its trigonal symmetry. Note that these parameters do not correspond to the true a, b, and c axes of the monoclinic C2/m unit cell. Normalized lattice constants of powder a) Mg₃Sb₂ and b) Mg₃Bi₂ before and after the phase transition. We have defined x as the [110] diagonal of the trigonal AP unit cell, as shown in the inset of panel. c) - d) A comparison of the normalized lattice constants and interatomic distance, x, of powder Mg₃Sb₂ and Mg₃Bi₂. The dashed lines in panel c) show the results of a prior computational study by Zhang et. al.[67]. Figure taken from W. Peng et al. [6].

The question of whether or not Mg_3Pn_2 (Pn = Sb, Bi) are layered structures has been under debate [80]. For a typical layered compound, the out-of-plane axis is significantly more compressible than the in-plane axis [177, 178, 179]. In fact, anisotropic compressibility is a key feature of layered structures, in particular those characterized by weak interlayer van der Waals bonding. However, even though Mg_3Pn_2 share the same structural features as the ternary layered AM_2X_2 compound family, the in-plane (Mg(2)-Pn) and out-of-plane (Mg(1)-Pn) bonding in Mg_3Pn_2 has been shown to be chemically similar despite their difference in the bonding environment. This was reported in a recent computational study of the pressure-dependence of AP-Mg_3Sb₂ by Zhang et al. [67] predicted nearly isotropic compressibility of the *a*- and *c*-axes. As shown in Figure 5.6 c), our experimental powder diffraction data (circle symbols) is consistent with Zhang's predictions (dashed lines) up to 8 GPa. Further, powder data for Mg_3Bi_2 up to 4 GPa (Figure 5.6 d)) reveals that the *a*-axis and *c*-axis of AP-Mg_3Bi₂ compress at near-identical rates, suggesting a even more isotropic behavior than AP-Mg_3Sb₂. The exact values and uncertainties of each powder data point in Figure 5.6 can be found in Tables A6-A9 in the Appendix.

When the ambient Mg₃*Pn*₂ structure ($P\bar{3}m1$) transforms to the high-pressure Mg₃*Pn*₂ structure (C2/m), the volume collapse is highly anisotropic with respect to the relative compression of the unit cell axes, as can be seen in Figure 5.6. At pressures above the phase transition, we continued to employ the unit cell axes from the trigonal $P\bar{3}m1$ phase to analyze the C2/m structure since the monoclinic cell is four-times the size of the trigonal cell and with axes re-defined in a different angle. The *c* lattice parameter is the out-of-plane direction, and the *a* lattice parameter is the in-plane directions. Here, we have newly defined *x* as the [110] diagonal of the trigonal unit cell, which is also an in-plane direction. In the $P\bar{3}m1$ structure, due to the fixed 120 degree angle, γ , between the *a* and *b* axes, the relationship x = a is fixed regardless of the pressure. From Figure 5.6, we can see that the phase transition in both compounds involves a collapse in the *c*- and *x*-direction, while *a* remains unchanged. The reduced symmetry of the C2/m structure allows the angle to deviate from 120 degrees, such that x < a after the phase transition. The drastic collapse along the *c*-direction

is a result of the transition of the distorted $[Mg(1)-Sb_6]$ octahedra to a square planar coordination environment. The experimental evidence of this statement can be found in the single crystal data in ref [165]. Furthermore, at pressures exceeding the phase transition, we find that the *c*-axis of the HP structure is more compressible than the *a*-axis, which is quite different from the isotropic compressibility of the AP structure.

Note that the nearly-isotropic in-plane and out-of-plane compressibility in ambient-pressure $P\bar{3}m1$ Mg₃*Pn*₂ (*Pn*=Sb, Bi) does not mean that the octahedral Mg(1)-*Pn* bonds are equal in strength to the tetrahedral Mg(2)-*Pn* bonds. The force constant calculations reported by J. Ding et al. have also shown that the octahedral Mg(1)-*Pn* bonds are significantly weaker than the tetrahedral Mg(2)-*Pn* bonds [180]. Experimentally, the single crystal data collected in the present study has also given similar result, in which the octahedral volume decreases more rapidly than the tetrahedral volume (The data can be found in the original paper.).

The relatively weak octahedral Mg(1)-Pn bonds help to explain the anomalously weak shear modulus and soft transverse phonon modes reported in Mg₃ Pn_2 compounds. These instabilities are in turn responsible for the low thermal conductivity and excellent thermoelectric performance of Mg₃ Pn_2 compounds [20, 180].

5.4 Compressibility and anisotropy of ternary *AM*₂*X*₂ compounds

Here, we show the pressure response of the unit cell volume and the lattice parameters of YbMg₂Bi₂, CaMg₂Sb₂, and EuAl₂Si₂, in comparison with the Mg₃Bi₂, Mg₃Sb₂ data with the same measurement and data processing approach in the prior section. The zero-pressure bulk modulus, K_0 of each compound were fitted with the 2nd-order Birch-Murnaghan equation of state, which are reproduced as solid curves shown in Figure 5.7 a). The K_0 obtained in this study for all compounds are comparable to those from high-temperature resonant ultrasound spectroscopy [20] and the DFT results (see table in Figure 5.7 b) [22].



Figure 5.7: a) The pressure-dependence of the unit cell volume for YbMg₂Bi₂, CaMg₂Sb₂, MgMg₂Bi₂, MgMg₂Sb₂, EuZn₂Sb₂, and EuAl₂Si₂. The solid lines are reproduced with the corresponding bulk modulus of each compound with the 2nd-order Birch-Murnaghan equation. b) A comparison of the bulk modulus obtained with different methods: Resonant ultrasound spectroscopy (RUS), density functional theory (DFT), and high-pressure X-ray diffraction.

From the RUS measurements, only the average bulk modulus in all directions is reflected. In contrast, the in-situ high-pressure measurements provide a convenient approach to track the progress of the relative compressibility along the a- and c-axis, which give information on which direction is

being affected the most. Here, we explored different types of AM_2X_2 compounds with the trigonal CaAl₂Si₂ structure type to study the relationship between anisotropy and the bulk modulus within this structure type.



Figure 5.8: a) The pressure-dependence of the c/a ratio for YbMg₂Bi₂, CaMg₂Sb₂, MgMg₂Bi₂, MgMg₂Bi₂, MgMg₂Sb₂, and EuAl₂Si₂. The slope of MgMg₂Bi₂ is significantly smaller compared to other compounds, which is an indication of a more isotropic behavior. b) The slopes of c/a are shown as vertical bars. The corresponding spatial dependence of Young's modulus from the Material-sProject.org is shown on top of each bar. The experimental anisotropy agrees qualitatively with the DFT results. Figure taken from W. Peng et al. [68].



Figure 5.9: a) Normalized lattice constants along a- or b-axis and b) c-axis for powder YbMg₂Bi₂, CaMg₂Sb₂, Mg₃Bi₂, Mg₃Sb₂, and EuAl₂Si₂. The discrepancies of the slope of a/a_0 between different compounds is significantly larger than that of c/c_0 . Figure taken from W. Peng et al. [68].

Figure 5.8 a) shows that the c/a ratio of all AM_2X_2 compounds are decreasing near-linearly with pressure but at different rates. Since all the compounds are in the same structure type, one might not

expect to see a major difference in the c/a trend with increasing pressure. However, as can be seen from Figure 5.8 a), the slope of the MgMg₂Bi₂ is almost zero, indicating a much higher isotropic behavior compared to other AM_2X_2 compounds. Our prior experimental study of the pressuredependence of Mg₃Sb₂ and Mg₃Bi₂ [165] observed near-isotropic compressibility of the *a*- and *c*-axes. The EuAl₂Si₂, in contrast, show a faster decreasing rate of c/a, which also corresponds with more anisotropic behavior. A faster rate suggests a bigger difference of the compressibility in the a-b plane compared to that along the c-axis, whereas a slower rate suggests a smaller difference, which in turn indicates a more isotropic behavior. To further illustrate this, Figure 5.8 b) shows the calculated spatial dependence of the Young's modulus from MaterialsProject.org database.

When we compare the c/a result with the bulk modulus values, a clear relationship can be found: A lower bulk modulus corresponds with more isotropic compressibility, whereas a higher bulk modulus corresponds with more anisotropic compressibility. This can be a result of less compressibility along the c-axis with decreasing anisotropy or more compressibility along the ab-plane with decreasing anisotropy. The normalized lattice constants, a/a_0 and c/c_0 (Figure 5.8), showed that the discrepancies of the slope of a/a_0 are significantly larger than that of c/c_0 . This indicates that the bond strength of M-X in the covalent slabs is a key factor in the anisotropy of the elastic moduli of AM_2X_2 compounds. The more ionic the M-X bond is, the weaker the covalent slab is, and therefore, the more isotropic the elastic modulus is.

5.5 High-pressure phase transition of ternary AM_2X_2

To investigate the relative stability of the AM_2X_2 compounds mentioned above, we kept adding pressure until the phase transition occurred. As shown in Figure 5.10, phase transitions of YbMg₂Bi₂, CaMg₂Sb₂, and EuAl₂Si₂ occured between 10.2 - 11.3 GPa, 14.1 - 19.1 GPa, and 13.7 - 16.0 GPa were observed, all of which were not previously reported. The peak bar for high-pressure phase of YbMg₂Bi₂ was made with the same structure as CaMn₂Bi₂ ($P2_1/m$) [176]. However, since we did not do single-crystal diffractions to confirm any of these three high-pressure compounds, we do



Figure 5.10: a) Powder diffraction patterns of $YbMg_2Bi_2$, b) $CaMg_2Sb_2$, and c) $EuAl_2Si_2$ with increasing pressure. Possible phase transitions were observed in all phases. The X-ray wavelength is 0.4133 Å for $YbMg_2Bi_2$ and $CaMg_2Sb_2$, and 0.4340 Å for $EuAl_2Si_2$. Figure taken from W. Peng et al. [68].

not know the exact high-pressure structures. As shown in Table 5.1, within selected the AMg_2Pn_2 (*Pn*=Sb,Bi) compounds, the transition pressure increases as the r_{cation} : r_{anion} increases, which is an indication of increasing phase stability.

Table 5.1: Transition pressure of AMg_2Pn_2 compounds and its relationship with the ionic radius. The transition pressure increases as the r_{cation} : r_{anion} increases.

	Mg ₃ Bi ₂	Mg ₃ Sb ₂	YbMg ₂ Bi ₂	CaMg ₂ Sb ₂
Transition pressure (GPa)	4.0 - 4.5	7.8 - 8.5	10.2 - 11.3	14.1 - 19.1
r _{cation} : r _{anion}	0.31	0.32	0.44	0.45

5.6 High-pressure high-temperature phase transition and intermediate phase exploration of EuAl₂Si₂ and SrAl₂Si₂

The CaAl₂Si₂ ($P\bar{3}m1$) structure type for AM_2X_2 compounds is one of the several structures that can be formed, which is also the structure type being discussed in the previous sections. Another structure type of AM_2X_2 compounds is the tetragonal ThCr₂Si₂ (I4/mmm). Studies have shown that smaller cations tend to form CaAl₂Si₂ structure type, whereas ThCr₂Si₂ structure is preferred when larger cations is presented [181, 45, 16]. The increase of pressure can result in an increase of coordination number (i.e. SiO₄ to SiO₆) [182]. The cation coordination is six in the CaAl₂Si₂ and eight in the ThCr₂Si₂ structure type, respectively. Pressure-induced polymorphism between these two structure types was first observed in ref [183], in which SrAl₂Si₂ transformed from CaAl₂Si₂ structure to ThCr₂Si₂ structure type above 3 GPa / 700 K with a multi-anvil press.

It has been pointed out by Huster et al. that a possible intermediate structure $BaCu_2S_2$ existed from a topological point of view [184], since there is no group-subgroup relation between the low-pressure trigonal phase and high-pressure tetragonal phase. However, no experimental studies have been done. In this study, our goal was to 1) collect in-situ X-ray diffraction data of $SrAl_2Si_2$ during heating to observe the transition process from $CaAl_2Si_2$ to $ThCr_2Si_2$ structure type. 2) Observe the phase transition of another $CaAl_2Si_2$ structure with big cations. For this purpose, we



Figure 5.11: a) Powder diffraction patterns of $EuAl_2Si_2$ at a fixed temperature around 600 °C. An abrupt phase transition from the trigonal ($P\bar{3}m1$) to tetragonal (I4/mmm) phase was observed. Note that the pressure shown on the right is the gas-membrane pressure. b) Powder diffraction patterns of $SrAl_2Si_2$ at a fixed pressure around 1.4 GPa. A gradual phase transition from the trigonal ($P\bar{3}m1$) to tetragonal (I4/mmm) phase was observed. Two-phase patterns can be spotted above ~700 °C. The X-ray wavelength is 0.3542 Å for both measurements. Figure taken from W. Peng et al. [68].

chose EuAl₂Si₂, as Eu has a similar ionic radius with Sr.

To explore the possible intermediate phase, we slowed down the reaction rate via two approaches. The first was to keep the system at a constant temperature, while gradually increasing pressure (Figure 5.11 a). Note that a high-enough temperature is kinetically necessary to activate the reaction due to the reconstructive nature of this phase transition. We have shown in Figure 5.10 c) that a different type of phase transition would take place when the system is not exposed to a high enough temperature. In this regard, we chose the temperature to be 600 - 700 °C for our first approach, which is high enough to drive the kinetics but low enough to allow a few pressure steps to observe the transition process. Two thermocouples were attached for temperature of 610 ± 10 °C. The thermocouple that was attached to the heater read a temperature 685 ± 10 °C. The ruby fluorescence spectrum is a function of temperature, which shifts and broadens as temperature increases. Using ruby as a pressure calibrate is not ideal at high-temperature. Therefore, the pressure of the gas-membrane instead of ruby pressure was used in Figure 5.11 a), which is positively correlated with the pressure of the DAC. Each data collection took approximately 5 minutes to complete.

The second approach is to keep the pressure fixed at around 1-2 GPa, while gradually increasing temperature, as shown in Figure 5.11 b). The room pressure reading was 1.4 GPa according to the ruby fluorescence. The pressure is expected to creep up a small amount with increasing temperature due to the thermal expansion of the pressure medium. One thermocouple was attached to the heater for temperature reading. Each data collection took approximately 5 minutes to complete.

As shown in Figure 5.11 a) the phase transition from trigonal (space group: $P\bar{3}m1$) to tetragonal EuAl₂Si₂ (space group: I4/mmm) was reported for the first time. The trigonal phase is a semiconductor, whereas the tetragonal phase is typically a superconductor. The successful observation of the high-pressure phase also represents the discovery of a new superconductor.

No intermediate phase was observed with both approaches. Figure 5.11 a) shows an abrupt transition between the two structures. In Figure 5.11 b), two-phase patterns can be spotted above \sim 700 °C, which can serve as further evidence that the reaction mechanism could be a fundamentally different pathway. However, we cannot exclude the possibility that an intermediate phase existed for a few seconds and we missed to capture it. Thus, we are planning to perform the same experiment at a higher energy beamline in the future, which can collect diffraction patterns in a matter of seconds. We also have an on-going collaboration with Dr. Stevanovic Vladan's group at Colorado School of Mines to computationally explore the transition pathway for a deeper understanding of this phase transition.

5.7 Concluding remarks

The present work observed the high-pressure phase transition of AM_2X_2 compounds in powder Mg_3Sb_2 , Mg_3Bi_2 , $CaMg_2Sb_2$, $YbMg_2Bi_2$, and $EuAl_2Si_2$ samples above 7.8 GPa, 4 GPa, 19.1 GPa, 11.3 GPa and 16.0 GPa, respectively. The reversibility of the phase transition was confirmed with powder Mg_3Bi_2 . Single-crystal diffraction at high pressure confirmed the monoclinic high-pressure structure (C2/m) of Mg_3Sb_2 and Mg_3Bi_2 , which is a distorted variant of the ambient-pressure structure. The transition to the high-pressure structure was shown to involve a highly anisotropic collapse of the lattice parameters along different crystallographic directions.

The anisotropy of the elastic moduli of the powder Mg_3Sb_2 , Mg_3Bi_2 , $CaMg_2Sb_2$, $YbMg_2Bi_2$, and $EuAl_2Si_2$ samples was compared within the ambient structures. Mg_3Sb_2 and Mg_3Bi_2 exhibit near-isotropic compressibility, whereas the ternary compounds are more anisotropic. When we compare the c/a decrease per GPa in powder Mg_3Sb_2 , Mg_3Bi_2 , $CaMg_2Sb_2$, $YbMg_2Bi_2$, and $EuAl_2Si_2$ samples, we found that the bond strength of *M*-*X* in the covalent slabs is a key factor in the anisotropy of the elastic moduli of AM_2X_2 compounds. The more ionic the *M*-*X* bond is, the weaker the covalent slab is, and therefore, more isotropic the elastic modulus is. The normalized lattice constants, a/a_0 and c/c_0 also confirmed that the discrepancies of the in-plane compressibility is significantly larger than that of the out-of-plane direction. Note that even though the ambient-pressure structures of Mg₃Sb₂ and Mg₃Bi₂ exhibit isotropic compressibility, analysis of the single crystal data shows that the octahedral Mg-*Pn* bonds does not have the same strength as the tetrahedral Mg-*Pn* bonds. The the octahedral ones are more compressible than the tetrahedral ones due to longer bond lengths.

For the high-temperature high-pressure phase transition of $EuAl_2Si_2$ and $SrAl_2Si_2$, no intermediate phase was observed, indicating that the reaction mechanism could be a fundamentally different pathway as Huster et al. predicted. However, we cannot exclude the possibility that an intermediate phase might existed for a few seconds and we missed to capture it. The phase transition from trigonal to tetragonal of $EuAl_2Si_2$ was reported for the first time. The successful observation of the high-pressure phase also represents the discovery of a new superconductor.

These high-pressure results provide a unique perspective and deeper understanding of the stability and bonding environment of AM_2X_2 compounds. We hope that this work will inspire the next generation of thermoelectric research to explore in the high-pressure dimension.

CHAPTER 6

LATTICE HARDENING DUE TO VACANCY DIFFUSION IN (GeTe)_mSb₂Te₃ ALLOYS

(Adapted from W. Peng et al. [71] "Lattice hardening due to vacancy diffusion in $(GeTe)_m Sb_2 Te_3$ alloys." 2019. Journal of Applied Physics, 126(5), 055106.)

6.1 GeTe-Sb₂Te₃ homologous series

To extend our understanding of the structure - property relationships in layered materials, we investigate the GeTe - Sb₂Te₃ homologous series. (GeTe)_mSb₂Te₃ alloys, also known as GST alloys, have been widely studied for nonvolatile memory storage applications due to their rapid and reversible transition between amorphous and crystalline phases with the accompanying changes in electrical and optical properties [185, 186, 187, 188, 189, 190, 191, 192, 193, 194]. The amorphous phase is achieved by rapid-quenching from the liquid state to the solid phase, whereas the cubic crystalline phase is obtained with a slower cooling rate. More recently, GST alloys have also attracted a great deal of excitement as *p*-type thermoelectric materials in the intermediate temperature range due to their low thermal conductivity, power factor up to 40 μ Wcm⁻¹K⁻², and impressive thermoelectric figure of merit (*zT*) in samples with optimized carrier concentrations [123, 195, 196, 197, 198, 199]. The highest *zT* values have been reported in Ge-rich alloys; J. Williams *et al.* reported a peak *zT* of 2.2 at 750 K in (GeTe)₁₇Sb₂Te₃ doped with an excess of 5% Sb [197], and Xu *et al.* achieved a *zT* of 2.4 at 773 K in undoped (GeTe)₁₇Sb₂Te₃ after extended annealing [198].

Compared to other other rock salt (e.g. GeTe, PbTe, and SnTe) and van der Waals (vdW) compounds (e.g. Bi_2Te_3 and Sb_2Te_3), one of fascinating features of GeTe-Sb₂Te₃ is their tunable layers. As shown in the phase diagram in Figure 6.1, up to about 7% of Sb2Te3 can be inserted into the GeTe structure within the solid-solution region to form the (GeTe)_m - Sb₂Te₃ homologous series.

Different thicknesses of layers in the building block can subtly affect the transport properties



Figure 6.1: The phase diagram of GeTe - Sb₂Te₃ [69].

within the different temperature range due to the complicated effect of phonon scattering, carrier concentration, interlayer bonding, defect layers, and phase transition temperatures. For example, in a study by Rosenthal et al. [200], they found that $(GeTe)_m - Sb_2Te_3$ compounds with high values of GeTe contents (i.e. high *m* values) typically have rather low *zT* values at low temperatures but reach the highest *zT* values in the high-temperature range. In contrast with the relatively simple scattering mechanism in most telluride thermoelectrics, GeTe-Sb₂Te₃ opens more opportunities to have the highest *zT* in the application range.

6.2 Structure and phase transitions of GeTe-Sb₂Te₃ alloys

In contrast to the amorphous - crystalline transition for memory applications, the phase transition for in this study and for thermoelectric applications in general is the rhombohedral to cubic transition within the solid-state.



Figure 6.2: a) Ambient-temperature rhombohedral structure of GeTe (R3m), b) Sb₂Te₃ (R3m), and c) (GeTe)_mSb₂Te₃ (R3m) with m = 3 used for illustrative purposes. The cation vacancies in (GeTe)_mSb₂Te₃ are relaxed into ordered layers, which resemble van der Waals gaps. Note that the hexagonal unit cell was employed here, with the c-axis perpendicular to the layers. d) At high temperature, (GeTe)_mSb₂Te₃ transitions to cubic symmetry with randomly distributed vacancies on the cation site. It can be visualized as stoichiometric occupancy of Ge, Sb, and vacancies on the cation site, while 100% of Te on the anion site [70]. Figure taken from W. Peng et al. [71].

As shown in Figure 6.2 a) and b), GeTe crystallizes in a distorted rocksalt structure with rhombohedral symmetry (R3m) at ambient temperature. At 643 K, GeTe transforms into the cubic rocksalt structure ($Fm\bar{3}m$) [72]. Pure Sb₂Te₃, in contrast, does not exhibit a temperature-dependent phase transition as a solid. It forms the layered tetradymite structure ($R\bar{3}m$) [201, 202], which is characterized by five-atom thick, Te-terminated covalent slabs separated by van der Waals (vdW) gaps, as shown in Figure 6.2 b).

 $(GeTe)_m Sb_2 Te_3$ alloys form a homologous series, which can be visualized as *m* layers of GeTe inserted into the covalent $Sb_2 Te_3$ slabs, expanding them into 2m+5 atomic-layer thick 3-D blocks [200, 203, 204, 205, 206], as illustrated in Figure 6.2 c). Like GeTe, GST alloys transform into the cubic rocksalt structure at high temperature. However, unlike the rapid displacive phase transition

found in pure GeTe, the phase transition in $(GeTe)_mSb_2Te_3$ alloys is reconstructive in nature, necessitating significant cation diffusion [207, 208, 209, 200, 198]. As illustrated in an *in* – *situ* study by Xu *et al*. [198], the vdW gaps in $(GeTe)_{17}Sb_2Te_3$ at low temperature can be thought of as ordered layers of cation vacancies, which spontaneously diffuse into the surrounding matrix with increasing temperature. This behavior is reversible; upon cooling, the vacancies re-order into layers, and the expanded tetradymite-like structure is recovered. The exceptional mobility of the cation vacancies in GST alloys, as well as the flexibility in spacing between vacancy layers has been demonstrated by several recent studies [205, 206].

6.3 Experimental

6.3.1 Synthesis

Samples of $(GeTe)_{17}Sb_2Te_3$, GeTe, Sb_2Te_3 , and Bi_2Te_3 were synthesized starting with stoichiometric quantities of Ge (zone-refined ingot, 99.9999%), Sb (6mm shot, 99.999%), Bi (granules, 1-2 mm, 99.997%) and Te (chunk, 99.999%) from Alfa Aesar. GeTe, Sb_2Te_3 , and Bi_2Te_3 were synthesized via direct ball-milling of the elements followed by spark plasma sintering (SPS). The powder was heated to 738 K in 5 minutes and held at the target temperature for 5 minutes for GeTe, to 738 K in 10 minutes and held for 15 minutes for Sb_2Te_3 , and to 723 K in 10 minutes and held for 5 min for Bi_2Te_3 under a uni-axial pressure of 31 MPa using a Dr. Sinter SPS-211LX spark plasma sintering (SPS) press. (GeTe)₁₇Sb₂Te₃ was synthesized by our collaborator, Jared Williams, with a slightly different approach (see Chapter 2 for details). The densities of all samples were obtained via measurements of mass and geometry, yielding at least 96% of the theoretical densities. Phase purity and compositions of the samples was confirmed via peak matching within the ICSD database, in which no impurity phase could be observed. More experimental details can be found in Chapter 2.

6.3.2 High-temperature resonant ultrasound spectroscopy

The temperature-dependent elastic moduli and speed of sound for the selected compositions were obtained by resonant ultrasound spectroscopy (RUS) [24]. The elastic moduli were measured in ~ 10 K intervals from room temperature up to 723 K for (GeTe)₁₇Sb₂Te₃, 530 K for Bi₂Te₃, and 600 K for Sb₂Te₃ and GeTe. The signal was lost for the GeTe sample above 600 K, so the elastic moduli above phase transition were not captured. More details of the high-temperatur RUS setup can be found in Chapter 2.

6.3.3 High-temperature X-ray diffraction

Thermal expansion of $(GeTe)_{17}Sb_2Te_3$ and Sb_2Te_3 were measured from 303 K to 673 K and 303 K to 573K, respectively, using a Rigaku Smartlab X-ray diffractometer equipped with the Rigaku HT1500 high-temperature stage. The samples showed no hysteresis upon further thermal cycling after the first cycle, in which a reversible phase transition between the rhombohedral and cubic rocksalt structure could be observed. More details can be found in Chapter 2.

6.4 Structural evolution with increasing temperature

High-temperature powder X-ray diffraction was used to investigate the evolution of the lattice parameters with increasing temperature in $(GeTe)_{17}Sb_2Te_3$ and Sb_2Te_3 . These results are compared with the corresponding data for GeTe from the previous literature [72]. The $(GeTe)_{17}Sb_2Te_3$ patterns share nearly the same peak positions both in the rhombohedral phase and in the cubic phase as the corresponding structure of GeTe without any superstructure peaks. The absence of a well-defined superstructure in the alloyed composition has been observed in several previous reports [198, 200]. Even though the vacancy layers (*i.e.*, van der Waals gaps) in $(GeTe)_mSb_2Te_3$ alloys are nominally spaced at 2m+5 atom intervals, the layer thickness exhibits a large degree of variability, which is dependent on *m* and the processing route. Samples with larger *m* and faster quenching lead to more variability. However, even afer two weeks of annealing, some variability of *m* can still be seen. Therefore, the GeTe unit cell was used for the refinement of the (GeTe)_{17}Sb_2Te_3



Figure 6.3: a) The c/a ratio, b) lattice parameter, a, and c) lattice parameter, c, of $(GeTe)_{17}Sb_2Te_3$ and GeTe. The GeTe data is taken from ref. [72]. A reversible phase transition from a rhombohedral structure (R3m) to cubic rocksalt $(Fm\bar{3}m)$ at roughly 623 K is observed in both materials. Figure taken from W. Peng et al. [71].

patterns.

Note that the hexagonal instead of rhombohederal notation are employed for all three compounds for the convenience of symmetry. As shown in Figure 6.2, with the hexagonal notation, the c-axis is perpendicular to the layers, while the a- and b-axes are parallel to the layers.

First compare the unit cell volume (per formula) of GeTe and the $(GeTe)_{17}Sb_2Te_3$. As shown in Figure 6.3 b) - c), the unit cell of $(GeTe)_{17}Sb_2Te_3$ is larger along the a-axis and smaller along the c-axis compared to GeTe in the entire temperature range below the phase transition. The expansion in the a-b plane for the $(GeTe)_{17}Sb_2Te_3$ is due to the substitution of the larger Sb cations on the Ge site, while the contraction along the c-axis is caused by the cation vacancy layer perpendicular to c. A reversible phase transition from the rhombohedral structure (R3m) to the cubic rocksalt structure $(Fm\bar{3}m)$ occurs in both GeTe and $(GeTe)_{17}Sb_2Te_3$ at ~623 K. The data in Figure 6.3 were measured during heating of the sample, the cooling data in Figurexx shows that the phase transition is fully reversible.

As shown in Figure 6.3 a), the c/a ratio, provides a convenient approach to track the progress of the phase transition, since cubic symmetry is achieved when $c/a = 2\sqrt{3/2}$. As the temperature approaches the transition to the cubic structure, GeTe has been shown previously to expand in the a-direction, while contracting in the c-direction, corresponding to the gradual opening of the rhombohedral angle [72]. Since the same rhombohedral-to-cubic phase transition occurs in (GeTe)₁₇Sb₂Te₃, one might expect to see a similar contraction along the c-axis approaching the transition temperature. However, as shown in Figure 6.4 b), the thermal expansion of the c-axis in (GeTe)₁₇Sb₂Te₃ is almost zero. This suggests that vacancy re-ordering is playing a role. In the high-temperature cubic phase, symmetry dictates that the cation vacancies be randomly dispersed. However, the transition from ordered vacancies to random vacancies cannot occur instantaneously at the transition temperature. Instead, the vacancy diffusion occurs gradually as temperature increases,



Figure 6.4: Normalized change in a) unit cell volume and b) lattice parameter along c-axis of $(GeTe)_{17}Sb_2Te_3$, GeTe, and Sb_2Te_3 . Data for GeTe was taken from ref. [72]. Similar volumetric thermal expansions is observed for the three compounds, despite drastic differences in the c-axis thermal expansion. Figure taken from W. Peng et al. [71].

leading to a gradual expansion of the structure along the c-axis.

To estimate the extent of vacancy re-ordering that occurs between 300 K and 620 K, we look to the c/a ratio. In the case of randomly dispersed vacancies, the c/a ratio in $(GeTe)_{17}Sb_2Te_3$ should be identical to that of GeTe, assuming that the rhombohedral distortion lessens at the same rate in both compounds and the size effect of the random vacancies dispersed into the structure can be ignored

due to their small amount. And indeed, with increasing temperature, we see that the c/a ratio of $(GeTe)_{17}Sb_2Te_3$ and GeTe slowly converge as we approach the phase transition temperature, indicating that the vacancy layers have mostly disappeared. Above the phase transition, the c/a ratio is necessarily identical in both compounds due to the cubic symmetry. The magnitude of the *a* and *c* in both compounds in the cubic symmetry are also similar, since the size-effect of the randomly distributed cation vacancies is mostly cancelled out by the partial substitution of the larger Sb on the Ge site.

For comparison, Figure 6.4 a) - b) shows the temperature-dependent unit cell volume and lattice parameter, c, of GeTe, Sb₂Te₃, and (GeTe)₁₇Sb₂Te₃, normalized to the room temperature values. Although the c-axis of Sb₂Te₃ expands more rapidly with increasing temperature, the volumetric thermal expansion of all three compounds is quite similar. The lattice parameters a and c for Sb₂Te₃ are shown separately in Figure 6.6.



Figure 6.5: a) A two-step phase transition can be observed during the first heating process. The cubic rocksalt structure transforms to a rhombohedral structure at 523 K, and then to a cubic rocksalt structure at 623 K. A single phase transition to rhombohedral structure occurred during the cooling process. b) The 2nd thermal cycle shows a reversible phase transition between the rhombohedral and cubic rocksalt structure around 623 K. Figure taken from W. Peng et al. [71].

Note that the as-synthesized sample need to be annealed in order to show the reversibility. Upon

cooling during the spark plasma sintering (SPS) process, the $(GeTe)_{17}Sb_2Te_3$ sample was essentially "quenched" in a meta-stable cubic phase $(Fm\bar{3}m)$ due to relatively slow kinetics of the diffusion process, as described in ref. [123]. During the first post-SPS heating cycle, a twostep phase transition can be observed: first, a phase transition from the metastable cubic rocksalt to the stable rhombohedral (R3m) structure occurs beginning at around 523 K (given sufficient time, annealing at a lower temperature would presumably have the same effect). The rhombohedral structure undergoes another phase transition to the cubic rocksalt structure at 623 K. During cooling, only one phase transition to the rhombohedral structure at 623 K occurred (Figure 6.5 a). The sample showed no hysteresis upon further thermal cycling after the first cycle, in which a phase transition between the rhombohedral and cubic rocksalt structure around 623 K can be observed both during heating and cooling, indicating stable structures and reversible transitions of (GeTe)₁₇Sb₂Te₃ (Figure 6.5 b).



Figure 6.6: a) Lattice parameter a, and b) lattice parameter, c of Sb₂Te₃ measured as a function of temperature. Figure taken from W. Peng et al. [71].

6.5 Temperature-dependent elastic moduli

Figure 6.7 a) - b) compares the calculated and experimental Young's modulus of polycrystalline rock salt compounds at room temperature. Density functional theory (materialsproject.org [22]), shown as the vertical bars, predicts i) that the distorted rock salt structure is softer than the cubic

rock salt structure, and ii) that the cubic structure becomes softer as we proceed to larger cations with longer bonds (consistent with room temperature experimental data for SnTe and PbTe from ref. [74, 73, 9, 10]). The average Ge-Te bond length in the distorted structure is longer than that in the cubic phase, leading to an overall weaker Young's modulus in comparison with the cubic structure. The distorted rock salt structure is also anisotropic (illustrated by the calculated 3D compressibility surfaces [22]) as a result of the distortion of the Ge position, which has three longer and three shorter Ge-Te bonds. This in turn leads to weaker bonds in the *c*-direction, and stronger bonding in the a - b plane. Note that RUS measurements using polycrystalline samples do not capture the anisotropy of rhombohedral GeTe, but they do confirm the prediction of softer Young's modulus compared with cubic compounds SnTe and PbTe.

A comparison of cubic PbTe and SnTe with rhombohedral GeTe reveals a slower rate of softening in GeTe (Figure 6.7 b)). In the absence of phase transitions, the rate of softening of a material is typically correlated with the degree of anharmonicity of the acoustic phonons [20, 17], which is usually correlated with thermal expansion. Structural changes, however, can have a greater impact on the elastic moduli than thermal expansion. In the case of GeTe, there is a phase transition from a distorted rocksalt structure to a cubic rocksalt structure. We attribute this anomalous slow softening to the gradual decrease in the rhombohedral distortion in GeTe with increasing temperature. In the current study, we did not obtain data for GeTe above the phase transition due to limitations of our RUS equipment, however, we would predict a step-like stiffening of the Young's modulus upon the transition to cubic symmetry. This step-like stiffening was observed in a previous investigation of single crystalline Ge_{0.2}Sn_{0.8}Te at the phase transition at 220 K [210].

We next turn to a comparison of the temperature-dependent shear and Young's moduli (*G* and *Y*, respectively) of GeTe, $(GeTe)_{17}Sb_2Te_3$, and Sb_2Te_3 (see Figure 6.8 a) - b). Although all three compounds have similar rates of volumetric thermal expansion, as established in Figure 6.4 a), they exhibit drastic differences in the temperature dependence of the elastic moduli. For comparison,



Figure 6.7: a) A comparison of the Young's modulus, Y, of cubic and distorted rock salt compounds shows that the distorted structure is softer. Bars show calculated data from ref. [22] and symbols are experimental data (present work: \star , literature data: \Box [73], \diamond [10], \triangle [74], \circ [9]). 3D surfaces show the compressibility of the two structure types [22]. b) The temperature dependence of Y for GeTe [present work], SnTe[10], and PbTe [74] show the slower rate of softening in GeTe. Figure taken from W. Peng et al. [71].

we also measured the high-temperature elastic moduli of Bi_2Te_3 , reported here for the first time. The rate of softening in Sb_2Te_3 and Bi_2Te_3 , which does not exhibit a phase transition at high temperature, is comparable to that of other thermoelectric materials such as PbTe [9] and SnTe [10].

The $(GeTe)_{17}Sb_2Te_3$ alloy is unique in that the elastic moduli actually harden gradually with increasing temperature. This gradual hardening is followed by an abrupt increase of the elastic moduli



Figure 6.8: The temperature dependence of the normalized a) Young's modulus, *Y*, and b) shear modulus, G, for GeTe, $(GeTe)_{17}Sb_2Te_3$, Sb_2Te_3 , and Bi_2Te_3 . All compounds besides $(GeTe)_{17}Sb_2Te_3$ soften with increasing temperature. c) The value of the Young's and shear moduli of $(GeTe)_{17}Sb_2Te_3$ across phase transition. Figure taken from W. Peng et al. [71].

at the transition from rhombohedral to cubic symmetry (Figure 6.8 c). Finally, at temperatures above the phase transition, softening of the elastic moduli can be observed, which is expected for

most compounds due to thermal expansion. Even though the abrupt increase in Y and G at the phase transition was expected, and is consistent with previously reported behavior for $Ge_{0.2}Sn_{0.8}Te$ as well as the *presumed* behavior of GeTe. The gradual hardening of $(GeTe)_{17}Sb_2Te_3$ leading up to the phase transition is unusual.

We attribute the gradual hardening of (GeTe)₁₇Sb₂Te₃ to two independent factors. The first is the gradually decreasing rhombohedral distortion with increasing temperature. As mentioned in the previous paragraphs, this effect also contribute to the relatively slow softening rate of GeTe compared to compounds with similar thermal expansion. The second and more significant effect is the dynamic reconfiguration of the cation vacancies with increasing temperature, which uniquely present in the alloy. When the vacancies are ordered into layers, the neighboring slabs are connected by weak Te-Te van der Waals interactions. Whenever a vacancy diffuse onto a cation site, a cation simultaneously diffuse onto the vacancy site. These local bondings formed between the cation and Te are stronger than the initial weak Te-Te van der Waals bonds. As temperature increases, more and more cations diffuse onto the vacancy sites, leading to stronger and stronger bonding between the slabs. This gradual diffusive re-ordering of the vacancies lead to the gradual stiffening of the lattice. The randomly distributed vacancies represent only 5% of the cation sites, which is not enough to have significant impact on the overall stiffness. Upon the phase transition, the elastic moduli of (GeTe)₁₇Sb₂Te₃ has an abrupt increase as the vacancy layers diminish. The behavior of the elastic moduli in (GeTe)₁₇Sb₂Te₃ is reversible, showing the same temperature-dependence during heating and cooling.

The lattice hardening due to the phase transition in $(GeTe)_{17}Sb_2Te_3$ leads to increasing speed of sound as a function of temperature (shown in Figure 6.9), in stark contrast to most solids. While the impact of lattice hardening is not significant enough to lead to increasing lattice thermal conductivity with temperature, since the the inverse temperature dependence of Umklapp scattering is simply too strong, it likely leads to a flatter lattice thermal conductivity. The relatively flat lattice



Figure 6.9: a) Longitudinal speed of sound and b) Transverse speed of sound of $(GeTe)_{17}Sb_2Te_3$, Sb_2Te_3 , GeTe, and Bi_2Te_3 measured from room temperature up to 600 K via resonant ultrasound spectroscopy. c) Longitudinal and shear speed of sound of $(GeTe)_{17}Sb_2Te_3$ measured from room temperature across phase transition. Figure taken from W. Peng et al. [71].

thermal conductivity of the $(GeTe)_{17}Sb_2Te_3$ sample used for this study is shown in Figure 6.10 c).

The stiffening of the elastic moduli with increasing temperature is expected to be a general feature of all GeTe-Sb₂Te₃ as well as GeTe-Bi₂Te₃ alloys [211], as long as they exhibit a rhombohedral-to-cubic transition involving vacancy diffusion. Further, we expect the stiffening rate to be more pronounced with increasing vacancy ratio in the structure (i.e., with decreasing value of m.)

Table 6.1: Experimental elastic moduli and speed of sound at 300 K for $(GeTe)_{17}Sb_2Te_3$, Sb_2Te_3 , GeTe, and Bi_2Te_3 samples measured using resonant ultrasound spectroscopy.

	$(GeTe)_{17}Sb_2Te_3$	Sb ₂ Te ₃	GeTe	Bi ₂ Te ₃
Young's modulus (GPa)	55	45	43	47
Shear modulus (GPa)	22	18	17	18
Longitudinal speed of sound (m/s)	3300	2950	2980	2800
Transvere speed of sound (m/s)	1900	1750	1740	1550
Theoretical density (g/cm ³)	6.09	6.12	5.91	7.47

6.6 Conclusions

In the current study, we have combined high-temperature X-ray diffraction and elasticity measurements to reveal anomalous lattice hardening in $(GeTe)_{17}Sb_2Te_3$, despite its positive thermal expansion coefficients. A positive thermal expansion coefficient is usually associated with lattice



Figure 6.10: The thermoelectric properties of the $(GeTe)_{17}Sb_2Te_3$ samples used in this study: a) Total thermal conductivity, lattice thermal conductivity, and electrical thermal conductivity; b) resistivity; c) Seebeck coefficient; and d) thermoelectric figure of merit. In contrast to the expectation of a decreasing trend of lattice thermal conductivity, as it is the case for most materials, the lattice thermal conductivity of $(GeTe)_{17}Sb_2Te_3$ remains roughly unchanged with increasing temperature before the phase transition. Figure taken from W. Peng et al. [71].

softening, since bonds weaken as they become longer. The elastic moduli of GeTe, Sb_2Te_3 and Bi_2Te_3 , in contrast, showed the expected softening behavior with increasing temperature. The unusual behavior of $(GeTe)_{17}Sb_2Te_3$ is assumed to originate from the gradual diffusion of vacancies that accompanies the phase transition from a layered structure to the cubic rocksalt structure. As the the ordered layers of vacancies switched sites with the cations, the attractions between neighboring layers presumably increases, which in turn stiffens the lattice. We expect this behavior to be a

generic feature of all GeTe-Sb₂Te₃ as well as GeTe-Bi₂Te₃ alloys, playing a fundamental role in the thermal conductivity in this important class of thermoelectric materials.

CHAPTER 7

CONCLUDING REMARKS

This work was focused largely on understanding the elastic moduli of two classes of layered thermoelectric materials: AM_2X_2 Zintl phases and GeTe - Sb₂Te₃ alloys. We learned that the stability of the bond controls the elastic moduli and anharmonicity, which is partially determined by the size ratio between the cation and anion, bond length, and bond type in the structure. In addition, approaching phase transitions have an impact on the elastic modulus of materials. In Figure 7.1, the data measured in this study is added to the literature temperature-dependent elastic moduli data of typical thermoelectric materials to illustrate the relationship between structure and elastic modulus.

In general, compounds with octahedral coordination, such as tetradymites and rock salts, are softer than those with tetrahedral coordination. This is because the bonds of a close-packed octahedron are typically longer than a close-packed tetrahedron according to Pauling's close-packed rule. In the case of AM_2X_2 compounds, the alternating layers of tetrahedral and octahedral coordination may explain their intermediate to low moduli. Within the same structure type, the differences in atomic sizes are the determining factor of the differences in the bond length and therefore have an impact on the stiffness of compounds. Among AM_2X_2 Zintls, for example, the Bi-based compounds are generally softer than Sb-analogues due to the larger size of Bi.

7.1 Possible explanations for the large anharmonicity of Mg₃Sb₂

 Mg_3Sb_2 and Mg_3Bi_2 , as outliers of the AM_2X_2 compounds, have a similar stiffness as the tetradymites structures due to their anomalously low shear moduli due to the small size of Mg. One of the main conclusions from our study of the elastic properties of AM_2X_2 compounds is that Mg_3Sb_2 and Mg_3Bi_2 have large anharmonicity and anomalously low lattice thermal conductivity. This finding is further confirmed by the comparison of Young's modulus, softening rate, thermal



Figure 7.1: Temperature-dependence of the Young's modulus, Y, of the selected thermoelectric material [7, 8, 71, 71, 9, 10, 75]. AM_2X_2 compounds, the alternating layers of tetrahedral and octahedral coordination may explain their intermediate moduli. Mg₃Sb₂ and Mg₃Bi₂, as outliers of the AM_2X_2 compounds, have a similar stiffness as the tetradymites structures. Figure taken from W. Peng et al. [6]

expansion, and mode Grüneisen parameters in the previous chapters. One possible explanation is the poor fit of the cation in the octahedral environment. In the sphere packing model proposed by Pauling for ionic solids, the smallest stable cation to anion radius for octahedral coordination is given by r_{cation} : r_{anion} =0.414 [154]. Figure 3.9 shows that for all the AM_2X_2 compounds, A = Mgones are the only compounds that have r_{cation} : r_{anion} below the stability limit, while compounds with larger cations are predicted to be stable in a six-fold coordinated environment. This results in large octahedral bond angle variances in Mg₃Sb₂ and Mg₃Bi₂ in order to depart the anions from touching and may explain why only compounds with A = Mg (not those with A=Ca, Sr, Yb, Eu) exhibit anomalous thermal properties. The unstable octahedra lead to a low shear modulus in Mg₃Sb₂ and Mg₃Bi₂. Another possible explanation is that the Mg(2)-Sb ionic bond is weaker than a typical M - X covalent bond in AM_2X_2 compounds, which leads to an overall less stable "covalent" slabs and lower in-plane thermal conductivity in Mg₃Sb₂. This idea was first reported by a DFT study by Zhang et. al [67]. Due to the high electronegativity of Mg compared to other possible element choices for the *M*-site, the Mg(2)-Sb bond is showing a stronger ionic character compared to most M-X bonds in a AM_2X_2 compound (e.g. CaZn₂Sb₂). Our results provide experimental evidence for this prediction. The *in-situ* high-pressure synchrotron X-ray diffraction showed that the bond strength of M-X in the covalent slabs is a key factor in the anisotropy of the elastic moduli of AM_2X_2 compounds. The more ionic the *M*-X bond is, the weaker the covalent slab is, and therefore, the more isotropic the elastic modulus is. A more isotropic elastic modulus results in a lower average elastic modulus and lower average lattice thermal conductivity.

7.2 Lattice hardening of GST alloys

Even though the phase transition of GST alloys has been previously investigated with *in-situ* TEM, the elastic moduli during the phase transition were reported for the first time in this study. Unlike most compounds that soften with increasing temperature, the elastic moduli of $(GeTe)_{17}$ - Sb₂Te₃ stiffen with increasing temperature before the phase transition. This is the only type of thermoelectric material that has observed to have this behavior due to a non-defect reason. Further, we observed the flattening of lattice thermal conductivity of $(GeTe)_{17}$ - Sb₂Te₃ as a result of the lattice stiffening. We concluded that the unusual behavior of $(GeTe)_{17}$ Sb₂Te₃ is originated from the gradual diffusion of vacancies that accompanies the phase transition from a layered structure to the cubic rocksalt structure. This behavior is expected to be a generic feature of all $(GeTe)_m$ Sb₂Te₃ and $(GeTe)_m$ Bi₂Te₃ alloys. Future works can be directed at investigating the temperature-dependent elastic moduli of other types of GST compounds to exploit the relationship between the rate of lattice stiffening with the thickness of the layer, as well as the impact of lattice stiffening on lattice thermal conductivity.

7.3 **Opportunities and challenges**

Temperature-dependent resonant ultrasound spectroscopy and *in-situ* high-pressure X-ray diffraction are powerful tools for the characterization of elastic properties and investigation of anharmonicity of materials. Few works have been directed at measuring and utilizing the elastic properties in the thermoelectric community so far. In addition, high-pressure characterization opens a new dimension to discover the unknown phase transitions of thermoelectrics. Combined with the property measurements through the phase transition, direct observation of the structure-property relationship can be achieved. Even though elastic moduli alone cannot be independently used predict the thermoelectric performance of materials, they can provide guidance for systematically searching high zT materials with low thermal conductivity wit DFT calculations. The main challenge of the ultrasound measurement is the limitations on the geometry of the sample and difficulty in solving the spectrum for low symmetry structures. Besides, the speed of sound and elastic moduli only contain information of the lowest frequency phonons. A further area of opportunity is to combine elasticity measurements with other in-situ techniques. For example, the frequencies of selected optical modes can be investigated via Raman spectroscopy and inelastic scattering can be used to target at any desired phonon mode.
APPENDIX

Table A1: Lattice parameters and R_{wp} values from refinements of powder XRD patterns of $(Ba_xCa_{1-x})Mg_2Sb_2$.

	After SPS		After annealing 10 days			
Х	a	с	R_{wp}	а	с	\mathbf{R}_{wp}
0	4.64913(18)	7.56089(2)	3.66	-	-	-
0.1	4.65967(10)	7.61872(15)	2.99	4.6563(3)	7.6121(4)	2.22
0.3	4.6821(2)	7.7356(4)	4.33	4.68539(15)	7.740300(3)	3.56
0.5	4.7077(10)	7.8544(16)	5.97	4.7046(2)	7.8483(4)	3.46
0.7	4.7328(2)	7.9790(4)	4.64	4.7328(2)	7.9790(5)	1.83
0.9	4.76027(14)	8.0907(3)	2.81	4.75453(16)	8.0838(3)	3.73
1	4.76767(15)	8.1293(3)	2.82	-	-	-

Table A2: Lattice parameters and R_{wp} values from refinements of powder XRD patterns of $(Ca_x Mg_{1-x})Mg_2Sb_2$.

	After SPS		After annealing 10 days			
Х	a	с	\mathbf{R}_{wp}	а	c	\mathbf{R}_{wp}
0	4.56436(14)	7.2310(2)	3.66	-	-	-
0.1	4.5760(2)	7.2631(2)	3.54	4.56854(18)	7.25428(17)	3.85
0.2	4.5856(2)	7.3033(4)	3.86	4.57815(16)	7.2932(2)	3.7
0.3	4.58928(15)	7.3319(2)	2.89	4.58691(11)	7.3304(2)	3.16
0.4	4.59639(11)	7.36216(17)	3.38	4.59622(11)	7.36684(17)	3.33
0.5	4.60429(12)	7.3853(2)	2.62	4.60254(11)	7.3905(18)	3.1
0.6	4.61042(9)	7.41467(14)	2.72	4.60919(11)	7.41438(18)	2.71
0.7	4.62359(10)	7.45927(17)	2.12	4.61850(7)	7.44851(13)	2.21
0.8	4.62980(7)	7.49189(14)	2.74	4.63103(16)	7.4971(2)	2.34
0.9	4.64026(8)	7.52549(14)	1.98	-	-	-
1	4.64913(18)	7.56089(2)	2.42	-	-	-

Table A3: Lattice parameters and R_{wp} values from refinements of powder XRD patterns of $(Sr_xMg_{1-x})Mg_2Sb_2$. With the exception of the x = 0.9 sample, all alloyed samples contain both a Sr-rich and a Mg-rich phase.

	After SPS					After annealing 10 days				
	Sr-rich phase		Mg-rich phase			Sr-rich phase		Mg-rich phase		
х	а	c	a	c	R_{wp}	a	c	a	с	R_{wp}
0	-	-	4.56436 (14)	7.2310(2)	3.66	-	-	-	-	-
0.2	4.6841 (2)	7.7482 (7)	4.57706 (10)	7.2805 (2)	2.9	4.6827(4)	7.7533(8)	4.56333(17)	7.2389(3)	2.28
0.4	4.6850 (3)	7.7570 (5)	4.5736 (3)	7.2721 (15)	2.19	4.6852(2)	7.7594(4)	4.5639(3)	7.2406(4)	2.92
0.6	4.68527 (19)	7.7568 (3)	4.5711 (4)	7.2599 (8)	1.9	4.68857(11)	7.7671(19)	4.5637(5)	7.2407(8)	1.81
0.7	4.68489 (17)	7.7597 (3)	4.5694 (6)	7.2643 (10)	1.83	4.6891(9)	7.765(15)	4.5664(2)	7.2377(7)	1.83
0.8	4.69262 (8)	7.78273 (17)	-	-	2.18	4.68644(19)	7.7651(3)	-	-	2.03
0.9	4.68927 (12)	7.7681 (2)	-	-	2.47	4.68727(9)	7.76557(16)	-	-	-
1	4.70068 (7)	7.82196(13)	-	-	1.59	-	-	-	-	-

Table A4: Lattice parameters and R_{wp} values from refinements of powder XRD patterns of $(Ba_xMg_{1-x})Mg_2Sb_2$. All alloyed samples separated into a Ba-rich and a Mg-rich phase, suggesting zero solubility.

	After SPS Ba-rich phase		Mg-rich phase			After annealing Ba-rich phase	g 10 days	Mg-rich phase		
х	a	с	a	с	R_{wp}	a	с	a	с	R_{wp}
0	-	-	4.56436 (14)	7.2310(2)	3.66	-	-	-	-	-
0.1	4.7615 (3)	8.1174 (8)	4.5649 (15)	7.2327 (18)	3.06	4.7647 (3)	8.1269 (10)	4.56246 (15)	7.22828 (19)	2.85
0.3	4.7645 (3)	8.1252 (5)	4.5653 (4)	7.2335 (5)	2.71	4.7642 (4)	8.1249 (8)	4.56622 (18)	7.2372 (3)	2.73
0.5	4.7716 (3)	8.1319 (2)	4.5682 (4)	7.2302 (9)	2.83	4.76237 (14)	8.1222 (3)	4.56307 (17)	7.2346 (4)	2.47
0.8	4.76800 (15)	8.1250 (3)	4.564 (4)	7.1924 (8)	3.64	4.7665 (3)	8.1236 (4)	-	-	3.31
0.9	4.7624 (18)	8.122 (3)	4.5746 (17)	7.2295 (5)	3.19	4.76172 (18)	8.1196 (3)	-	-	3.8
1	4.76767 (15)	8.1293 (3)	-	-	2.82	-	-	-	-	-

Table A5: The parameters from the 2nd-order Birch–Murnaghan EOS fit for Mg₃Sb₂ and Mg₃Bi₂ corresponding to Figure 5.5. The V₀ for the ambient structures ($P\bar{3}m1$) were obtained via Rietveld refinement of the corresponding room temperature XRD pattern. For the high-pressure phase (C2/m), V₀ is unknown, so it was treated as an open fitting parameter in the Birch–Murnaghan EOS fit.

	AP - Mg_3Sb_2	$C2/m Mg_3Sb_2$	AP - Mg_3Bi_2	$C2/m Mg_3Bi_2$
V_0 (Å ³)	130.44	122.5	138.79	128.7
K ₀ (GPa)	38.4	45.7	36.9	48.9
\mathbf{K}_p (GPa)	4	4	4	4

Table A6: Lattice parameters and uncertainties of the $P\bar{3}m1$ Mg₃Sb₂ phase from powder XRD refinements using PDXL2. The lattice parameters, and peak shape parameters are refined. P₁ and P₂ are pressure readings before and after the measurement of each pattern. The deviation of the average value between P₁ and P₂ is used as the pressure uncertainty for the Birch–Murnaghan equation of state fit.

P ₁ (GPa)	P ₂ (GPa)	a (Å)	c (Å)	V (Å ³)
0.58	0.58	4.5376(17)	7.195(3)	128.29(8)
0.64	0.64	4.5337(17)	7.185(3)	127.90(8)
0.73	0.75	4.5304(16)	7.180(3)	127.62(8)
0.91	0.88	4.5269(18)	7.170(3)	127.25(9)
1.26	1.26	4.513(2)	7.146(3)	126.02(9)
1.94	1.94	4.4919(18)	7.107(3)	124.19(9)
3.06	3.06	4.464(2)	7.055(3)	121.73(10)
3.38	3.38	4.452(2)	7.038(3)	120.78(9)
3.90	3.90	4.4403(16)	7.016(4)	119.80(9)
4.36	4.36	4.4274(15)	6.997(3)	117.53(9)
4.81	4.90	4.4122(18)	6.971(3)	117.53(9)
5.48	5.57	4.3986(19)	6.954(16)	116.51(13)
6.70	6.70	4.3792(17)	6.913(4)	114.81(9)

Table A7: Lattice parameters and uncertainties of the C2/m Mg₃Sb₂ phase from powder XRD refinements using PDXL2. The lattice parameters, peak shape parameters, z and x are refined. The deviation of the average value between P₁ and P₂ (pressures measured before and after sample exposure) is used as the pressure uncertainty for the Birch–Murnaghan equation of state fit.

P ₁ (GPa)	P_2 (GPa)	a (Å)	b (Å)	c (Å)	V (Å ³)	beta (deg)
8.43	8.60	15.062(11)	4.201(3)	7.599(3)	425.8(4)	117.67(2)
9.08	9.11	15.012(15)	4.187(4)	7.595(4)	423.0(6)	117.62(3)
10.25	10.44	14.910(16)	4.169(4)	7.549(3)	415.7(6)	117.63(4)
13.33	13.53	14.693(19)	4.144(5)	7.479(4)	403.4(7)	117.65(5)
15.02	15.29	14.638(16)	4.126(4)	7.420(3)	396.4(6)	117.79(4)
17.48	17.65	14.495(16)	4.094(4)	7.348(4)	385.8(6)	117.78(4)
18.56	18.70	14.450(18)	4.085(5)	7.322(4)	382.2(7)	117.84(4)

Table A8: Lattice parameters and uncertainties of the $P\bar{3}m1$ Mg₃Bi₂ phase from powder XRD refinements using PDXL2. The lattice parameters, and peak shape parameters are refined. The deviation of the average value between P₁ and P₂ (pressures measured before and after sample exposure) is used as the pressure uncertainty for the Birch–Murnaghan equation of state fit.

P ₁ (GPa)	P ₂ (GPa)	a (Å)	c (Å)	V (Å ³)
1.49	1.49	4.6005(12)	7.293(8)	133.67(16)
2.48	2.55	4.5672(11)	7.236(7)	130.73(13)
2.92	3.00	4.5559(11)	7.217(7)	129.74(13)
3.52	3.59	4.5365(11)	7.185(7)	128.06(13)

Table A9: Lattice parameters and uncertainties of the C2/m Mg₃Bi₂ phase from powder XRD refinements using PDXL2. The lattice parameters, peak shape parameters, z and x are refined. The deviation of the average value between P₁ and P₂ is used as the pressure uncertainty for the Birch–Murnaghan equation of state fit.

P ₁ (GPa)	P ₂ (GPa)	a (Å)	b (Å)	c (Å)	V (Å ³)	beta (deg)
4.51	4.6	15.618(19)	4.329(3)	7.907(3)	475.4(7)	117.20(6)
5.21	5.25	15.548(15)	4.327(2)	7.8773(19)	471.0(5)	117.27(4)
5.80	5.91	15.481(13)	4.315(2)	7.850(2)	466.2(5)	117.24 (4)
6.56	6.68	15.426(14)	4.310(2)	7.831(2)	462.9(5)	117.26(4)
7.10	7.26	15.388(15)	4.292(3)	7.801(2)	457.7(5)	117.34(4)
8.00	8.00	15.320(14)	4.281(2)	7.7722(19)	452.7(5)	117.36(4)
8.60	8.60	15.284(14)	4.276(2)	7.7573(19)	450.1(5)	117.39(4)
9.30	9.3	15.233(13)	4.269(2)	7.7368(18)	446.6(5)	117.40(4)
10.02	10.02	15.181(14)	4.260(2)	7.7143(18)	442.8(5)	117.42(4)

BIBLIOGRAPHY

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- [1] Robert Berman and Paul G Klemens. Thermal conduction in solids. *Physics Today*, 31:56, 1978.
- [2] Terry M Tritt. *Thermal conductivity: theory, properties, and applications*. Springer Science & Business Media, 2005.
- [3] Yoko Suzuki, Jonathan B Levine, Albert Migliori, Jim D Garrett, Richard B Kaner, Victor R Fanelli, and Jonathan B Betts. Rhenium diboride's monocrystal elastic constants, 308 to 5 K. *The Journal of the Acoustical Society of America*, 127(5):2797–2801, 2010.
- [4] W.C. Overton Jr. and John Gaffney. Temperature variation of the elastic constants of cubic elements. I. Copper. *Physical Review*, 98(4):969, 1955.
- [5] Lattice dynamics and local structure in AMg₂Sb₂ thermoelectric Zintl phases. 2020 (In preparation).
- [6] Wanyue Peng, Ashiwini Balodhi, and Alexandra Zevalkink. High-temperature elastic moduli: a tool for understanding chemical bonding in thermoelectric materials. 2020 (in preparation).
- [7] Norihiko L Okamoto, Takahiro Nakano, Katsushi Tanaka, and Haruyuki Inui. Mechanical and thermal properties of single crystals of the type-I clathrate compounds Ba₈Ga₁₆Ge₃₀ and Sr₈Ga₁₆Ge₃₀. *Journal of Applied Physics*, 104(1):013529, 2008.
- [8] G Rogl, A Grytsiv, M Gürth, A Tavassoli, C Ebner, A Wünschek, S Puchegger, V Soprunyuk, W Schranz, E Bauer, et al. Mechanical properties of half-heusler alloys. *Acta Materialia*, 107:178–195, 2016.
- [9] Fei Ren, Eldon D Case, Joseph R Sootsman, Mercouri G Kanatzidis, Huijun Kong, Ctirad Uher, Edgar Lara-Curzio, and Rosa M Trejo. The high-temperature elastic moduli of polycrystalline Pb Te measured by resonant ultrasound spectroscopy. *Acta Materialia*, 56(20):5954–5963, 2008.
- [10] Robert D Schmidt, Eldon D Case, Jennifer E Ni, Rosa M Trejo, Edgar Lara-Curzio, Rachel J Korkosz, and Mercouri G Kanatzidis. High-temperature elastic moduli of thermoelectric SnTe_{1±x}-y SiC nanoparticulate composites. *Journal of Materials Science*, 48(23):8244–8258, 2013.
- [11] R.B. Schwarz and J.F. Vuorinen. Resonant ultrasound spectroscopy: applications, current status and limitations. *Journal of Alloys and Compounds*, 310(1-2):243–250, 2000.
- [12] Udo Lang, Nicola Naujoks, and Jurg Dual. Mechanical characterization of PEDOT: PSS thin films. *Synthetic Metals*, 159(5-6):473–479, 2009.

- [13] Baoyang Lu, Hyunwoo Yuk, Shaoting Lin, Nannan Jian, Kai Qu, Jingkun Xu, and Xuanhe Zhao. Pure PEDOT: PSS hydrogels. *Nature communications*, 10(1):1–10, 2019.
- [14] Francesco Greco, Alessandra Zucca, Silvia Taccola, Arianna Menciassi, Toshinori Fujie, Hiroki Haniuda, Shinji Takeoka, Paolo Dario, and Virgilio Mattoli. Ultra-thin conductive free-standing pedot/pss nanofilms. *Soft Matter*, 7(22):10642–10650, 2011.
- [15] Dean Cheikh, Kathleen Lee, Wanyue Peng, Alexandra Zevalkink, Jean-Pierre Fleurial, and Sabah K Bux. Thermoelectric properties of scandium sesquitelluride. *Materials*, 12(5):734, 2019.
- [16] Wanyue Peng, Sevan Chanakian, and Alexandra Zevalkink. Crystal chemistry and thermoelectric transport of layered AM_2X_2 compounds. *Inorganic Chemistry Frontiers*, 5(8):1744– 1759, 2018.
- [17] Alex Zevalkink, David M Smiadak, Jeff L Blackburn, Andrew J Ferguson, Michael L Chabinyc, Olivier Delaire, Jian Wang, Kirill Kovnir, Joshua Martin, Laura T Schelhas, et al. A practical field guide to thermoelectrics: Fundamentals, synthesis, and characterization. *Applied Physics Reviews*, 5(2):021303, 2018.
- [18] Zhaohui Dong and Yang Song. Novel pressure-induced structural transformations of inorganic nanowires. In *Nanowires-Fundamental Research*. InTech, 2011.
- [19] M Martinez-Ripoll, A Haase, and G Brauer. The crystal structure of α-Mg₃Sb₂. Acta Crystallographica Section B: Structural Crystallography and Crystal Chemistry, 30(8):2006–2009, 1974.
- [20] Wanyue Peng, Guido Petretto, Gian-Marco Rignanese, Geoffroy Hautier, and Alexandra Zevalkink. An unlikely route to low lattice thermal conductivity: small atoms in a simple layered structure. *Joule*, 2(12):1879–1893, 2018.
- [21] G Ceder and K Persson. The materials project: A materials genome approach. *DOE Data Explorer, osti. gov/dataexplorer/biblio/1077798*, 2010.
- [22] Maarten De Jong, Wei Chen, Thomas Angsten, Anubhav Jain, Randy Notestine, Anthony Gamst, Marcel Sluiter, Chaitanya Krishna Ande, Sybrand Van Der Zwaag, Jose J Plata, et al. Charting the complete elastic properties of inorganic crystalline compounds. *Scientific Data*, 2:150009, 2015.
- [23] Eric S Toberer, Alex Zevalkink, and G Jeffrey Snyder. Phonon engineering through crystal chemistry. *Journal of Materials Chemistry*, 21(40):15843–15852, 2011.
- [24] G Li and JR Gladden. High temperature resonant ultrasound spectroscopy: a review. *International Journal of Spectroscopy*, 2010.
- [25] Wanyue Peng and Alexandra Zevalkink. Limits of Cation Solubility in AMg₂Sb₂ (A = Mg, Ca, Sr, Ba) Alloys. *Materials (Basel, Switzerland)*, 12(4), 2019.

- [26] Shalabh Gupta, Ashok K Ganguli, and John D Corbett. Mg_{5.23}Sm_{0.77}Sb₄: an ordered superstructure derived from the Mg₃Sb₂ structure type. *Inorganic Chemistry*, 45(20):8175– 8178, 2006.
- [27] Tessera Alemneh Wubieneh, Pai-Chun Wei, Chien-Chih Yeh, Szu-yuan Chen, and Yang-Yuan Chen. Thermoelectric Properties of Zintl Phase Compounds of $Ca_{1-x}Eu_xZn_2Sb_2$. *Journal of Electronic Materials*, 45(3):1942–1946, 2016.
- [28] Jing Shuai, Yumei Wang, Zihang Liu, Hee Seok Kim, Jun Mao, Jiehe Sui, and Zhifeng Ren. Enhancement of thermoelectric performance of phase pure zintl compounds Ca_{1-x}Yb_xZn₂Sb₂, Ca_{1-x}Eu_xZn₂Sb₂, and Eu_{1-x}Yb_xZn₂Sb₂ by mechanical alloying and hot pressing. *Nano Energy*, 25:136–144, 2016.
- [29] Alexander Ovchinnikov and Svilen Bobev. Zintl phases with group 15 elements and the transition metals: A brief overview of pnictides with diverse and complex structures. *Journal of Solid State Chemistry*, 270:346–359, 2019.
- [30] Jing Shuai, Zihang Liu, Hee Seok Kim, Yumei Wang, Jun Mao, Ran He, Jiehe Sui, and Zhifeng Ren. Thermoelectric properties of Bi-based Zintl compounds $Ca_{1-x}Yb_xMg_2Bi_2$. *Journal of Materials Chemistry A*, 4(11):4312–4320, 2016.
- [31] Franck Gascoin, Sandra Ottensmann, Daniel Stark, Sossina M Haïle, and G Jeffrey Snyder. Zintl phases as thermoelectric materials: tuned transport properties of the compounds $Ca_xYb_{1-x}Zn_2Sb_2$. Advanced Functional Materials, 15(11):1860–1864, 2005.
- [32] Qigao Cao, Hui Zhang, Meibo Tang, Haohong Chen, Xinxin Yang, Yuri Grin, and Jingtai Zhao. Zintl phase $Yb_{1-x}Ca_xCd_2Sb_2$ with tunable thermoelectric properties induced by cation substitution. *Journal of Applied Physics*, 107(5):053714, 2010.
- [33] Hui Zhang, Michael Baitinger, Mei-Bo Tang, Zhen-Yong Man, Hao-Hong Chen, Xin-Xin Yang, Yi Liu, Ling Chen, Yuri Grin, and Jing-Tai Zhao. Thermoelectric properties of Eu(Zn_{1-x}Cd_x)₂Sb₂. *Dalton Transactions*, 39(4):1101–1104, 2010.
- [34] Ting Zhou, Jun Mao, Jing Jiang, Shaowei Song, Hangtian Zhu, Qing Zhu, Qinyong Zhang, Wuyang Ren, Zhiming Wang, Chao Wang, et al. Large reduction of thermal conductivity leading to enhanced thermoelectric performance in p-type Mg₃Bi₂-YbMg₂Bi₂ solid solutions. *Journal of Materials Chemistry C*, 7, 2019.
- [35] Gerhard Cordier and Herbert Schäfer. Neue intermetallische Verbindungen im anti-Ce₂O₂S-Strukturtyp. / New Intermetallic Compounds in the anti-Ce₂O₂S-Structure Type. Zeitschrift für Naturforschung B, 31(11):1459–1461, 1976.
- [36] Peter Klüfers and Albrecht Mewis. AB₂X₂-Verbindungen im CaAl₂Si₂-Typ, III Zur Struktur der Verbindungen CaZn₂P₂, CaCd₂P₂, CaZn₂As₂ und CaCd₂As₂/AB₂X₂ Compounds with the CaAl₂Si₂ Structure, III / The Crystal Structure of CaZn₂P₂, CaCd₂P₂, CaZn₂As₂, and CaCd₂As₂. Zeitschrift für Naturforschung B, 32(7):753–756, 1977.

- [37] Peter Klüfers and Albrecht Mewis. Zur Struktur der Verbindungen BaZn₂P₂ und BaZn₂As₂
 / The Crystal Structure of BaZn₂P₂ and BaZn₂As₂. *Zeitschrift für Naturforschung B*, 33(2):151–155, 1978.
- [38] Albrecht Mewis. ₂-Verbindungen im CaAl₂Si₂-Typ, IV Zur Struktur der Verbindungen CaZn₂Sb₂, CaCd₂Sb₂, SrZn₂Sb₂ und SrCd₂Sb₂ / AB₂X₂ Compounds with the CaAl₂Si₂ Structure, IV The Crystal Structure of CaZn₂Sb₂, CaCd₂Sb₂, SrZn₂Sb₂, and SrCd₂Sb₂. *Zeitschrift für Naturforschung B*, 33(4):382–384, 1978.
- [39] Albrecht Mewis. AB₂X₂-Verbindungen im CaAl₂Si₂-Typ, V Zur Struktur der Verbindungen CaMn₂P₂, CaMn₂As₂, SrMn₂P₂ und SrMn₂As₂ / AB₂X₂-Compounds with the CaAl₂Si₂ Structure, V The Crystal Structure of CaMn₂P₂, CaMn₂As₂, SrMn₂P₂, and SrMn₂As₂. *Zeitschrift für Naturforschung B*, 33(6):606–609, 1978.
- [40] Erwin Brechtel, Gerhard Cordier, and Herbert Schäfer. Neue ternäre Erdalkaliverbindungen des Arsens mit Mangan / New Ternary Alkaline Earth Compounds of Arsenic with Manganese. Zeitschrift für Naturforschung B, 33(7):820–822, 1978.
- [41] Erwin Brechtel, Gerhard Cordier, and Herbert Schäfer. Darstellung und Kristallstruktur von BaMn₂Sb2, BaZn₂Sb₂ und BaCd₂Sb₂ / Preparation and Crystal Structure of BaMn₂Sb₂, BaZn₂Sb₂ and BaCd₂Sb₂. *Z. Naturforsch. B*, 34(7):921–925, 1979.
- [42] R Rühl and W Jeitschko. New pnictides with Ce₂O₂S-type structure. *Materials Research Bulletin*, 14(4):513–517, 1979.
- [43] Inga Schellenberg, Matthias Eul, Wilfried Hermes, and Rainer Pöttgen. A ¹²¹Sb and ¹⁵¹Eu Mössbauer spectroscopic investigation of EuMn₂Sb₂, EuZn₂Sb₂, YbMn₂Sb₂, and YbZn₂Sb₂. Zeitschrift für anorganische und allgemeine Chemie, 636(1):85–93, 2010.
- [44] AV Morozkin, O Isnard, P Henry, S Granovsky, R Nirmala, and P Manfrinetti. Synthesis and magnetic structure of the YbMn₂Sb₂ compound. *Journal of Alloys and Compounds*, 420(1):34–36, 2006.
- [45] Peter Klüfers and Albrecht Mewis. AB₂X₂-Verbindungen mit CaAl₂Si₂-Struktur. *Zeitschrift für Kristallographie-Crystalline Materials*, 169(1-4):135–148, 1984.
- [46] Peter Klüfers, Hermann Neumann, Albrecht Mewis, and Hans-Uwe Schuster. AB2X2-Verbindungen im CaAl₂Si₂-Typ, VIII [1] / AB₂X₂ Compounds with the CaAl₂Si₂ Structure, VIII [1]. Zeitschrift für Naturforschung B, 35(10):1317–1318, 1980.
- [47] Peter Klüfers, Albrecht Mewis, and Hans-Uwe Schuster. AB₂X₂-Verbindungen im CaAl₂Si₂-Typ, VI Zur Struktur von ThCu₂P₂, YbZn₂P₂ und YbZnCuP₂ sowie der verwandten Verbindungen YbCu₃P₂ und YbCu₂P₂. Zeitschrift für Kristallographie-Crystalline Materials, 149(3-4):211–225, 1979.
- [48] Gerhard Zwiener, Hermann Neumann, and Hans-Uwe Schuster. Magnetische Eigenschaften von AB₂X₂-Verbindungen im CaAl₂Si₂-Typ/Magnetic Properties of AB₂X₂ Compounds with the CaAl₂Si₂ Structure. *Zeitschrift für Naturforschung B*, 36(9):1195–1197, 1981.

- [49] A. Nateprov, J. Cisowski, J. Heimann, and I. Mirebeau. A new ternary compound YbZn₂As₂ with mixed valency of Yb. *Journal of Alloys and Compounds*, 290(1):6–9, 1999.
- [50] Zelinska, O. Ya and Tkachuk, A.V. and Grosvenor, A.P. and Mar, A. Structure and physical properties of YbZn₂Sb₂ and YbCd₂Sb₂. *Chemistry of metals and alloys*, (1):204–209, 2008.
- [51] A. Artmann, A. Mewis, M. Roepke, and G. Michels. AM₂X₂-Verbindungen mit CaAl₂Si₂-Struktur. XI. Struktur und Eigenschaften der Verbindungen ACd₂X₂ (A: Eu, Yb, X: P, As, Sb). Zeitschrift für anorganische und allgemeine Chemie, 622(4):679–682, 1996.
- [52] Robert Juza and Reinhard Kroebel. Über eine Hochtemperaturmodifikation des Magnesiumarsenids und eine ternäre Phase Mg₂MnAs₂ gleicher Struktur. *Zeitschrift für anorganische und allgemeine Chemie*, 331(3-4):187–199, 1964.
- [53] E. Zintl and E. Husemann. Bindungsart und Gitterbau binärer Magnesiumverbindungen. *Zeitschrift für physikalische Chemie*, 21(1):138–155, 1933.
- [54] Klaus Deller and Brigitte Eisenmann. Ternäre Erdalkali-Element (V)-Verbindungen AMg₂B₂ mit A= Ca, Sr, Ba und B= As, Sb, Bi/Ternary Alkaline Earth-Element (V)-Compounds AMg₂B₂ with A= Ca, Sr, Ba and B= As, Sb, Bi. Zeitschrift für Naturforschung B, 32(6):612–616, 1977.
- [55] Andrew F. May, Michael A. McGuire, David J. Singh, Radu Custelcean, and Gerald E. Jellison Jr. Structure and properties of single crystalline CaMg₂Bi₂, EuMg₂Bi₂, and YbMg₂Bi₂. *Inorganic Chemistry*, 50(21):11127–11133, 2011.
- [56] Franziska Wartenberg, Christian Kranenberg, Regina Pocha, Dirk Johrendt, Albrecht Mewis, Rolf-Dieter Hoffmann, Bernd D Mosel, and Rainer Poettgen. Neue pnictide im CaAl₂Si₂-Typ und dessen existenzgebiet / New pnictides with the CaAl₂Si₂ type structure and the stability range of this type. *Zeitschrift für Naturforschung B*, 57(11):1270–1276, 2002.
- [57] A.A. Murav'eva, O.S. Zarechnyuk, and E.I. Gladyshevskii. Systems Y–Al–Si (Ge, Sb) in the range 0 to 33.3 at percent Y. Technical report, Lvov State Univ., 1971.
- [58] Reinhard Xesper and Hans Georg von Schnering. GdAl₂Si₂, eine unerwartete Verbindung im CaAl₂Si₂-Typ / GdAl₂Si₂, an Unexpected Compound of the CaAl₂Si₂-Type. Zeitschrift für Naturforschung B, 37(12):1514–1517, 1982.
- [59] C. Kranenberg, D. Johrendt, and A. Mewis. Untersuchungen zum Existenzgebiet des CaAl₂Si₂-Strukturtyps bei ternären Siliciden. Zeitschrift für anorganische und allgemeine Chemie, 625(11):1787–1793, 1999.
- [60] Christian Kranenberg, Dirk Johrendt, Albrecht Mewis, Rainer Pöttgen, Gunter Kotzyba, Carsten Rosenhahn, and Bernd D Mosel. Structure and properties of the compounds LnAl₂X₂ (Ln= Eu, Yb, X= Si, Ge). Solid State Sciences, 2(2):215–222, 2000.
- [61] Nataliya Muts, Roman Gladyshevskii, and Evgen Gladyshevskii. Crystal structures of the compounds PrAl₂Si₂, Pr₃Al₄Si₆ and PrAlSi₂. *Journal of Alloys and Compounds*, 402(1):66– 69, 2005.

- [62] SJ Andersen, CD Marioara, A Frøseth, R Vissers, and HW Zandbergen. Crystal structure of the orthorhombic U₂-Al₄Mg₄Si₄ precipitate in the Al–Mg–Si alloy system and its relation to the β ' and β " phases. *Materials Science and Engineering: A*, 390(1):127–138, 2005.
- [63] P. Schobinger-Papamantellos and F. Hulliger. The magnetic structure of EuAl₂Si₂. *Journal of the Less Common Metals*, 146:327–335, 1989.
- [64] H. Flandorfer, D. Kaczorowski, J. Gröbner, P. Rogl, R. Wouters, C. Godart, and A. Kostikas. The systems Ce–Al–(Si, Ge): phase equilibria and physical properties. *Journal of Solid State Chemistry*, 137(2):191–205, 1998.
- [65] Christian Kranenberg, Dirk Johrendt, and Albrecht Mewis. The stability range of the CaAl₂Si₂-type structure in case of LnAl₂Ge₂ compounds. *Solid State Sciences*, 4(2):261– 265, 2002.
- [66] Olaf Reckeweg and Francis J DiSalvo. About binary and ternary alkaline earth metal nitrides. *Zeitschrift für anorganische und allgemeine Chemie*, 627(3):371–377, 2001.
- [67] Jiawei Zhang, Lirong Song, Mattia Sist, Kasper Tolborg, and Bo Brummerstedt Iversen. Chemical bonding origin of the unexpected isotropic physical properties in thermoelectric Mg₃Sb₂ and related materials. *Nature Communications*, 9(1):1–10, 2018.
- [68] Wanyue Peng, Mario Calderón-Cueva, Mingda Lyu, Benjamin Brugman, Gill Levental, Ashiwini Balodhi, Megan Rylko, Susannah Dorfman, and Alexandra Zevalkink. Highpressure behavior of layered AM_2X_2 compounds. 2020 (in preparation).
- [69] Yougui Liao. Practical electron microscopy and database, 2006.
- [70] Jamo Momand, Felix R.L. Lange, Ruining Wang, Jos E. Boschker, Marcel A. Verheijen, Raffaella Calarco, Matthias Wuttig, and Bart J. Kooi. Atomic stacking and van-der-Waals bonding in GeTe–Sb₂Te₂ superlattices. *Journal of Materials Research*, 31(20):3115–3124, 2016.
- [71] Wanyue Peng, David M. Smiadak, Michael G. Boehlert, Spencer Mather, Jared B. Williams, Donald T. Morelli, and Alexandra Zevalkink. Lattice hardening due to vacancy diffusion in (GeTe)_mSb₂Te₃ alloys. *Journal of Applied Physics*, 126(5):055106, 2019.
- [72] H. Wiedemeier and P.A. Siemers. The thermal expansion of GeS and GeTe. Zeitschrift für anorganische und allgemeine Chemie, 431(1):299–304, 1977.
- [73] Y. Gelbstein, G. Gotesman, Y. Lishzinker, Z. Dashevsky, and MP Dariel. Mechanical properties of PbTe-based thermoelectric semiconductors. *Scripta Materialia*, 58(4):251– 254, 2008.
- [74] Jennifer E. Ni, Eldon D. Case, Kristen N. Khabir, Ryan C. Stewart, Chun-I. Wu, Timothy P. Hogan, Edward J. Timm, Steven N. Girard, and Mercouri G. Kanatzidis. Room temperature Young's modulus, shear modulus, Poisson's ratio and hardness of PbTe-PbS thermoelectric materials. *Materials Science and Engineering: B*, 170(1-3):58–66, 2010.

- [75] Mathias Woydt and Hardy Mohrbacher. The tribological and mechanical properties of niobium carbides (NbC) bonded with cobalt or Fe3Al. *Wear*, 321:1–7, 2014.
- [76] Francis J. DiSalvo. Thermoelectric cooling and power generation. *Science*, 285(5428):703– 706, 1999.
- [77] Bradley Orr and Aliakbar Akbarzadeh. Prospects of waste heat recovery and power generation using thermoelectric generators. *Energy Procedia*, 110:250–255, 2017.
- [78] George Schmidt, Leonard Dudzinski, and Thomas Sutliff. Radioisotope power: A key technology for deep space exploration. In *6th International Energy Conversion Engineering Conference (IECEC)*, page 5640, 2011.
- [79] Ajay Misra. Overview of nasa program on development of radioisotope power systems with high specific power. In *4th International Energy Conversion Engineering Conference and Exhibit (IECEC)*, page 4187, 2006.
- [80] Jiawei Zhang, Lirong Song, and Bo Brummerstedt Iversen. Insights into the design of thermoelectric Mg₃Sb₂ and its analogs by combining theory and experiment. *Npj Computational Materials*, 5(1):76, 2019.
- [81] G. Jeffrey Snyder and Eric S. Toberer. Complex thermoelectric materials. In *Materials for* sustainable energy: a collection of peer-reviewed research and review articles from Nature Publishing Group, pages 101–110. World Scientific, 2011.
- [82] Zhiting Tian, Jivtesh Garg, Keivan Esfarjani, Takuma Shiga, Junichiro Shiomi, and Gang Chen. Phonon conduction in PbSe, PbTe, and PbTe_{1-x}Se_x from first-principles calculations. *Physical Review B*, 85(18):184303, 2012.
- [83] Robert E. Newnham. *Properties of materials: anisotropy, symmetry, structure*. Oxford University Press on Demand, 2005.
- [84] Wolfgang G. Zeier, Alex Zevalkink, Zachary M. Gibbs, Geoffroy Hautier, Mercouri G. Kanatzidis, and G. Jeffrey Snyder. Thinking like a chemist: intuition in thermoelectric materials. *Angewandte Chemie International Edition*, 55(24):6826–6841, 2016.
- [85] Yaniv Gelbstein. $Pb_{1-x}Sn_x$ Te alloys: Application considerations. *Journal of electronic materials*, 40(5):533–536, 2011.
- [86] David G. Cahill and Robert O. Pohl. Lattice vibrations and heat transport in crystals and glasses. *Annual review of physical chemistry*, 39(1):93–121, 1988.
- [87] P.G. Klemens. Theory of the thermal conductivity of solids. *Thermal conductivity*, 1:1–68, 1969.
- [88] Micheline Roufosse and P.G. Klemens. Thermal conductivity of complex dielectric crystals. *Physical Review B*, 7(12):5379, 1973.
- [89] G. Leibfried and E. Schl. Omann thermal conductivity of dielectric solids by a variational technique nachr. *Akad. Wiss. G€ ottingen II a (4)*, 71, 1954.

- [90] Carl L. Julian. Theory of heat conduction in rare-gas crystals. *Physical Review*, 137(1A):A128, 1965.
- [91] Glen A. Slack and S. Galginaitis. Thermal conductivity and phonon scattering by magnetic impurities in CdTe. *Physical Review*, 133(1A):A253, 1964.
- [92] E. Grüneisen. Theory of solid state of monatomic elements. *Annalen der Physik*, 39:257–306, 1912.
- [93] Matthias Agne, Shashwat Anand, and G. Jeffrey Snyder. Inherent anharmonicity of harmonic solids. *submitted*, 2020.
- [94] Günther Leibfried and Wolfgang Ludwig. Theory of anharmonic effects in crystals. In *Solid state physics*, volume 12, pages 275–444. Elsevier, 1961.
- [95] Hassel Ledbetter, Ming Lei, Allen Hermann, and Zhengzhi Sheng. Low-temperature elastic constants of YBa₂Cu₃O₇. *Physica C: Superconductivity*, 225(3-4):397–403, 1994.
- [96] Teahoon Park, Chihyun Park, Byeonggwan Kim, Haejin Shin, and Eunkyoung Kim. Flexible pedot electrodes with large thermoelectric power factors to generate electricity by the touch of fingertips. *Energy & Environmental Science*, 6(3):788–792, 2013.
- [97] D.S. Sanditov and M.V. Darmaev. Effective Modulus of Elasticity and Grüneisen Parameter of Chalcogenide Glasses in the As–Tl–S System. *Inorganic Materials*, 55(6):617–622, 2019.
- [98] D.S. Sanditov and V.N. Belomestnykh. Relation between the parameters of the elasticity theory and averaged bulk modulus of solids. *Technical Physics*, 56(11):1619–1623, 2011.
- [99] Vladimir Nikolaevich Belomestnykh and Elena Pavlovna Tesleva. Interrelation between anharmonicity and lateral strain in quasi-isotropic polycrystalline solids. *Technical physics*, 49(8), 2004.
- [100] Vladimir Nikolaevich Belomestnykh. The acoustical grüneisen constants of solids. *Technical Physics Letters*, 30(2):91–93, 2004.
- [101] G.J. Miller and S.M. Kauzlarich. Chemistry, Structure, and Bonding of Zintl Phases and Ions. *Kauzlarich, S., Eds*, 1996.
- [102] Chong Zheng, Roald Hoffmann, Reinhard Nesper, and Hans Georg Von Schnering. Site preferences and bond length differences in CaAl₂Si₂-type Zintl compounds. *Journal of the American Chemical Society*, 108(8):1876–1884, 1986.
- [103] Susan Mary Kauzlarich. *Chemistry, structure, and bonding of Zintl phases and ions*. VCH Publishers, 1996.
- [104] Jürgen Evers. Zintl Phases: Principles and Recent Developments, volume 139. Springer Science & Business Media, 2011.
- [105] E. I. Gladyshevskii, P. I. Kipyakevich, and O.I. Ukr. Fiz. Zh. Bodak. Crystal structure of CaAl₂Si₂ and its analogs.

- [106] Jeremy K. Burdett and Gordon J. Miller. Fragment formalism in main-group solids: applications to aluminum boride (AlB₂), calcium aluminum silicide (CaAl₂Si₂), barium-aluminum (BaAl₄), and related materials. *Chemistry of Materials*, 2(1):12–26, 1990.
- [107] Chong Zheng and Roald Hoffmann. Complementary local and extended views of bonding in the ThCr₂Si₂ and CaAl₂Si₂ structures. *Journal of Solid State Chemistry*, 72(1):58–71, 1988.
- [108] Jiawei Zhang, Lirong Song, Aref Mamakhel, Mads Ry Vogel Jørgensen, and Bo Brummerstedt Iversen. High-performance low-cost n-type Se-doped Mg₃Sb₂-based Zintl compounds for thermoelectric application. *Chemistry of Materials*, 29(12):5371–5383, 2017.
- [109] Zhang Jiawei, Song Lirong, Madsen Georg K.H., Fischer Karl F.F., Zhang Wenqing, Shi Xun, and Iversen Bo B. Designing high-performance layered thermoelectric materials through orbital engineering. *Nature Communications*, 7:10892, 2016.
- [110] Jing Shuai, Jun Mao, Shaowei Song, Qinyong Zhang, Gang Chen, and Zhifeng Ren. Recent progress and future challenges on thermoelectric zintl materials. *Materials Today Phys.*, 1:74–95, 2017.
- [111] Jing Shuai, Huiyuan Geng, Yucheng Lan, Zhuan Zhu, Chao Wang, Zihang Liu, Jiming Bao, Ching-Wu Chu, Jiehe Sui, and Zhifeng Ren. Higher thermoelectric performance of Zintl phases $(Eu_{0.5}Yb_{0.5})_{1-x}Ca_xMg_2Bi_2$ by band engineering and strain fluctuation. *Proceedings* of the National Academy of Sciences, page 201608794, 2016.
- [112] Alex Zevalkink, Wolfgang G. Zeier, Ethan Cheng, Jeffrey Snyder, Jean-Pierre Fleurial, and Sabah Bux. Nonstoichiometry in the Zintl phase $Yb_{1-\delta}Zn_2Sb_2$ as a route to thermoelectric optimization. *Chemistry of Materials*, 26(19):5710–5717, 2014.
- [113] Kazuki Imasato, Stephen Dongmin Kang, Saneyuki Ohno, and G. Jeffrey Snyder. Band engineering in Mg₃Sb₂ by alloying with Mg₃Bi₂ for enhanced thermoelectric performance. *Materials Horizons*, 5(1):59–64, 2018.
- [114] Effects of Lanthanum Substitution on Thermoelectric Properties of YbZn₂Sb₂, author=Zhang, Xiong and Peng, Kunling and Guo, Lijie and Yan, Yanchi and Zhan, Hen and Lu, Xu and Gu, Haoshuang and Zhou, Xiaoyuan. *Journal of Electronic Materials*, 46(5):2611–2615, 2017.
- [115] Xiao-Jun Wang, Mei-Bo Tang, Hao-Hong Chen, Xin-Xin Yang, Jing-Tai Zhao, Ulrich Burkhardt, and Yuri Grin. Synthesis and high thermoelectric efficiency of zintl phase YbCd_{2-x}Zn_xSb₂. Applied Physics Letters, 94(9):092106, 2009.
- [116] Vijay Ponnambalam and Donald T Morelli. Thermoelectric Properties of Light-Element-Containing Zintl Compounds CaZn_{2-x}Cu_xP₂ and CaMnZn_{1-x}Cu_xP₂ (x=0.0–0.2). *Journal* of Electronic Materials, 43(6):1875–1880, 2014.
- [117] Kai Guo, Qigao Cao, and Jingtai Zhao. Zintl phase compounds AM₂Sb₂ (A=Ca, Sr, Ba, Eu, Yb; M=Zn, Cd) and their substitution variants: a class of potential thermoelectric materials. *Journal of Rare Earths*, 31(11):1029–1038, 2013.

- [118] Hiromasa Tamaki, Hiroki K. Sato, and Tsutomu Kanno. Isotropic conduction network and defect chemistry in $Mg_{3+x}Sb_2$ -based layered zintl compounds with high thermoelectric performance. *Advanced Materials*, 28(46):10182–10187, 2016.
- [119] Jiawei Zhang, Lirong Song, Steffen Hindborg Pedersen, Hao Yin, Le Thanh Hung, and Bo Brummerstedt Iversen. Discovery of high-performance low-cost n-type Mg₃Sb₂-based thermoelectric materials with multi-valley conduction bands. *Nature Communications*, 8:13901, 2017.
- [120] Jing Shuai, Jun Mao, Shaowei Song, Qing Zhu, Jifeng Sun, Yumei Wang, Ran He, Jiawei Zhou, Gang Chen, David J Singh, and Zhifeng Ren. Tuning the carrier scattering mechanism to effectively improve the thermoelectric properties. *Energy & Environmental Science*, 10(3):799–807, 2017.
- [121] Saneyuki Ohno, Kazuki Imasato, Shashwat Anand, Hiromasa Tamaki, Stephen Dongmin Kang, Prashun Gorai, Hiroki K Sato, Eric S Toberer, Tsutomu Kanno, and G Jeffrey Snyder. Phase Boundary Mapping to Obtain n-type Mg₃Sb₂-Based Thermoelectrics. *Joule*, 2, 2017.
- [122] Jimmy Jiahong Kuo, Stephen Dongmin Kang, Kazuki Imasato, Hiromasa Tamaki, Saneyuki Ohno, Tsutomu Kanno, and G. Jeffrey Snyder. Grain boundary dominated charge transport in mg₃sb₂-based compounds. *Energy & Environmental Science*, 11(2):429–434, 2018.
- [123] Jared B Williams and Donald T Morelli. Understanding the superior thermoelectric performance of Sb precipitated Ge₁₇Sb₂Te₂₀. *Journal of Materials Chemistry C*, 4(42):10011– 10017, 2016.
- [124] HJ McSkimin. Ultrasonic methods for measuring the mechanical properties of liquids and solids. *Physical Acoustics*, 1(part A):271–334, 1964.
- [125] Robert G Leisure and FA Willis. Resonant ultrasound spectroscopy. *Journal of Physics: Condensed Matter*, 9(28):6001, 1997.
- [126] Brian J. Zadler, Jérôme H.L. Le Rousseau, John A. Scales, and Martin L. Smith. Resonant ultrasound spectroscopy: theory and application. *Geophysical Journal International*, 156(1):154–169, 2004.
- [127] Harold H Demarest Jr. Cube-resonance method to determine the elastic constants of solids. *The Journal of the Acoustical Society of America*, 49(3B):768–775, 1971.
- [128] Integrated X-ray powder diffraction software. *The Rigaku Journal*, 26(1), 2010.
- [129] PDXL Version. 2.0. 3.0 Integrated X-ray Powder Diffraction Software. *Rigaku Corporation*, *Tokyo, Japan*, pages 196–8666, 2011.
- [130] HaM Rietveld. A profile refinement method for nuclear and magnetic structures. *Journal of applied Crystallography*, 2(2):65–71, 1969.

- [131] Rostislav Hrubiak, Stanislav Sinogeikin, Eric Rod, and Guoyin Shen. The laser micromachining system for diamond anvil cell experiments and general precision machining applications at the High Pressure Collaborative Access Team. *Review of Scientific Instruments*, 86(7):072202, 2015.
- [132] Guoyin Shen, Yanbin Wang, Agnes Dewaele, Christine Wu, Dayne E. Fratanduono, Jon Eggert, Stefan Klotz, Kamil F. Dziubek, Paul Loubeyre, Oleg V. Fat'yanov, et al. Toward an international practical pressure scale: A proposal for an IPPS ruby gauge (IPPS-Ruby2020). *High Pressure Research*, pages 1–16, 2020.
- [133] Ross J. Angel, Matteo Alvaro, and Javier Gonzalez-Platas. Eosfit7c and a fortran module (library) for equation of state calculations. *Zeitschrift für Kristallographie*, 229(5):405–419, 2014.
- [134] Xavier Gonze, J.M. Beuken, R. Caracas, F. Detraux, M. Fuchs, G.M. Rignanese, Luc Sindic, Matthieu Verstraete, G. Zerah, F. Jollet, et al. First-principles computation of material properties: the ABINIT software project. *Computational Materials Science*, 25(3):478– 492, 2002.
- [135] Xavier Gonze, Bernard Amadon, P-M Anglade, J.M. Beuken, François Bottin, Paul Boulanger, Fabien Bruneval, Damien Caliste, Razvan Caracas, Michel Côté, et al. ABINIT: First-principles approach to material and nanosystem properties. *Computational Materials Science*, 180(12):2582–2615, 2009.
- [136] Xavier Gonze, François Jollet, F. Abreu Araujo, Donat Adams, Bernard Amadon, Thomas Applencourt, Christophe Audouze, J.M. Beuken, Jordan Bieder, A. Bokhanchuk, and E. Bousquet. Recent developments in the ABINIT software package. *Computer Physics Communications*, 205:106–131, 2016.
- [137] Stefano Baroni, Stefano de Gironcoli, Andrea Dal Corso, and Paolo Giannozzi. Phonons and related crystal properties from density-functional perturbation theory. *Reviews of Modern Physics*, 73:515–562, 2001.
- [138] Xavier Gonze. First-principles responses of solids to atomic displacements and homogeneous electric fields: Implementation of a conjugate-gradient algorithm. *Phys. Rev. B*, 55:10337– 10354, 1997.
- [139] Xavier Gonze and Changyol Lee. Dynamical matrices, born effective charges, dielectric permittivity tensors, and interatomic force constants from density-functional perturbation theory. *Physical Review B*, 55:10355–10368, 1997.
- [140] D. R. Hamann, Xifan Wu, Karin M. Rabe, and David Vanderbilt. Metric tensor formulation of strain in density-functional perturbation theory. *Physical Review B*, (3).
- [141] John P. Perdew, Adrienn Ruzsinszky, Gábor I. Csonka, Oleg A. Vydrov, Gustavo E. Scuseria, Lucian A. Constantin, Xiaolan Zhou, and Kieron Burke. Restoring the density-gradient expansion for exchange in solids and surfaces. *Physical Review Letters*, 100:136406, 2008.

- [142] Lianhua He, Fang Liu, Geoffroy Hautier, Micael J. T. Oliveira, Miguel A. L. Marques, Fernando D. Vila, J. J. Rehr, G.-M. Rignanese, and Aihui Zhou. Accuracy of generalized gradient approximation functionals for density-functional perturbation theory calculations. *Physical Review B*, 89:064305, 2014.
- [143] D. R. Hamann. Optimized norm-conserving vanderbilt pseudopotentials. *Physical Review B*, 88:085117, 2013.
- [144] Michiel Van Setten, Matteo Giantomassi, Eric Bousquet, Matthieu J. Verstraete, Donald R Hamann, Xavier Gonze, and Gian-Marco Rignanese. The PseudoDojo: Training and grading a 85 element optimized norm-conserving pseudopotential table. *Computer Physics Communications*, page 10.1016/j.cpc.2018.01.012, 2018.
- [145] Hendrik J. Monkhorst and James D. Pack. Special points for Brillouin-zone integrations. *Physical Review B*, 13(12):5188–5192, 1976.
- [146] Guido Petretto, Xavier Gonze, Geoffroy Hautier, and Gian-Marco Rignanese. Convergence and pitfalls of density functional perturbation theory phonons calculations from a highthroughput perspective. *Computational Materials Science*, 144:331–337, 2018.
- [147] Guido Petretto, Shyam Dwaraknath, Henrique P. C. Miranda, Donald Winston, Matteo Giantomassi, Michiel J. Van Setten, Xavier Gonze, Kristin A. Persson, Geoffroy Hautier, and Gian-Marco Rignanese. High-throughput density functional perturbation theory phonons for inorganic materials. *Scientific data*, 5:180065, 2018.
- [148] Georg K. H. Madsen, Ankita Katre, and Chandan Bera. Calculating the thermal conductivity of the silicon clathrates using the quasi-harmonic approximation. *Physica status solidi* (*A*), 213(3):802–807, 2015.
- [149] Alex Zevalkink, Wolfgang G. Zeier, Ethan Cheng, Jeffrey Snyder, Jean-Pierre Fleurial, and Sabah Bux. Nonstoichiometry in the Zintl phase $Yb_{1-x}Zn_2Sb_2$ as a route to thermoelectric optimization. *Chemistry of Materials*, 26(19):5710–5717, 2014.
- [150] Shaowei Song, Jun Mao, Jing Shuai, Hangtian Zhu, Zhensong Ren, Udara Saparamadu, Zhongjia Tang, Bo Wang, and Zhifeng Ren. Study on anisotropy of n-type Mg₃Sb₂-based thermoelectric materials. *Applied Physics Letters*, 112(9):092103, 2018.
- [151] Wolfgang G. Zeier. New tricks for optimizing thermoelectric materials. *Current Opinion in Green and Sustainable Chemistry*, 4:23–28, 2017.
- [152] Guodong Li, Umut Aydemir, Max Wood, Qi An, William A. Goddard III, Pengcheng Zhai, Qingjie Zhang, and G. Jeffrey Snyder. Deformation mechanisms in high-efficiency thermoelectric layered zintl compounds. *Journal of Materials Chemistry A*, 5:9050–9059, 2017.
- [153] Mansura Khatun, Stanislav S. Stoyko, and Arthur Mar. Quaternary Arsenides AM_{1.5}Tt_{0.5}As₂ (A= Na, K, Rb; M= Zn, Cd; Tt= Si, Ge, Sn): Size Effects in 2-and ThCr₂Si₂-Type Structures. *Inorganic chemistry*, 52(6):3148–3158, 2013.

- [154] Linus Pauling. *The Nature of the Chemical Bond*, volume 260. Cornell university press Ithaca, NY, 1960.
- [155] C. Giacovazzo. Editor. Fundamentals of Crystallography. IUCr, 1992.
- [156] R.D. T. Shannon and C. Tfc Prewitt. Effective ionic radii in oxides and fluorides. (*IUCr*) Acta Crystallographica Section B, 25(5):925–946, 1969.
- [157] G. S. Pomrehn, A. Zevalkink, W. G. Zeier, A. van de Walle, and G. J. Snyder. Defectcontrolled electronic properties in AZn₂Sb₂ Zintl phases. *Angewandte Chemie International Edition*, 53(13):3422–6, 2014.
- [158] Alan R. Denton and Neil W. Ashcroft. Vegard's law. *Physical Review A*, 43(6):3161, 1991.
- [159] D.A. Goodman, L.H. Bennett, and R.E. Watson. Valency effects and relative solubilities in transition metal alloys. *Scripta metallurgica*, 17(1):91–96, 1983.
- [160] Geoffrey Vincent Raynor. XII. Atomic and ionic radii.—III. Polarization effects in alloys. *The London, Edinburgh, and Dublin Philosophical Magazine and Journal of Science*, 26(173):152–165, 1938.
- [161] William Hume-Rothery and Geoffrey Vincent Raynor. XI. Atomic and ionic radii.—II. Application to the theory of solid solubility in alloys. *The London, Edinburgh, and Dublin Philosophical Magazine and Journal of Science*, 26(173):143–152, 1938.
- [162] Zhijun Wang, Yunhao Huang, Yong Yang, Jincheng Wang, and CT Liu. Atomic-size effect and solid solubility of multicomponent alloys. *Scripta Materialia*, 94:28–31, 2015.
- [163] Prashun Gorai, Brenden R. Ortiz, Eric S. Toberer, and Vladan Stevanović. Investigation of ntype doping strategies for Mg₃Sb₂. *Journal of Materials Chemistry A*, 6(28):13806–13815, 2018.
- [164] S.W. Song, J. Mao, M. Bordelon, R. He, Y.M. Wang, J. Shuai, JY Sun, X.B. Lei, S. Ren, Z.S and Chen, et al. Joint effect of magnesium and yttrium on enhancing thermoelectric properties of n-type Zintl Mg_{3+δ}Y_{0.02}Sb_{1.5}Bi_{0.5}. *Materials Today Physics*, 8:25–33, 2019.
- [165] Mario Calderón-Cueva*, Wanyue Peng*, Samantha M. Clarke, Jingxuan Ding, Benjamin Brugman, Gill Levental, Ashiwini Balodhi, Megan Rylko, Olivier Delaire, James P. S. Walsh, Susannah Dorfman, and Alexandra Zevalkink. Anisotropic structural collapse of Mg₃Sb₂ and Mg₃Bi₂ at high pressure. *Chemistry of Materials (submitted)*, 2020.
- [166] John V. Badding. High-pressure synthesis, characterization, and tuning of solid state materials. *Annual Review of Materials Research*, 28(1):631–658, 1998.
- [167] Maxwell Wood, Jimmy Jiahong Kuo, Kazuki Imasato, and Gerald Jeffrey Snyder. Improvement of Low-Temperature zT in a Mg₃Sb₂–Mg₃Bi₂ Solid Solution via Mg-Vapor Annealing. *Advanced Materials*, 31(35):1902337, 2019.

- [168] Jun Mao, Yixuan Wu, Shaowei Song, Qing Zhu, Jing Shuai, Zihang Liu, Yanzhong Pei, and Zhifeng Ren. Defect Engineering for Realizing High Thermoelectric Performance in n-Type Mg₃Sb₂-Based Materials. ACS Energy Letters, 2(10):2245–2250, 2017.
- [169] Cathie L. Condron, Susan M. Kauzlarich, Franck Gascoin, and G. Jeffrey Snyder. Thermoelectric properties and microstructure of Mg₃Sb₂. *Journal of Solid State Chemistry*, 179(8):2252–2257, 2006.
- [170] Vijay Ponnambalam and Donald T Morelli. On the thermoelectric properties of Zintl compounds Mg₃Bi_{2-x}Pnx (Pn= P and Sb). *Journal of electronic materials*, 42(7):1307– 1312, 2013.
- [171] Saneyuki Ohno, Kazuki Imasato, Shashwat Anand, Hiromasa Tamaki, Stephen Dongmin Kang, Prashun Gorai, Hiroki K Sato, Eric S Toberer, Tsutomu Kanno, and G Jeffrey Snyder. Phase boundary mapping to obtain n-type Mg₃Sb₂-based thermoelectrics. *Joule*, 2(1):141– 154, 2018.
- [172] Jun Mao, Hangtian Zhu, Zhiwei Ding, Zihang Liu, Geethal Amila Gamage, Gang Chen, and Zhifeng Ren. High thermoelectric cooling performance of n-type Mg₃Bi₂-based materials. *Science*, 365(6452):495–498, 2019.
- [173] Weiwei Xie, Michał J. Winiarski, Tomasz Klimczuk, and Robert Joseph Cava. A tetragonal polymorph of SrMn₂P₂ made under high pressure-theory and experiment in harmony. *Dalton Transactions*, 46(21):6835–6838, 2017.
- [174] Alex Zevalkink, Matej Bobnar, Ulrich Schwarz, and Yuri Grin. Making and breaking bonds in superconducting sral_{4-x}si_x ($0 \le x \le 2$). *Chem. Mater.*, 29(3):1236–1244, 2017.
- [175] Masashi Tanaka, Shuai Zhang, Kei Inumaru, and Shoji Yamanaka. High-Pressure synthesis and superconductivity of the laves phase compound Ca(Al,Si)₂ composed of truncated tetrahedral cages Ca@(Al, Si)₁₂. *Inorganic Chemistry*, 52(10):6039–6045, 2013.
- [176] Xin Gui, Gregory J. Finkelstein, Keyu Chen, Tommy Yong, Przemyslaw Dera, Jinguang Cheng, and Weiwei Xie. Pressure-Induced Large Volume Collapse, Plane-to-Chain, Insulator to Metal Transition in CaMn₂Bi₂. *Inorganic Chemistry*, 58(14):8933–8937, 2019.
- [177] R.J. Riedner, S.R. Srinivasa, L. Cartz, T.G. Worlton, R. Klinger, and R. Beyerlein. Anisotropic thermal expansion and compressibility of black phosphorus. In *AIP Conference Proceedings*, volume 17, pages 8–20. American Institute of Physics, 1974.
- [178] You Xiang Zhao and Ian L Spain. X-ray diffraction data for graphite to 20 GPa. *Physical Review B*, 40(2):993, 1989.
- [179] S. Stølen, A. Grzechnik, T. Grande, and M. Mezouar. Anisotropic compressibility and expansivity in layered GeSe₂. *Solid State Communications*, 115(5):249–252, 2000.
- [180] Jingxuan Ding, Tyson Lanigan-Atkins, Mario Calderon-Cueva, Arnab Banerjee, Douglas L. Abernathy, Ayman Said, Alexandra Zevalkink, and Olivier Delaire. Anharmonic lattice dynamics in Zintl AMg₂X₂ (A =Mg, Ca, Yb; X =Sb, Bi. In preparation, 2020.

- [181] Mansura Khatun, Stanislav S Stoyko, and Arthur Mar. Quaternary Arsenides AM_{1.5}Tt_{0.5}As₂ (A= Na, K, Rb; M= Zn, Cd; Tt= Si, Ge, Sn): Size Effects in CaAl₂Si₂-and ThCr₂Si₂-Type Structures. *Inorganic chemistry*, 52(6):3148–3158, 2013.
- [182] Charles T. Prewitt and Robert T. Downs. High-pressure crystal chemistry. *Reviews in Mineralogy and Geochemistry*, 37:284–318, 1998.
- [183] Alex Zevalkink, Matej Bobnar, Ulrich Schwarz, and Yuri Grin. Making and Breaking Bonds in Superconducting $SrAl_{4-x}Si_x$ ($0 \le x \le 2$). *Chemistry of Materials*, 29(3):1236–1244, 2017.
- [184] J. Huster and W. Bronger. α und β -BaCu₂X₂ (X = S, Se)–Darstellung von Einkristallen in Kaliumchalkogenocyanat-Schmelzen. *Zeitschrift für anorganische und allgemeine Chemie*, 625(12):2033–2040, 1999.
- [185] G.I. Meijer. Who wins the nonvolatile memory race? *Science*, 319(5870):1625–1626, 2008.
- [186] Matthias Wuttig and Noboru Yamada. Phase-change materials for rewriteable data storage. *Nature Materials*, 6(11):824, 2007.
- [187] Geoffrey W. Burr, Matthew J. Breitwisch, Michele Franceschini, Davide Garetto, Kailash Gopalakrishnan, Bryan Jackson, Bülent Kurdi, Chung Lam, Luis A. Lastras, Alvaro Padilla, et al. Phase change memory technology. *Journal of Vacuum Science & Technology B*, 28(2):223–262, 2010.
- [188] Simone Raoux, Geoffrey W. Burr, Matthew J. Breitwisch, Charles T. Rettner, Y.C. Chen, Robert M. Shelby, Martin Salinga, Daniel Krebs, S.H. Chen, H.L. Lung, et al. Phase-change random access memory: A scalable technology. *IBM Journal of Research & Development*, 52(4.5):465–479, 2008.
- [189] G. Bruns, P. Merkelbach, C. Schlockermann, M. Salinga, M. Wuttig, T.D. Happ, J.B. Philipp, and M. Kund. Nanosecond switching in GeTe phase change memory cells. *Applied Physics Letters*, 95(4):043108, 2009.
- [190] J Hegedüs and SR Elliott. Microscopic origin of the fast crystallization ability of Ge–Sb–Te phase-change memory materials. *Nature Materials*, 7(5):399, 2008.
- [191] Bong-Sub Lee, John R. Abelson, Stephen G. Bishop, Dae-Hwan Kang, Byung-ki Cheong, and Ki-Bum Kim. Investigation of the optical and electronic properties of Ge₂Sb₂Te₅ phase change material in its amorphous, cubic, and hexagonal phases. *Journal of Applied Physics*, 97(9):093509, 2005.
- [192] Stanford R Ovshinsky. Reversible electrical switching phenomena in disordered structures. *Physical Review Letters*, 21(20):1450, 1968.
- [193] Zhimei Sun, Jian Zhou, Andreas Blomqvist, Börje Johansson, and Rajeev Ahuja. Formation of large voids in the amorphous phase-change memory Ge₂Sb₂Te₅ alloy. *Physics Review Letters*, 102(7):075504, 2009.

- [194] Wei Zhu, Ruisheng Yang, Yuancheng Fan, Quanhong Fu, Hongjing Wu, Peng Zhang, Nian-Hai Shen, and Fuli Zhang. Controlling optical polarization conversion with Ge₂Sb₂Te₅based phase-change dielectric metamaterials. *Nanoscale*, 10(25):12054–12061, 2018.
- [195] Ho-Ki Lyeo, David G. Cahill, Bong-Sub Lee, John R. Abelson, Min-Ho Kwon, Ki-Bum Kim, Stephen G. Bishop, and Byung-ki Cheong. Thermal conductivity of phase-change material Ge₂Sb₂Te₅. *Applied Physics Letters*, 89(15):151904, 2006.
- [196] Juan Li, Zhiwei Chen, Xinyue Zhang, Yongxing Sun, Jiong Yang, and Yanzhong Pei. Electronic origin of the high thermoelectric performance of gete among the p-type group iv monotellurides. NPG Asia Materials, 9(3):e353, 2017.
- [197] Jared B. Williams, Spencer P. Mather, Alexander Page, Ctirad Uher, and Donald T. Morelli. Increasing the thermoelectric power factor of Ge₁₇Sb₂Te₂₀ by adjusting the Ge/Sb ratio. *Journal of Applied Physics*, 122(4):045105, 2017.
- [198] Xiao Xu, Lin Xie, Qing Lou, Di Wu, and Jiaqing He. Boosting the Thermoelectric Performance of Pseudo-Layered Sb₂Te₃(GeTe)_n via Vacancy Engineering. Advanced Science, 5(12):1801514, 2018.
- [199] Tobias Rosenthal, Philipp Urban, Kathleen Nimmrich, Ludwig Schenk, Johannes de Boor, Christian Stiewe, and Oliver Oeckler. Enhancing the Thermoelectric Properties of Germanium Antimony Tellurides by Substitution with Selenium in Compounds $Ge_nSb_2(Te_{1-x}Se_x)_{n+3}$ ($0 \le x \le 0.5$; $n \le 7$). *Chemistry of Materials*, 26(8):2567–2578, 2014.
- [200] Tobias Rosenthal, Matthias N. Schneider, Christian Stiewe, Markus Doblinger, and Oliver Oeckler. Real structure and thermoelectric properties of GeTe-rich germanium antimony tellurides. *Chemistry of Materials*, 23(19):4349–4356, 2011.
- [201] THOMAS L Anderson and H BRIGITTE Krause. Refinement of the Sb₂Te₃ and Sb₂Te₂Se structures and their relationship to nonstoichiometric Sb₂Te_{3-y}Se_y compounds. (*IUCr*) Acta Crystallographica Section B, 30(5):1307–1310, 1974.
- [202] Peter Bayliss. Crystal chemistry and crystallography of some minerals in the tetradymite group. *American Mineralogist*, 76(1-2):257–265, 1991.
- [203] Matthias N. Schneider, Markus Seibald, Patrick Lagally, and Oliver Oeckler. Ambiguities in the structure determination of antimony tellurides arising from almost homometric structure models and stacking disorder. *Journal of Applied Crystallography*, 43(5):1012–1020, 2010.
- [204] O.G. Karpinsky, L.E. Shelimova, M.A. Kretova, and J.P. Fleurial. An X-ray study of the mixed-layered compounds of (GeTe)_n (Sb₂Te₃)_m homologous series. *Journal of alloys and compounds*, 268(1):112–117, 1998.
- [205] Andriy Lotnyk, Torben Dankwort, Isom Hilmi, Lorenz Kienle, and Bernd Rauschenbach. *In-situ* observations of the reversible vacancy ordering process in van der Waals-bonded Ge-Sb-Te thin films and GeTe-Sb₂Te₃ superlattices. *Nanoscale*, 11(22):10838–10845, 2019.

- [206] Jamo Momand, Ruining Wang, Jos E. Boschker, Marcel A. Verheijen, Raffaella Calarco, and Bart J. Kooi. Dynamic reconfiguration of van der Waals gaps within GeTe-Sb₂Te₃ based superlattices. *Nanoscale*, 9(25):8774–8780, 2017.
- [207] Peter Zalden, Karl Simon Siegert, Stephane Rols, Henry E. Fischer, Franziska Schlich, Te Hu, and Matthias Wuttig. Specific Heat of $(GeTe)_x(Sb_2Te_3)_{1-x}$ Phase-Change Materials: The Impact of Disorder and Anharmonicity. *Chemistry of Materials*, 26(7):2307–2312, 2014.
- [208] Juarez L.F. Da Silva, Aron Walsh, and Hosun Lee. Insights into the structure of the stable and metastable $(GeTe)_m(Sb_2Te_3)_n$ compounds. *Physical Review B*, 78(22):224111, 2008.
- [209] Andriy Lotnyk, Isom Hilmi, Ulrich Ross, and Bernd Rauschenbach. Van der Waals interfacial bonding and intermixing in GeTe-Sb₂Te₃-based superlattices. *Nano Research*, 11(3):1676– 1686, 2018.
- [210] T. Seddon, J.M. Farley, and G.A. Saunders. An acoustic anomaly at the phase transition in GeTe SnTe alloy single crystals. *Solid State Communications*, 17(1):55–57, 1975.
- [211] Naor Madar, Tom Givon, Dmitry Mogilyansky, and Yaniv Gelbstein. High thermoelectric potential of Bi₂Te₃ alloyed GeTe-rich phases. *Journal of Applied Physics*, 120(3):035102, 2016.