ON THERMAL TRANSPORT AND ITS RELATIONSHIP WITH BOND-STIFFNESS IN MATERIALS FOR THERMOELECTRIC APPLICATIONS

By

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ABSTRACT

The lattice thermal conductivity, $\kappa_{\rm L}$, is a fundamental physical property which characterizes the heat transport due to the solid's lattice vibrations (*phonons*). This intrinsic property is of great importance for the performance of a wide variety of devices, such as thermal barrier coating, electronics, optoelectronic, and thermoelectrics. In thermoelectrics, i.e., materials that convert heat to electricity or vice versa, having low $\kappa_{\rm L}$ is critical for efficient thermal-to-electrical energy conversion. The heat transport by phonons which, in turn control the phonon group velocities and scattering rates, are related to the solid's bond stiffness and anharmonicity. To study these effects, a combination of high-pressure synchrotron X-ray diffraction (HP-XRD) and high-temperature resonant ultrasound spectroscopy (HT-RUS) was used to quantify both local and average bond stiffness and anharmonic effects.

High-pressure experiments were carried out to investigate the stability and bond stiffness of AM_2X_2 Zintl phases. For this purpose, single- and poly-crystals of several compounds, including Mg₃Bi₂, Mg₃Sb₂, CaMg₂Bi₂, and YbMg₂Bi₂, were synthesized. These samples were hydrostatically compressed inside diamond anvil cells for *in-situ* synchrotron radiation X-ray diffraction. As a result, the compressibility of the unit cell, lattice parameters, and individual bonds were obtained. It is shown that the octahedral *A* cation sites on all compositions are more compressible than the tetrahedral *M* cation sites. Furthermore, the influence of ionic radii on the compressibility was investigated. Additionally, reversible high-pressure phase transitions were discovered, and the high-pressure structures were solved, which are shown to be monoclinic, with space group *C2/m*.

In the second part of this thesis, HT-RUS was used to investigate the average bond stiffness (e.g., as quantified by the elastic constants) as a function of temperature and composition in the $(GeSe)_{1-x}$ - $(AgBiSe_2)_x$ (x=0, 0.1, 0.2, 0.3, 0.4) system. The crystal structure progressively transitions from an orthorhombic *Pnma*, to a rhombohedral *R3m*, to a cubic *Fm3m* arrangement, with marked consequences on the lattice thermal conductivity. With temperature, all the compositions eventually evolve to the rock-salt phase. From the HT-RUS experiments, it was determined that the cubic structure shows, on average, stiffer bonds compared to the other symmetries (rhombohedral and

orthorhombic) present in this material system, which ultimately increases κ_L . In contrast, using scattering rate estimations, it is shown that an increase in alloying leads to a suppression of κ_L , mainly due to alloy scattering. From these observations, it is demonstrated how κ_L is suppressed by the combined influence of the softening of elastic constants and an increase in the scattering rate.

I dedicate this work to my sister, Amelia. Don't you let them get you to trade your heroes for ghosts, hot ashes for trees, hot air for a cool breeze, cold comfort for change.

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CHAPTER 1

BACKGROUND AND INTRODUCTION

1.1 Fundamentals of Thermoelectrics

It is imperative to find efficient energy conversion strategies to limit the increase of global energy use and, incidentally, decrease the greenhouse emissions [1, 2]. One strategy, for example, to tackle this impending issue, is to recover *waste* energy. Even in the most recent US energy flow chart, as shown in Figure 1.1, the quantity of waste energy (labeled as *rejected energy*) amounts to more than 67% of the total energy consumed.



Figure 1.1: US consumption and use of energy in the year 2021, in units of quad (1 quad = 10^{15} BTU $\approx 1.1 \times 10^{18}$ J). Figure from [3].

Since the majority of the rejected energy, more than 70%, is waste heat [4], it is of major importance to implement strategies to recover thermal energy. For this purpose, thermoelectric devices are great candidates to harvest that rejected heat and convert it into electricity. The thermoelectric effect, first discovered by T. J. Seebeck in the early 1820s [5], is a two-way process: either the generation of an electric current upon application of a temperature gradient in the material (known as the *Seebeck effect*), or the production of a temperature gradient inside the solid when subjected to an electric current (the *Peltier effect*). The latter effect, named after the observations by J. C. A. Peltier in 1834 [6], was demonstrated by H. F. E. Lenz to have a heating or cooling effect depending on the direction of the applied current [7]. The Seebeck effect, expressed by the Seebeck coefficient (*S*), can be quantified in terms of the induced voltage (V) in response

to an applied temperature gradient (ΔT). Mathematically, this coefficient is $S = V/\Delta T$, which is commonly expressed in units of $\mu V/K$. Similarly, the Peltier coefficient (Π) is defined as the induced temperature change (due to the heat transferred) in response to an electric current applied to the material, as $\Pi = Q/I$, where Q and I are the induced heat and the current at the junction, respectively. These observations led W. Thomson (Lord Kelvin) to explain the thermodynamic relation governing the Seebeck and Peltier effect [8], namely: $\Pi = ST$. Additionally, Thomson observed a third effect, now known as the *Thomson effect*, which is the heating or cooling of the material which is simultaneously subjected to a temperature gradient and an electric current. This effect is described in terms of the Thomson coefficient τ as: $\tau = S dS/dT$.

Technologically, the electric generation from heat is achieved by a thermoelectric generator (TEG), schematically shown in Figure 1.2. It consists of one p- and one n-type thermoelectric bulk materials (known as *legs* in light blue) connected to metal conductors (in dark blue) to the heat source and the heat sink. The term *p-type* refers to a thermoelectric material whose majority electrical carriers are electron holes (electron deficiency), or simply holes. Conversely, *n-type* thermoelectrics have electrons as their majority carriers. In a TEG, when a temperature gradient is applied, the holes in a p-type leg travel from the hot to the cold side, and the electrons travel from the hot to the cold end. A real thermoelectric device consists of many alternating p- and n-type legs electrically connected in series and thermally connected in parallel.

For an idealized device, i.e., when the thermoelectric properties are constant, the maximum conversion efficiency of heat to power (η_{max}) is given by:

$$\eta_{\text{max}} = \frac{T_{\text{H}} - T_{\text{C}}}{T_{\text{H}}} \frac{\sqrt{1 + \overline{ZT} - 1}}{\sqrt{1 + \overline{ZT}} + \frac{T_{\text{C}}}{T_{\text{H}}}}$$
(1.1)

where T_H , T_C , and \overline{ZT} are the hot-side temperature, the cold-side temperature, and the device's thermoelectric figure of merit (ZT) averaged, respectively. Note that the first term in Equation 1.1 is the Carnot efficiency–the maximum efficiency of a heat engine that operates between temperatures T_H and T_C . The thermoelectric performance of the device, ZT, which includes electrical and thermal



Figure 1.2: Schematic of a thermoelectric device.

contact resistances, is given by:

$$ZT = \frac{S^2}{RK}T$$
(1.2)

where S is the Seebeck coefficient, R the electrical resistance, K the thermal conductance and T the absolute temperature. To increase the device's thermoelectric efficiency (ZT), the major challenge currently [9] is to improve the *material* figure of merit zT. The metric to assess such performance is the *material thermoelectric figure of merit* zT expressed by:

$$zT = \frac{\sigma S^2}{\kappa} T \tag{1.3}$$

where σ , κ , S, and T are the electrical conductivity, the thermal conductivity, the Seebeck coefficient, and the temperature, respectively. The thermal conductivity can be separated into the lattice (κ_L) and electronic (κ_e) contributions as: $\kappa = \kappa_L + \kappa_e$. From Equation 1.3, it is clear that a high Seebeck coefficient (S), high electrical conductivity (σ), and a low thermal conductivity (κ), are desired for thermoelectric applications. The figure of merit, *zT*, of some of commonly used thermoelectric materials are depicted in Figure 1.3.

It is not easy to achieve all these requirements, since these materials properties are highly correlated. The present research will focus on the κ_L and its relation to crystal structure, and



Figure 1.3: Thermoelectric figure of merit of a) n-type and b) p-type materials. Adapted from [10].

therefore, bonding properties.

1.2 Factors That Impact Thermal Conductivity

As previously mentioned, $\kappa_{\rm L}$ is dictated by the material's lattice dynamics, i.e., *phonons*. Phonons exist in a range of frequency, from 0 to the Debye frequency, $\omega_{\rm D}$, and the allowed frequencies and momentum are quantified by dispersion relations. Mathematically, the phonon thermal conductivity ($\kappa_{\rm L}$) can be expressed as:

$$\kappa_{\rm L} = \frac{1}{3} C_{\rm V} v^2 \tau \tag{1.4}$$

where C_V is the heat capacity, v is the phonon velocity, and τ is the phonon relaxation time. The phonon velocity, namely its group velocity (v_g) , is determined by the local energy gradient $(E_{qj} = \hbar \omega_{qj})$ with respect to the phonon momentum with the *dispersion relation*:

$$\mathbf{v}_{\mathbf{q}\mathbf{j}} = \hbar \frac{\partial \omega_{\mathbf{q}\mathbf{j}}}{\partial \mathbf{q}} \tag{1.5}$$

where ω is the angular frequency, h is the reduced Planck constant (h/2 π) and **q** is the momentum. Equation 1.5 highlights the dependence of the v_g on the phonon branch (j). Traditionally, due to the difficulty of experimentally obtaining v_g, it is commonly approximated to the (low-frequency) wave propagation speed inside the material, i.e., *the speed of sound*, v_s. By using this approximation, it is possible to use the following relation, which is ubiquitous in the present study: v_s $\propto \sqrt{(E/\rho)}$. This is a crucial equation which shows the dependence of the speed of sound as a function of E (the appropriate *elastic modulus*) and ρ (its density). The elastic moduli and its relation with κ_L will be discussed in detail in the following section.

1.2.1 Elasticity

Elasticity is the reversible deformation below a certain threshold—known as the *elastic limit*— of the material as a response to stress. This intrinsic property is expressed in terms of its stiffness tensor C, with components C_{ij} (in matrix notation) [11]. The number of components needed to fully describe the elastic tensor is dependent on the symmetry of the crystal (ranging from 3 for cubic to 21 for triclinic symmetries [12]). For polycrystalline, bulk materials, there are only two independent constants, namely C_{11} and C_{44} . This so-called *isotropic approximation* is valid when the sample dimensions are much bigger than the size of their grains, and when the crystallographic orientations of such grains are random [13]. Experimentally, C_{11} and C_{44} can be obtained by measuring the elastic wave propagation inside the solid, i.e., by measuring the speed of sound (v_s), as mentioned in the previous section. v_s is the *average* speed of sound, and is composed of longitudinal (v_l) and transverse (v_t) components. In the case of a longitudinal wave, the oscillating mass particles of the medium move in the same direction as the wave itself. In contrast, the transverse wave has a direction of propagation perpendicular to the displacement of the particles. The longitudinal and transverse components of the speed of sound are related to v_s by:

$$\mathbf{v}_{\rm s} = \left(\frac{1}{3} \left[\frac{1}{\mathbf{v}_1^3} + \frac{2}{\mathbf{v}_t^3}\right]\right)^{-\frac{1}{3}} \tag{1.6}$$

For convenience, we will utilize the more familiar engineering moduli, the bulk modulus (B) and the shear modulus (G), instead of the matrix components C_{11} and C_{44} . Using the isotropic approximation, i.e., with $C_{11} = B + \frac{4}{3}G$ and $C_{44} = G$, v_1 and v_t are:

$$\mathbf{v}_{1} = \sqrt{\frac{\mathbf{B} + \frac{4}{3}\mathbf{G}}{\rho}} \tag{1.7a}$$

$$v_t = \sqrt{\frac{G}{\rho}}$$
(1.7b)

where ρ is the density of the solid.

In order to relate the previous equations to microscopic quantities, we introduce the mass-andspring model. In this model, the crystal is treated as a linear chain of spheres of mass (m) connected by spring constants (K). The solution of the equation of motion for that model introduces the angular frequency, ω , expressed as:

$$\boldsymbol{\omega} = \sqrt{\frac{\mathrm{K}}{\mathrm{m}}} \tag{1.8}$$

Although this model has to be modified for the case of polyatomic crystal lattices, the inverse proportionality of ω to the root of the (average) mass holds true. It is worth mentioning that $\omega \propto \sqrt{K}$ is applicable to the 3D, polyatomic case.

From Equation 1.8, it becomes evident that a soft bond (low K) leads to lower ω , and thus to lower v_g, which ultimately leads to a low κ_L in Eq. 1.4. In addition, every crystallographically unique bond present in the material has a unique stiffness. For example, in Mg₃Bi₂ and Mg₃Sb₂ there are 3 unique types of bonds. This means that, in order to fully describe K, it is necessary to establish *individual* bond strength. Experimentally, the *average* elastic modulus can be readily determined using polycrystalline samples via resonant ultrasound spectroscopy or sound velocity measurements [14]; however, the characterization of individual bond strengths require single crystals and more involved experiments. In this work, we take advantage of high-pressure X-ray diffraction to accomplish this.

1.2.2 Anharmonicity and Phonon Scattering

To continue the discussion of the lattice dynamics of the material, let us consider a small displacement **R** applied to the material. As a consequence of this displacement, the solid's response can be described in terms of a Taylor series expansion of its potential energy $U(\mathbf{R})$ in terms of the atomic displacement from its equilibrium position \mathbf{R}_0 as:

$$U(\mathbf{R}) = U(\mathbf{0}) + A_2 (\mathbf{R} - \mathbf{R}_0)^2 + A_3 (\mathbf{R} - \mathbf{R}_0)^3 + \dots$$
(1.9)

where A_2 and A_3 are the magnitudes of its harmonic and first anharmonic terms, respectively. The anharmonicity of the system is quantified by the ratio A_3/A_2 , or A_4/A_2 if the A_3 term vanishes due

to the crystal symmetry. If we take the second derivative of Eq. 1.9 with respect to displacement, the modulus of elasticity (E) —known as the *force constant*— of the material is obtained:

$$\mathbf{E} = \frac{1}{\mathbf{R}_0} \nabla \mathbf{U} \bigg|_{\mathbf{R} = \mathbf{R}_0} \tag{1.10}$$

This can be thought of as the linear response to the force that the system exerts to bring the atoms back to their equilibrium position after a small atomic displacement. If we take the harmonic term only, the modulus of elasticity, E, would be constant. However, E becomes smaller with increasing potential energy (U), atomic displacement (**R**), and temperature. Furthermore, from Eq. 1.10 and 1.9, it becomes evident why A_3/A_2 is a measure of anharmonicity.

To continue the analysis of Equation 1.4, we consider now the relaxation time, τ . This is a measure of phonon scattering in the material. It is composed of a number of terms, where the *Umklapp* contribution (τ_L) is the most important for high temperature applications. Umklapp scattering refers to the interaction between two or more phonons that creates phonons that travel in the opposite direction of the heat flow [15]. The inclusion of the third-order term (the first anharmonic contribution) in Equation 1.9 gives rise to Umklapp scattering. This means that if a compound is highly anharmonic, its κ_L may be suppressed considerably. For our study, since we are interested in the heat transport well above the Debye temperature, it is often safe to approximate the total relaxation time (τ_{Tot}) as the relaxation time due to Umklapp scattering (τ_U). Although there are many forms to express the Umklapp-dominated relaxation time, the following equation is used due to its universality [16, 17]:

$$\tau_{\rm U} \propto \frac{{\rm M}{\rm v}^3}{{\rm V}^{1/3} \omega^2 \gamma^2 {\rm T}} \tag{1.11}$$

where M, V, ω , T, and γ are the average mass, the unit cell volume, the angular frequency, and the Grüneisen parameter, respectively. It is worth mentioning that τ_U has a strong temperature dependence while the other scattering mechanisms do not. The Grüneisen parameter can be expressed as the change in pressure as a function of internal energy at constant volume. Thus, γ is a measure of the change in ω as a function of the unit cell volume as shown in Equation 1.12:

$$\gamma_{i}(q) = -\frac{\partial \ln \omega(q)_{i}}{\partial \ln V}$$
(1.12)

Based on this last relation, γ accounts for the variation of lattice dynamics as a function of temperature, since V increases as a function of the temperature in most solids. Experimentally, γ_i can be measured using the *linewidth* of the phonon dispersion from inelastic neutron scattering (INS) or inelastic X-ray scattering (IXS) measurements on single-crystals [18].

For the present study, due to the experimental complexity of a direct measurement of τ_u , the Grüneisen parameter (γ) is used to account for the bonding anharmonicity in the system. This approach, based on $\tau_U \propto \gamma^{-2}$ (from Eq. 1.11), utilizes the rate at which the elastic constants vary with temperature, and thermal expansion of the solids. Specifically, there are three methods (averaged over all modes) to calculate the Grüneisen parameter. The first method takes into account the Poisson's ratio, μ , and the corresponding equation is:

$$\gamma_{\mu} = \frac{3}{2} \frac{1+\mu}{2-3\mu} \tag{1.13}$$

The second method, known as the Ledbetter method [19] which for, high-temperature applications, is mathematically expressed as:

$$\frac{\partial \mathbf{K}}{\partial \mathbf{T}} = \frac{3\mathbf{k}_{\mathbf{B}}}{\mathbf{V}_{\mathbf{a}}} \boldsymbol{\gamma}_{\mathbf{L}} \left(\boldsymbol{\gamma}_{\mathbf{L}} + 1 \right) \tag{1.14}$$

where K, T, k_B , and V_a are any elastic modulus, temperature, Boltzmann constant, and volume per atom, respectively. The third method, the most used one to estimate the Grüneisen parameter, is based on the volumetric thermal expansion coefficient (α_V), the bulk modulus (B), the heat capacity at constant volume C_V , and the solid's density rho, which uses the equation:

$$\gamma_{\alpha} = \frac{\alpha_{\rm V} B}{C_{\rm V} \rho} \tag{1.15}$$

Although the three different methods to calculate the Grüneisen parameter may give different results, they are useful to draw general conclusions on the trends of the selected materials of this study. The next sections will introduce the materials studied in the present work

1.3 Introduction to AM_2X_2 Zintl Phases and (GeSe)_{1-x}-(AgBiSe₂)_x Thermoelectrics

The present work will focus on two different classes of materials, namely AM_2X_2 (where A = Ca, Mg, Yb, M = Mg, and X = Bi, Sb) and the $(GeSe)_{1-x}$ - $(AgBiSe_2)_x$ system. Both classes

bridge the gap between three-dimensional (3D) and layered crystal structures, and the in-plane vs. out-of-plane bond strength can be controlled by tuning the composition.

1.3.1 AM_2X_2 Zintl Phases

In recent years, one of the most studied thermoelectric materials for its impressive zT is the Zintl phase Mg₃*Pn*₂ (*Pn*=Sb, Bi) [20–22]. Although these compounds were discovered in the 1930s [23], their popularity has dramatically increased in the past decade, in part due to their abnormally low κ_L . In the present study, we will focus on the lattice dynamics and the crystal structure of binary and ternary Zintl phases for thermoelectric applications. Specifically, the present study focuses on the compounds CaMg₂Bi₂, YbMg₂Bi₂, Mg₃Sb₂, and Mg₃Bi₂ to understand the effect of replacing the Mg atom with Ca or Yb in the cation site.

Formally, Zintl compounds are composed of an alkali element (group 1 in the periodic table) or alkaline-earth (group 2) and a main-group element with high electronegativity. The latter can be either a metal, a semi-metal, or a semiconductor of small bandgap. In general terms, a Zintl phase has closed electronic shells, due to the complete electronic transfer between the group 1 or group 2 and the electronegative elements. This electronic balance is achieved by the formation of covalent bonds or lone pairs of electrons among the electronegative elements [24]. Usually, Zintl phases exhibit semiconducting or poor electric conductivity behavior, high melting points, and higher brittleness than other intermetallic compounds. [25].

Zintl phases that crystallize in the CaAl₂Si₂ structure type (with space group $P\bar{3}mI$) are widely studied in the field of thermoelectrics. These compounds, often referred as *122s*, consist of alternating layers of electropositive (A^{2+}) elements and $[M_2X_2]^{2-}$ slabs, as depicted in Figure 1.4. In the aforementioned figure, the cation (A, in yellow) is a rare-earth or alkaline-earth element, a transition metal or a group-13 element (M, in orange) and an element from groups 14 or 15 (X, in blue).

Particularly, compounds in the form AM_2Pn_2 (where A = Ca, Mg, Eu, Yb; M = Mg, Zn; Pn = Bi, Sb) for their high figure of merit ($zT \ge 1$) [26–30]. Of particular interest are compounds that have

Mg in the cation and the metal site, for their remarkably high thermoelectric performance (zT > 1.5 at 724 K [31–33]) are compounds. In the search for tellurium-free compounds, these 122s have attracted great attention in recent years because they challenge the decades-long reign of Bi₂Te₃ in the low-to-mid temperature range [34, 35].



Figure 1.4: AM_2X_2 crystal structure.

In contrast, the binary Mg₃*Pn*₂ (*Pn*= Sb, Bi) Zintl compounds appear to contradict the origin of a low κ_L . For instance, at 50°C, κ_L in Mg₃Sb₂ is ~ 1.4 W/mK, comparable to that of Bi₂Te₃ [36] despite their substantial density difference ($\rho_{Mg_3Bi_2} = 3.94 \text{ g/cm}^3 \text{ vs. } \rho_{Bi_2Te_3} = 7.47 \text{ g/cm}^3$). Additionally, as previously discussed, although the structure of Mg₃*Pn*₂ is significantly less complex than other Zintl compounds, such as $A_{14}MPn_{11}$ and $A_9M_4Pn_9$ [37–40], they exhibit low intrinsic κ_L . Moreover, the ternary (AMg_2Pn_2) compounds have higher κ_L compared to their binary counterparts (Mg₃*Pn*₂). Since the origin of low κ_L cannot be elucidated by density and structural complexity for binary AMg_2Pn_2 , we turn to the bonding environment and its effects on intrinsic thermal transport.

The other source of low κ_L stems from low v_g , which is usually present in compounds that have a complex chemistry, high density, and soft bonds [41, 42]. In Bi₂Te₃, a well-studied layered thermoelectric, κ_L is ~ 0.6 W/mK in the direction of its van der Waals bonds. For this same material, κ_L rises to ~ 1.5 W/mK perpendicular to the direction of the van der Waals bonds [43]. The discrepancy of κ_L in Bi₂Te₃ lies in the bond strength: *soft* interlayer van der Waals bonds vs. stronger, mainly covalent, interlayer bonds between Bi-Te [44]. Another example of Zintl phases that exhibit intrinsic low κ_L are the $A_{14}MPn_{11}$ compounds (A=Ca, Ba, Yb; M=Al, Mn; Pn=Sb, Bi). Specifically, $Yb_{14}MnPn_{11}$ shows remarkably low κ_L (~ 0.6 W/mK) due to its complex structure and the presence of heavy elements [45–47]. The unit cell of $Yb_{14}MnPn_{11}$ exhibits a combination linear chains of *Pn* atoms, *MPn*₄ tetrahedra, and isolated *Pn* atoms [45].

Recently, it has been confirmed that the origin of the anomalously low κ_L in Mg₃Sb₂ and Mg₃Bi₂ arises from soft phonon transverse modes in the acoustic branches as well as anharmonic effects in the optical and some acoustic phonon branches [48–50]. Although these findings show unequivocal proof of the presence of anharmonicity and isotropic compressibility in the binary Mg₃Bi₂ and Mg₃Sb₂ compounds as a possible origin of the low κ_L , an experimental validation of these predictions was missing. This study presents a direct observation of the origin of the soft phonon modes rooted in the chemical bonding environment. With the aid of high-pressure X-ray diffraction (XRD), we present experimental evidence of the influence of *bond-strength* in binary Mg₃Pn₂ as the origin of the intrinsically low κ_L .

1.3.2 The (GeSe)_{1-x}-(AgBiSe₂)_x System

Inherently low κ_L is observed in compounds where the phonon scattering rate (τ^{-1}) is large and the phonon group velocity (v_g) is low. A large τ is associated with lattice instabilities because that meta-stable bonding environments increase the interaction of phonons (three-phonon mechanisms in the phase-space) and result in strong anharmonicity and, therefore, low κ_L . One important example of lattice instabilities is SnSe, a layered orthorhombic structure (*Pnma*) below 810 K. The unit cell of SnSe is composed of two Sn-Se bilayers along the *a*-direction and soft interlayer bonds. These interlayer bonds have been identified as the source of the bonding network instability of the Se atoms that dramatically suppresses κ_L [51].

SnSe is a member of the so-called semiconducting IV-VI chalcogenides, i.e., compounds that contain the elements: Ge, Sn, or Pb (group IV) and S, Se, or Te (group VI), which are of great importance in thermoelectrics for their high performance [52–54, 54, 55]. Among these IV-VI materials, (Sn,Pb)Te, as well as Pb(S,Se), crystallize in the cubic $Fm\bar{3}m$ (*rock-salt*) structure-type [56] at room temperature, while (Ge,Sn)Se are orthorhombic (*Pnma*) at ambient conditions. On the other hand, GeTe, is rhombohedral at 300 K and experiences a spontaneous phase transition to $Fm\bar{3}m$ above 625 K [57]. Interestingly, GeSe also transforms to the rock-salt structure, but at a

higher temperature, namely at \approx 925 K[58, 59].

Most of the high-performing thermoelectrics contain Te [60–62], a scarce element throughout Earth's crust [63]. One remarkable example of such high-zT, tellurium-based compounds are the so-called TAGS, i.e., GeTe-AgBiTe₂ alloys. As shown in Fig. 1.3a, these p-type compounds show exceptional zT in the temperature range between 600 K and 800 K (known as the *mid-temperature* range in thermoelectrics). Although TAGS have been extensively studied for over 50 years [64–68], the need for high-efficiency, n-type, Te-free materials is still pending. Over the past decade, SnSe has emerged as a promising candidate to the task, with single-crystalline samples that exhibit zTof 2.6 at 923 K [69], which has been attributed to its intrinsically low $\kappa_{\rm L}$ [70]. Motivated by this high thermoelectric performance, a more recent study predicted a theoretical zT in GeSe that would exceed that of SnSe [71]. Using Density Functional Theory (DFT), researchers claimed that the optimization in the carrier concentration in GeSe would yield record values of zT at 800 K. However, the experiments revealed a zT value of only 0.2 at 700 K, where the low carrier concentration was identified as the reason for such low thermoelectric performance [72]. To overcome this issue, recent studies have shown promising results by alloying GeSe with AgBiSe₂, where the thermoelectric properties improve considerably [73]. One of the most interesting features of the $(GeSe)_{1-x}$ -(AgBiSe₂)_x system is it that exhibits four crystal structures at room temperature as a function of alloying. As mentioned before, GeSe is orthorhombic (Pnma). By gradually adding AgBiSe₂, this structure evolves into a rhombohedral symmetry (space group R3m) above 10% alloying, and becomes cubic (space group $Fm\bar{3}m$) above 30% alloying [74]. Interestingly, the rhombohedral and orthorhombic structures morph into the rock-salt structure with temperature. The other end member of the system, AgBiSe₂, is trigonal ($P\bar{3}mI$), and transforms into a rhombohedral symmetry ($R\bar{3}m$ at 390 K and to the rock-salt structure at 560 K [75].

Previous studies on this material system have shown that by only adding 10% of AgBiSe₂ to GeSe, κ_L reduces from ~ 1.8 W/mK to ~ 0.5 W/mK at room temperature [74, 76]. Furthermore, these values remain similar for x = 0.2, 0.3, 0.4, and 1.0 compositions [77, 77]. To date, the influence of crystal structure and alloying on κ_L has not been fully explained. Due to the variety of structures

in a relatively small temperature and composition range, the $(GeSe)_{1-x}$ - $(AgBiSe_2)_x$ system provides a unique opportunity to study the interplay between crystal structure and chemistry (composition alloying), and how this relation determines the thermal transport properties of the system.

1.4 Goals of the Present Work

As previously discussed, the bonding environment can profoundly affect the intrinsic thermal transport properties in promising thermoelectric materials. Although Zintl phases and the $(GeSe)_{1-x}$ -(AgBiSe₂)_x system have been extensively studied, the link between bond strength, crystal structure, and lattice thermal conductivity in each of them is missing. Therefore, the focus of the present research is to study the interplay between the chemical bonds and thermal transport in these materials. Herein, we have used *in-situ* high-pressure synchrotron X-ray diffraction to investigate the stiffness and stability of AM_2X_2 compounds to better understand the interplay between structural features and lattice thermal conductivity. The structure-property relationship of the $(GeSe)_{1-x}$ - $(AgBiSe_2)_x$ system was studied by a combination of high-temperature X-ray diffraction and high-temperature resonant ultrasound spectroscopy. The experiments conducted in the present research, show the effect of the crystal structure and alloying on the elastic properties of this material system. By conducting these experiments, we were able to investigate the phonon transport in the material, by characterizing the bond stiffness and scattering rates as decoupled factors on the lattice dynamics. The results of this research contribute to the understanding of the mechanisms that control $\kappa_{\rm L}$ in the (GeSe)_{1-x}-(AgBiSe₂)_x alloys, arising from bond strength and from different phonon scattering mechanisms.

CHAPTER 2

EXPERIMENTAL DETAILS

2.1 Materials Synthesis

2.1.1 Synthesis of AM₂Pn₂ (A=Ca, Mg, Yb, Pn=Sb, Bi) Zintl phases

The present study required the synthesis of single crystals and polycrystalline samples of AMg_2Pn_2 compounds; the effect on κ_L was then analyzed by substituting Mg for another element in the cation site (*A* atom). For this purpose, the compositions Mg_3Sb_2, Mg_3Bi_2, CaMg_2Bi_2, and YbMg_2Bi_2, were chosen. Experimentally, the purpose of synthesizing high-quality single crystals is to analyze *individual* bond strengths. For this reason, all the aforementioned AMg_2Pn_2 compounds were synthesized as single and poly crystals.

2.1.1.1 Synthesis of Polycrystalline Samples

For the synthesis of polycrystalline samples, the spark plasma sintering (SPS) method was employed using the Dr. Sinter SPS-211LX at MSU. For this purpose, stoichiometric amounts of the corresponding elements were weighed inside the Argon-filled glovebox. The elements and three 10-mm steel balls were then loaded in a stainless-steel jar and ball-milled for one hour in a high-energy SPEX mill. The resulting powder was then placed in graphite dies and subjected to 31 MPa of pressure; the target temperature was reached in 5 minutes and maintained for 10 minutes. The target sintering temperatures for Mg₃Sb₂, Mg₃Bi₂, CaMg₂Bi₂, and YbMg₂Bi₂ are 850 °C, 700 °C, 650 °C, and 600 °C, respectively. The SPS synthesis parameters for Mg₃Sb₂ and Mg₃Bi₂ were chosen from Refs. [78]. For the CaMg₂Bi₂ and YbMg₂Bi₂, the maximum temperatures for the SPS process were calculated as 80% of the melting temperatures reported in Ref. [27]. Then, the pressure was released and the sintering chamber allowed to cool down to approximately 40 °C. The phase purity of the samples was then confirmed via powder X-ray diffraction (PXRD) using a Rigaku Smartlab X-ray diffraction system with Cu-K α radiation at MSU as exemplified in Figure 2.1.



Figure 2.1: PXRD pattern of CaMg₂Sb₂ from SPS. The obtained samples contained less that 5% secondary phase (Bi).

2.1.1.2 AM₂Pn₂ Single-Crystal Growth

Single crystals were synthesized using two methods, the self-flux growth method and the Bridgman method [79].

 AM_2Pn_2 Bridgman Growth In the Bridgman method, single crystals of the desired phase are obtained via slow, directional solidification from the melt. Experimentally, this is realized by slowly moving the vacuum-sealed quartz ampule ($v_a \sim 3mm/h$) that contains the elements from the furnace region which is above T_M to the bottom of the furnace, where the temperature is below T_M . The experimental setup, shown in Figure 2.2, consists of a vertical tubular furnace kept at a temperature (T_F) above the melting temperature (T_M) of the desired phase. For all experiments reported here, $T_F = 200 \text{ °C} + T_M$. Although T_F is kept constant, a temperature gradient is created by thermally insulating the top of the furnace while keeping the bottom part open to air. At the beginning of the experiment, the alumina (Al_2O_3) crucible with the elements is kept at the top of the furnace for 12 hours to ensure that the melt is homogeneous. The crystal starts to solidify at the tip of the tapered crucible and, if the crystallization speed is smaller than v_a , the crystal will grow as one grain.



Figure 2.2: Mg_3Sb_2 clusters of crystals grown via CVT adhered to inner wall of Al_2O_2 crucible. **Self-Flux Growths** The self-flux growth, also known as the molten-metal flux, is a single-crystal growth technique for intermetallic compounds that takes advantage of improved diffusion of atoms in the liquid solvent (known as the *flux*) and a reduced synthesis temperature of the desired phase [80]. To illustrate the working principle of this synthesis technique, let us consider the following phase diagram of Mg_3Sb_2 (Figure 2.3), modified from [81, 82]:

The aforementioned phase diagram shows that Mg₃Sb₂ solidifies at 1227°C, which would be the necessary temperature to obtain such phase if the starting ratio of Mg:Sb was 3:2. The desired trigonal phase, α -Mg₃Sb₂, crystallizes at around 930 °C, above which the β -Mg₃Sb₂ phase exists (as a body-centered cubic unit cell [83]). If, for instance, the starting stoichiometry of Mg:Sb was 3:7, Mg₃Sb₂ would start to crystallize at approx. 690°C. Evidently, the choice of the starting stoichiometric amounts of the two elements in question demonstrate technological advantages for the synthesis of the desired phase, such as reduction of almost 50% of the temperature of the furnace. At the same time, the phase diagram demonstrates that, at the ratio of Mg:Sb = 3:7, between 580°C and 690°C, solid α -Mg₃Sb₂ coexists with the liquid phase (L). If the sample is further allowed to cool, i.e., below 580°C, the sample will exist as a solid solution of Sb and α -Mg₃Sb₂. For this reason, the solvent (or flux) has to be separated from the α -Mg₃Sb₂ crystals. This is achieved by chemical or mechanical means. For the present work, mechanical separation of the flux was



Figure 2.3: Phase diagram for the Mg-Sb system. Dashed blue lines denote the α - and β -phases of Mg₃Sb₂. Solid blue lines show special temperatures of the system. L represents the area where a liquid is thermodynamically stable.

performed, which, experimentally, is achieved by centrifugation at the temperature range where the liquid and the desired phase coexist. The experimental details for all samples synthesized via the self-flux method are shown in Figure 2.4:

For the purpose of centrifugation, an alumina Canfield crucible set was used (Fig. 2.4a, which consists of two cups coaxially aligned by a disc with small holes [84]. At the beginning of the growth, the bottom crucible of the set (labeled as *growth crucible* in Fig. 2.4b), contains the elements while the top crucible (the *catch crucible*) is empty. The space between the Canfield set and the ampule is filled with quartz wool to keep the crucible assembly in place during centrifugation. The quartz container is then vacuum-sealed and placed in the furnace and heated to around 100°C above the melting temperature of the initial stoichiometry of the elements. At that point, the furnace temperature is slowly brought down to a temperature where the desired phase and the liquid are present ($T_{mix} T_{mix}$). The temperature is kept constant at T_{mix} for several days to promote the



(c) Effect of centrifugation on sample position inside Canfield set.



growth of single crystals. After that period, the ampule is quickly removed from the furnace and placed in the centrifuge, where it is centrifuged at ~ 2400 rpm for two minutes. The process of centrifugation at T_{mix} results in the mechanical separation of the flux from the single crystals, as depicted in 2.4c. At T_{mix} , the growth crucible contains single crystals with liquid flux and the catch crucible is empty. During centrifuging, the liquid flows through the holed disc (the sieve). After this decanting step, the ampule is allowed to cool to room temperature and single crystals are found on the growth crucible contains crystals only, while the other crucible has flux in solid form.

 Mg_3Pn_2 Crystal Growth Mg_3Sb_2 single crystals were grown as a byproduct of a directional solidification method (modified Bridgman technique) using a Sb flux. The starting composition was 3:4.5 of Mg:Sb. Tapered (bottom) and cylindrical (top) alumina crucibles were used as containers for the starting material. The single crystals that adhered to the top crucible, as shown in Figure 2.5, were broken under liquid nitrogen. It is believed that the crystals formed via chemical vapor

transport (CVT). Wee-faceted specimens of around 50 μ m (Figure 2.6) in their longest dimensions



Figure 2.5: Mg₃Sb₂ clusters of crystals grown via CVT adhered to inner wall of Al₂O₂ crucible. were selected under a microscope. The samples that were removed from the crucible at room temperature showed indications of plastic deformation in the XRD patterns, i.e., streaking of the diffraction spots. For this reason, the crucibles containing the samples were kept in liquid nitrogen for at least 5 minutes before being gently tapped to separate the single crystals for XRD scans.

 AM_2Pn_2 Crystal Growth On the other hand, single crystals of the ternary compositions, namely CaMg₂Bi₂ and YbMg₂Bi₂, were grown using the self-flux method in Al₂O₃ with starting compositions of CaMg₄Bi₆ and YbMg₄Bi₆. The initial mass for both compounds was 5 g. For the CaMg₂Bi₂ compound, the oven was heated to 900°C, cooled to 800°C in one hour, and then cooled to 650°C in a 40-hour period. After a 24-hour period at 650°C, the ampules were centrifuged to remove the flux. For YbMg₂Bi₂, the furnace was set to 900°C, cooled to 850°C in 1 hour, cooled



Figure 2.6: Optical-microscopy image of Mg_3Sb_2 (a) and Mg_3Bi_2 (b) single crystals grown via chemical vapor transport.



Figure 2.7: Optical-microscopy images of a) $CaMg_2Bi_2$ and b) $YbMg_2Bi_2$ single crystals grown via the self-flux method. Note clear facets and clean surfaces of samples.

to 750°C in 10 hours, and then cooled to 650° C in 36 hours. The furnace was held at 650° C for 72 hours before the ampules were extracted and centrifuged. The slight modification of the temperature program for the YbMg₂Bi₂ compound was done to replicate the procedure reported in [85]. It is worth noting that both compositions yielded large crystals, approximately 1 mm in their longest direction as shown in Figure 2.7. Unlike binary Zintl phases, the CaMg₂Bi₂ and YbMg₂Bi₂ crystals do not need to be broken under liquid nitrogen. The ternary compounds are relatively brittle, and breaking them into smaller pieces at room temperature does not cause them to deform plastically. The XRD patterns of the ternary AMg₂Pn₂ do not show streaking of the diffraction spots.

2.1.2 Synthesis of (GeSe)_{1-x}-(AgBiSe₂)_x

For the $(GeSe)_{1-x}$ - $(AgBiSe_2)_x$ system, Ge, Ag, Bi, and Se were weighted inside an Ar-filled glovebox to prepare precursor ingots of GeSe (x=0) and AgBiSe₂ (x=100). Then, the elements were placed in quartz ampules and sealed under running vacuum (at less than 10^{-4} Torr). After sealing, the GeSe (AgBiSe₂) compound was heated in a box furnace to 800°C (900°C) and slowly cooled to ambient temperature. At that point, the resulting ingots were ground to fine powders using a mortar and pestle. Thereafter, stoichiometric amounts for the desired compositions, i.e., for x=0, 0.1, 0.2, 0.3, 0.4 were mixed. The powder was then consolidated into solid, dense disks using the Spark

Plasma Sintering (SPS) technique, using the same apparatus for the synthesis of the 122 Zintls compounds.

2.2 Characterization

2.2.1 Resonant Ultrasound Spectroscopy

Resonant ultrasound spectroscopy (RUS) is a non-destructive, reliable, and highly precise technique to measure the elastic constants in a material [86–88]. Unlike other ultrasonic tools, such as pulse echo, RUS is capable of determining the whole elastic tensor (using single-crystals) in one measurement [89]. Another important feature of RUS is that only a very small sample is needed [90]. Although the samples can be small, they have to be regular-shaped, e.g., parallelepipeds, spheres, or cylinders. A significant deviation from the regular shape, as well as other imperfections need to be avoided since they will create perturbations in the peak positions [91]. When significant geometrical defects are present in the sample, such as cracks, voids, or chipped edges, the peak positions of the pattern will be altered. These imperfections may result in significant errors at ambient and, to a greater extend, at high temperature.

The principle of operation of this technique is the identification of the resonance frequencies, i.e., the normal modes of the compound, as a response to external vibrations applied to the sample. These resonance frequencies, the *resonance peaks*, are a function of the density, geometry, and elastic constant of the sample. Experimentally, the external vibrations are applied to the sample by a piezoelectric transducer (the emitter, in Fig. 2.8b) and collected by another transducer (the receiver). The emitter sweeps acoustic frequencies (usually in the range of 10 to 400 kHz) which are picked up by the receiver to generate the pattern shown in Fig. 2.8a.

The first step to obtain the elastic constants is to create a model of the expected resonance peaks. This model is created by generating a pattern of the peak positions using the geometry and experimental density of the sample, and with a first guess of the elastic constants C_{11} and C_{44} . This model is iteratively refined by adjusting C_{11} and C_{44} until the positions of resonances in the observed pattern match with the positions predicted peaks [92, 93].





(a) RUS pattern at room temperature, inset corresponds to frequency change with temperature.

(b) Basic components of RT AND HT RUS stage.

Figure 2.8: Resonant ultrasound spectroscopy (RUS) a) pattern, where peaks are indicative of resonant frequencies of the material. These peaks are marked by blue triangles. In this RUS setup (b), a sample (gray disk) is balanced between a piezoelectric transducer that emits a frequencies in a spectrum (typically between 10-400 kHz), and a piezoelectric transducer that picks up the signal.

In the present study, RUS was used to determine the elastic moduli of the $(GeSe)_{1-x}$ - $(AgBiSe_2)_x$ system at room temperature (RT) and at high temperature (HT). For RT and HT measurements, thin disks (approx. 4 mm in height, 10 mm in diameter) of polycrystalline samples of $(GeSe)_{1-x}$ - $(AgBiSe_2)_x$ (x=0, 0.1, 0.2, 0.3, 0.4) were prepared. RT measurements were carried out using a portable stage from Alamo Creek Engineering (ACE) as shown in Fig. 2.9[94]. This design allows light contact between the transducers and the sample to allow free oscillations of the sample. The HT-experiments were conducted using also a two-point contact stage (designed by ACE), in a resistive heating furnace under flowing Ar. In this set-up, longer alumina buffer rods are adhered to the transducers, as shown in Fig 2.8b. These buffer rods extend from the sample to the outside of the heated chamber. Data was collected from ambient temperature to 400°C in steps of 10°C for each sample.

Both the RT and HT stages were connected to the electronics system that amplifies the signal and returns two components of the sinusoidal signal (in-phase and quadrature). The peak positions for each RUS pattern were identified using the complex Lorentzian function fit of the LabVIEWTM-



Figure 2.9: 3D printed, hinged-arm stage, by Alamo Creek Engineering RT-RUS stage. Perspective view (left) and front view, with sample balanced between transducers (left). Figure from [94].

based ResonanceSpectrometer Software [95–97]. The elastic moduli were calculated using the Cyl.exe software[14].

2.2.2 X-ray Diffraction Experiments

X-ray diffraction (XRD) is a widely-used, powerful tool in materials science used to characterize the structural features of the crystalline materials. It uses the equation: $n\lambda = 2d \sin \theta$ (*Bragg's Law*), where n is a positive integer, λ is the wavelength, θ the diffraction angle, and d the interatomic plane distance, to determine lattice parameters, phases, structures, thermal expansion, among other crystallographic features [98].

For the present study, three *types* of X-ray diffraction were used: single-crystal X-ray diffraction (SC-XRD), poly-crystal X-ray diffraction (PXRD) (both instruments at MSU) and synchrotron radiation X-ray diffraction (SXRD) at Argonne National Laboratory.

2.2.2.1 Ambient Temperature SC-XRD

Single-crystal X-ray diffraction has additional capabilities compared to PXRD. As a characterization technique, it can provide information about single-crystallinity (e.g., twinning), atomic positions, accurate atomic site and occupancy, and bond lengths [99]. SC-XRD experiments were carried out in the Chemistry Department at MSU, using a Rigaku XtaLAB Synergy diffractometer, using a Mo K α ($\lambda = 0.7107$ Å) and a Cu K α source (wavelength $\lambda = 1.5406$ Å). As shown in Fig. 2.11, small

samples of approx. 50 μ m in their longest direction were mounted on nylon loops, and screened for composition, single-crystallinity, and ambient-pressure lattice parameters.

An example of a high-quality single crystal that meets the aforementioned criteria is shown in Figure 2.10, i.e., the diffraction spots show no evidence of twinning nor plastic deformation.



Figure 2.10: Precession images of Mg₃Sb₂.



Figure 2.11: Face-indexing (black lines) of $YbMg_2Bi_2$ single crystal. The crystal is on top of the nylon loop, highlighted by solid white lines.

The data analysis was performed in Crysalis Pro [100], and the individual atomic positions were subsequently refined in SHELXT [101] and OLEX2 [102].

2.2.2.2 Ambient- and High-Temperature PXRD

In the present study, polycrystalline samples, either in the form of consolidated pucks or powders, were investigated at room-temperature (RT) and high-temperature (HT). For RT and HT diffraction experiments, a Rigaku SmartLab Diffractometer, with a Cu K α was employed (see 2.12.

The HT stage of the Rigaku Smartlab Diffractometer, as shown in Fig. 2.12, was used to investigate the $(GeSe)_{1-x}$ - $(AgBiSe_2)_x$ system in a temperature range from 25°C to 300°C. These experiments served to obtain the volumetric thermal expansion coefficients (α_V), the lattice parameter vs. temperature, and to pinpoint the phase transition temperatures. For these HT experiments, samples were ground into fine powders with a mortar and pestle, and were placed on the platinum sample tray. The accuracy of the temperature readings on the sample was ensured by placing the thermocouple in close contact with the Pt tray, shown in the inset in Figure 2.12. XRD patterns were collected every 10-20°C, with a temperature increase/decrease rate of 10°C per minute. The sample temperature homogeneity was ensured by waiting 10 minutes between the target temperature was reached and the XRD pattern was acquired. For all PXRD experiments, the Rietveld refinement



Figure 2.12: Rigaku SmartLab Diffractometer with high-temperature stage and Pt sample tray (inset).

method was implemented, using the PDXL[103] and GSASII [104] suites.

2.2.3 High-pressure research

High pressure research is of great importance for the fundamental understanding of materials properties, for it allows to modify bonding environments and electronic orbitals by reducing interatomic distances. Unlike temperature, pressure allows precise physical and chemical measurements through significant volume changes without the introduction of disorder, phase separation, melting, etc [105, 106]. Additionally, pressure, as a fundamental thermodynamic property, enables the formation of structures that do not occur at ambient conditions through the variation of energy stability in the compound. [107, 108].

2.2.3.1 Diamond Anvil Cells

The main categories in high pressure research are static or dynamic compression techniques. The dynamic compression is generated by shock waves and can reach pressures above several thousand GPa [109]. In the static pressure category, two main devices are used: the large anvil cell (LAC) and the diamond anvil cell (DAC). LACs, first developed by P. W. Bridgman in the beginning of the 20th century [110, 111], can reach pressures up to \approx 90 GPa and accommodate samples of around 10-100 cm³ [107]. DACs, developed in the 1950s [112, 113] can reach pressures of almost two orders of magnitude larger than that of LACs, albeit with smaller samples, in a range from 10^{-9} to 10^{-6} cm³ [107]. Currently, DACs are the most used devices for high-pressure studies [114], for a diversity of reasons, such as from the compactness of the device, versatility of in-situ measurements, rapid development of the spectroscopic techniques it relies on, among others. Many in-situ techniques have been implemented in conjunction with DACs, such as Brillouin, Raman, Mössbauer, fluorescence, optical reflectance/absorption [115–119]. In the present study, high-pressure X-ray diffraction (HP-XRD) of single crystals and polycrystalline samples will be discussed.

One of the main advantages to use DACs in HP-XRD experiments is diamond's high transmittance in the X-ray frequency range, as well as in a considerable portion from the infrared to the ultraviolet frequency electromagnetic spectrum [105].

A typical DAC is shown in Figure 2.13, which displays the basic components of the devices used for the present work. In the DAC shown in the aforementioned figure, a sample and a ruby are placed between two diamonds. The volume between the two diamonds is filled with a pressure medium, typically a noble gas, and sealed with a gasket (usually made of rhenium). By manually rotating the screws, a linear force is applied on the diamond *table* face, i.e. the side that is in contact with the backing plate. This force, results in a greatly amplified pressure on the other side of the



Figure 2.13: Components of a DAC.

diamond, i.e., on the *culet*. Because of the pressure medium, the linear force on the culet results in hydrostatic pressure applied on the sample. The choice of culet size depends on the desired pressure to be applied on the sample. Since the materials investigated here are probed in pressures up to approx. 30 GPa, diamond culets were chosen in diameter range from 300-800 μ m, which are below the reported failure pressure of diamonds [120]. For single crystal experiments, conical support anvils are used to maximize the aperture and capture wide-angle diffraction spots [121].

2.2.3.2 Synchrotron-Radiation XRD

For the synchrotron XRD experiments, 300 μ m diamond anvil culets and rhenium gaskets were pre-indented to ~ 50 μ m in thickness. Using an electrical discharge machine (EDM) at MSU, holes of ~ 120 μ m were drilled in the rhenium gaskets. Next, the single-crystalline samples were placed and centered on the culet in the diamond anvil cell (DAC) as illustrated in Figure 2.14.

We conducted *in-situ* XRD-experiments at the Advanced Photon Source (APS) in Argonne National Laboratory, Sector 13 (GeoSoilEnviroCARS), beamline 13-BM-C. At APS, before our experiments, the DAC chamber was filled with neon to create an environment in which the sample experiences a hydrostatic pressure. This process is known as *gas-loading*. The DAC containing the Mg₃Sb₂ single crystal was exposed to a X-ray beam with wavelength of 0.4340 Å. The pressure was measured by the fluorescence of the ruby in the DAC [122]. This technique is based on the peak shift of the lines (*sharp R-lines*) in the ruby *luminescence* spectrum (electromagnetic radiation from

the transition of an electron from an excited to the ground state) [123]. The detector collects the intensity of the luminescence emitted from a ruby ($\alpha - Al_2O_3 : Cr^{3+}$ when irradiated with a laser beam). The emitted radiation by the ruby is collected at a detector and this luminescence spectrum is fitted in real time by the T-rax software [124]. This technique is widely used in high-pressure research due to the precise calibration of the ruby peak positions as a function of pressure as well as for the limited available space inside a DAC. The DAC was subjected to a φ scan per each detector



Figure 2.14: Mg₃Sb₂ single crystal inside diamond anvil cell for high-pressure synchrotron XRD. position, namely $\delta = 0$ v = 0, $\delta = 20$ v = 0, and $\delta = 0$ v = 5. The configuration is illustrated in Figure 2.15. For high-pressure experiments, the presence of the DAC restricts the total available φ



Figure 2.15: Main components of beamline for high-pressure XRD experiments at Sector 13-BM-C.

from approximately 55° to 135°. This reduced available physical space for diffraction translates into a limited reciprocal space. This imposes the need to have multiple detector positions for each φ -scan.

We collected XRD scans from 1 to 10 GPa in steps of approximately 2 GPa between each point. We refined the unit cell and integrated the reflections in the software APEX [125] and then created CIF files of the structure solutions in the OLEX software [126].

2.2.3.3 Data Analysis

Single crystal structures data were analyzed using Bruker APEX and Rigaku CrysalisPro. Structures were refined in OLEX, using the Least Squares Method (L.S) within the SHELXL routine. The detailed procedure is presented next, and further information can be found in Ref. [127].

Unit Cell Determination First, the diffraction spots were gathered by selecting the left-hand-side tab Evaluate \rightarrow Determine Unit Cell and adjusting the Min. Intensity/sigma(I) to an appropriate value (usually between 3-5 for the experiments of this study), such that the diffraction spots arising from the sample only are harvested. By tuning said value, the diamond diffraction peaks (large and irregular spots) as well as the DAC and gasket diffraction rings are excluded. To identify the desired diffraction spots, the tab View Reciprocal Lattice was selected. Then, the 3D diffraction space was rotated such that the diffraction spots are aligned in a series of equidistant planes, as shown in Fig. 2.16a. At that point, the Lattice Overlay Tool is selected (on the right-hand side) to mark diffraction spots from the sample–the ones that lie on the lattice lines–and the rest of *stray* diffraction spots that lie on the plane along one orientation, but are revealed not to belong to the sample (see Fig. 2.16c). After this step, the unit cell parameters and Bravais lattice are determined by selecting the tab Determine Unit Cell, and clicking on Index, followed by Bravais, and finally, Refine. The results of a good unit cell solution are displayed in Fig. 2.16d.

Data Reduction Once satisfactory unit cell parameters are determined, the data need to be integrated. This step is necessary to obtain a highly precise orientation matrix and a reflection profile, which, in turn, determine the *hkl* components (and uncertainties) of each reflection [128]. The data integration in the APEX3 Suite is shown in Figure 2.17. The first part of this process consists of clicking on the Integrate Images Tab (left side of Fig. 2.17a) and input an appropriate


(a) Diffraction spots after harvest.



(c) Diffraction sphere is rotated to exclude stray diffraction spots from other orientations.



(b) Selection of relevant diffraction spots using lattice overlay: Green spots correspond to sample, white spots from DAC/diamonds, gasket, etc.



(d) Statistics of unit cell solution.

Figure 2.16: Example of unit cell determination procedure in the Bruker APEX3 Suite from high-pressure single-crystal XRD experiments.

resolution limit (as displayed on the right side of the same figure). For the experiments of this study, a resolution limit of approx. 0.7 Å yielded the best results. Once the integration is done, it is important to verify the data integration statistics results, shown in Fig. 2.17b. Particularly, it is crucial to check that the average correlation coefficient (top left panel) is high (i.e., close to 1), and that spot shape profile (bottom left panel) has a circular shape, centered around x, y, and z.

Once the integration step is complete, the data needs to be scaled. This process serves to determine the background, to further improve the unit cell parameters, and to minimize systematic errors of the apparatus and the sample's centering [128]. In the APEX3 Suite, the data scaling is done by selecting the Scale tab, and using the .raw files generated in the integration step. If known, it is advisable to select the known Laue and point groups for the scaling process, as shown in Fig. 2.18a. Then, the value in the Number of Refinement Cycles box is increased to 500, as shown in Fig. 2.18b, and, for the YbMg₂Bi₂ composition in this study, to select the Absorption Type as

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(b) Data integration statistics.

Figure 2.17: Data integration example in the Bruker APEX3 Suite for high-pressure single-crystal XRD experiments.

Strong Absorber. Additionally, if the results are not satisfactory, the Mean I/ σ Threshold field can be increased–usually a value of 3.0 would suffice.



(a) Parameter setup for data scaling, including Laue and point group selection.



(b) Selection of settings for data scaling, including absorption type, number of cycles, and resolution threshold, using the parameters determined in a).

Figure 2.18: Data scaling procedure example in the Bruker APEX3 Suite for high-pressure single-crystal XRD experiments.

After performing the scaling, the results can be visually assessed by examining the shape of the curves of Figure 2.19a. There, the left y-axis (error, denoted as R[%]) should smoothly decrease and stabilize as a function of increasing cycle number (the x-axis). In contrast, the Mean Weight (right y-axis) should steadily increase and stabilize as a function of cycle number. It is worth noting that the ideal value is 1 and 0 for the Mean Weight and the R[%], respectively. The final statistics

of the data scaling are displayed in Fig. 2.19b. For the experiments reported here, the number of reflections per run are between 100 and 300.



(a) Convergence curves for the data mean weight (dark blue curve, right y-axis) and error percentage (light blue curve, left y-axis) as a function of cycle number.



(b) Data scaling statistics separated by batch number (i.e., data run), including number of reflections, scale factors, and error percentage.

Figure 2.19: Data scaling results example in the Bruker APEX3 Suite for high-pressure single-crystal XRD experiments.

Space Group Determination Once the data has been integrated and scaled, in other words, the data has been reduced, the file that contains all reflections (known as the *hkl-file*) and the data collection parameter file (p4p-file) are used to determine the space group. For this purpose, the .hkl and .p4p files are used as input, as shown in Fig. 2.20a. In this step, the radiation wavelength of the experiments and the sample's composition need also to be completed. The process of the

determination of the space group starts by selecting first the centering. In this example, as shown in Fig. 2.20b, the data points to a P-centered unit cell.



(a) Input and output files relevant to space group determination.



(b) Lattice type determination.

Figure 2.20: Space group determination setup example in the Bruker APEX3 Suite for high-pressure single-crystal XRD experiments.

Next, the Bravais lattice and the space group need to be selected, as displayed in Fig. 2.21a. Note that the likeliness of a space group is evaluated by the CFOM (the *combined figure of merit*), among other parameters. Usually, the lower the CFOM value, the better. After the selection of the space group has been done, the statistics for the dataset are displayed (see Fig. 2.21b), including the overall weighted error (R(int)), uncertainty (R(sigma)), and the statistics based on the resolution ranges, in Å.

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(a) Space group (bottom) and Bravais lattice (top) selection.

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	7	1.42 - 1.35	3	3	100.0	2.67	12.3	20.45	0.0369	0.0338		
	8	1.35 - 1.27	5	7	71.4	3.14	171.1	43.72	0.0343	0.0240		
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Surface and the second s	10	1.20 - 1.16	5	6	83.3	3.00	15.0	26.35	0.0229	0.0319		
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(b) Reflection statistics as a function of resolution (in Å).

Figure 2.21: Space group determination procedure in the Bruker APEX3 Suite for high-pressure single-crystal XRD experiments.

At this point, the instruction file (*ins-file*), as well as a .prp file (which contains the details of what was done during the XPREP routine [129]) are generated, as exemplified in Figure 2.22a. The .ins and .hkl are then used in OLEX for the final data refinement and to generate a cif file (see Fig. 2.22b).



(b) Structure refinement example results in the OLEX2 Software, showing the statistics of the data on the right-hand side.

Figure 2.22: Structure refinement example in the Bruker APEX3 Suite and OLEX2 Software for high-pressure single-crystal XRD experiments.

The process described in this section was performed for each data point for every single-crystal

XRD experiment of the present study.

CHAPTER 3

COMPRESSIBILITY AND HIGH-PRESSURE STRUCTURE OF Mg₃Bi₂ AND Mg₃Sb₂ 3.1 Abstract

Alloys between Mg₃Sb₂ and Mg₃Bi₂ have recently been shown to be exceptional thermoelectric materials due in part to their anomalously low thermal conductivity. In the present study, *in-situ* high-pressure synchrotron X-ray diffraction was used to investigate the structure and bonding in Mg₃Sb₂ and Mg₃Bi₂ at pressures up to 50 GPa. Our results confirm prior predictions of isotropic in-plane and out-of-plane compressibility, but reveal large disparities between the bond strength of the two distinct Mg sites. Using single crystal diffraction, we show that the octahedral Mg-Sb bonds are significantly more compressible than the tetrahedral Mg-Sb bonds in Mg₃Sb₂, which lends support to prior arguments that the weaker octahedral Mg bonds are responsible for the anomalous thermal properties of Mg₃Sb₂ and Mg₃Bi₂. Further, we report the discovery of a displacive and reversible phase transition in both Mg₃Sb₂ and Mg₃Bi₂ above 7.8 GPa and 4.0 GPa, respectively. The transition to the high-pressure structure involves a highly anisotropic volume collapse, in which the out-of-plane axis compresses significantly more than the in-plane axes. Single crystal diffraction at high pressure was used to solve the monoclinic high-pressure structure (*C*2/*m*), which is a distorted variant of the ambient-pressure structure containing four unique Mg coordination environments.

3.2 Introduction

The compound Mg₃Sb₂ was discovered by Edward Zintl in 1933 before falling into almost complete obscurity for more than 70 years [23]. In the past five years, however, alloys between Mg₃Sb₂ and Mg₃Bi₂ have emerged as exceptional room temperature thermoelectric materials, threatening to overthrow the decades-long reign of Bi₂Te₃ [20–22, 49, 130, 131]. Mg₃Sb₂ and Mg₃Bi₂ are binary members of the CaAl₂Si₂ structure type ($P\bar{3}m1$) shown in Figure 3.8a, making them part of a broader family of AM_2X_2 Zintl compounds that are traditionally considered to be layered materials [132–134]. Many compounds in this family are well-described as consisting of covalent [M_2X_2]²⁻ slabs with the ionically-bonded interlayer A^{2+} cations providing charge neutrality [135]. However, this picture is not suitable in the case of Mg_3Sb_2 and Mg_3Bi_2 ; in these binary compounds, Mg resides in both the octahedrally-coordinated Mg1 site (i.e., the cation site) and the tetrahedrally-coordinated Mg2 site (typically occupied by a more electronegative post-transition metal) [136]. First principles chemical bonding analysis has suggested that the Mg1-Sb and Mg2-Sb bonds in Mg₃Sb₂ are quite similar with respect to the degree of charge transfer from Mg to Sb [137]. This prediction of quasi-isotropic bonding in Mg₃Sb₂ was accompanied by first principles calculations of nearly isotropic compressibility in the in-plane (*a-b* plane) and out-ofplane (*c*-axis) directions under pressure [137]. An improved understanding of chemical bonding is particularly germane to Mg₃Sb₂ and Mg₃Bi₂, since the low thermal conductivity of these materials is thought to arise from soft and anharmonic bonding between the octahedrally-coordinated Mg1 atoms and pnictogen species [48].

In the present study, we investigate these questions experimentally using *in-situ* diffraction of Mg₃Sb₂ and Mg₃Bi₂ at pressures up to ~50 GPa. The application of high pressure allows investigation of bonding environments without varying chemical composition or introducing the complications associated with high temperature (i.e., large entropy, phase separation, thermal excitations, etc.) [105, 138]. In particular, the compressibility of individual bonds can be directly measured, shedding light on structural instabilities that can lead to desirable phonon behavior. Despite intense interest in these compounds in recent years, no experimental high-pressure investigation exists to date. In fact, there have been only a handful of high-pressure studies of compounds in the CaAl₂Si₂ structure type, [139–143] despite their long history and potential technological importance. Here we report on the discovery of a previously unrecognized high-pressure phase transition in Mg₃*Pn*₂ (*Pn* = Sb, Bi) using *in-situ* high-pressure synchrotron X-ray diffraction combined with first principles calculations. Through high-pressure single-crystal X-ray diffraction, we extract the pressure-dependent volume change of the polyhedra of the ambient structure and solve the structure of the high-pressure phase, revealing large disparities between the bond strength of the two distinct Mg sites.

3.3 Experimental

3.3.1 Synthesis

Polycrystalline Mg_3Sb_2 and Mg_3Bi_2 samples were synthesized by direct ball-milling of the elements followed by spark plasma sintering. Stoichiometric quantities of Mg (granules, Alfa Aesar 99.8%), Bi (shot, 99.99% RotoMetal), and Sb (shot, 99.99% Alfa Aesar) were cut into small pieces in an argon-filled glove box, loaded into stainless steel vials with two 10 mm diameter stainless balls, and milled under argon for one hour using a SPEX mill. The powder was then loaded into graphite dies and sintered at 31 MPa using a Dr. Sinter SPS-211LX. The Mg_3Sb_2 and Mg_3Bi_2 powders were heated to 850 °C and 650 °C in 5 minutes, and then holding at the target temperature for 10 minutes. The pressure was removed immediately when cooling started. The samples were ground into fine powders, the phase purity of which was confirmed using a Rigaku Smartlab X-ray diffraction system with Cu K α radiation. Based on relative peak intensities, Mg_3Sb_2 and Mg_3Bi_2 powders contain less than 1% of Sb, and less than 3% of Bi as impurity phases, respectively.

Small Mg₃Sb₂ single crystals (~100 μ m) grown via chemical vapor transport were also used in this study. These were obtained as a byproduct of an attempt to grow larger Mg₃Sb₂ crystals from a flux. Elemental Mg (granules, Alfa Aesar 99.8%) and Sb (shots, 99.99% Alfa Aesar) were mixed in a molar ratio of 2:3 Mg:Sb, loaded into an Al₂O₃ crucible with a second Al₂O₃ crucible on top serving as a cap. These were sealed in a quartz ampule under vacuum (~ 10⁻³ Torr). The ampule was heated to 800°C in a tube furnace during an 8-hour period, and then moved upwards through the furnace at a rate of 1.8 mm h⁻¹. Upon inspection, small Mg₃Sb₂ single crystals were found to be deposited on the top crucible, as shown in Figure 3.1. Selected crystals, not bigger than ~100 μ m in their longest dimension, were broken under liquid N, and screened by single-crystal XRD using a Bruker AXS Diffractometer at ambient pressure.

3.3.2 High-pressure X-ray diffraction

In-situ high-pressure X-ray diffraction experiments were conducted at the Advanced Photon Source (APS), beamlines 13-BM-C (GSECARS) and 16-BM-D (HPCAT) at Argonne National Laboratory.



Figure 3.1: Optical microscopy of as-grown mass of Mg_3Sb_2 crystals, deposited on an Al_2O_3 crucible.

The distance and orientation of the detector was calibrated using a CeO₂ standard. The beam size was 12 μ m (horizontal) × 18 μ m (vertical) FWHM at GSECARS and 4 μ m × 4 μ m FWHM at HPCAT. The detector was an online Pilatus 1M at GSECARS and a Mar345 image plate at HPCAT. Diamond anvils with culets of diameter 300 and 800 μ m were used, with rhenium gaskets from H-Cross pre-indented to thicknesses of ~45 μ m (see Figure 3.2c). To form the sample chamber, the gaskets were drilled using the laser micro-machining system at HPCAT [144]. The polycrystalline samples were ground into powder and then pressed into flakes before loading into the DACs. A ~40×40 μ m Mg₃Sb₂ single crystal was screened for crystallinity at APS before loading into a diamond anvil cell (DAC), as shown in Figure 3.2d). Ruby was placed next to each sample for pressure readings. Neon was loaded as the hydrostatic pressure medium using the COMPRES/GSECARS gas loading system for all samples. For powder 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 [145]. All experiments were carried out at ambient temperature. Further experimental details specific to beamline 13-BM-C can be found in ref. [146].

Raw single-crystal and powder diffraction patterns were pre-processed in Bruker APEX3

software suite [125] and Dioptas [147], respectively. The high-pressure structure was solved with the OLEX2 software [126] using the high-pressure Mg₃Sb₂ single-crystal data. The crystallographic details can be found in Tables 3.1 and 3.2. Powder data Rietveld refinement was performed using the PDXL2 software [148]. Equation of state fits were performed in the EosFit7 software [149]. Vesta was used for structural visualization and crystallographic analysis [150].

3.3.3 Density Functional Theory (DFT) Simulations

Density Functional Theory (DFT) simulations were performed using the Vienna Ab initio Simulation Package (VASP) [151], [152], [153]. We used the generalized gradient approximation (GGA) of Perdew-Burke-Ernzerhof modified for solid (PBEsol)[154], [155] for the exchange-correlation functional. The plane-wave energy cut-off was set to 400 eV. The conventional cells of the ambientpressure (AP) structure (5 atoms) were fully relaxed. The high-pressure (HP) structures (20 atoms) were determined by fixing volume and relaxing the lattice parameters and the ionic positions. For the AP structure under pressure, we applied isotropic compression and relaxed the structure with fixing volume. The energy convergence criterion for the self-consistency loop was 10^{-8} eV and the lattice parameters and atomic positions were optimized until the forces on all atoms were smaller than 10^{-3} eV Å⁻¹. The electronic k-points were $8 \times 8 \times 5$ (AP) and $4 \times 8 \times 6$ (HP). Phonon calculations were performed using Phonopy[156] with $4 \times 4 \times 2$ and $1 \times 4 \times 2$ supercells of the AP and HP structures, respectively (both containing 160 atoms), and using electronic k-point meshes of $4 \times 3 \times 3$ and $3 \times 3 \times 3$, respectively. The charge density difference was evaluated as $\Delta \rho = \rho_{Mg_3Sb_2} - \rho_{Mg} - \rho_{Sb}$ where $\rho_{Mg_3Sb_2}$, ρ_{Mg} , and ρ_{Sb} are the charge density of the full unit cell or the cell with only Mg or Sb atoms. The electronic k-points for density calculations were $22 \times 22 \times 12$ and $6 \times 22 \times 12$, respectively.

3.3.4 Error Propagation Calculation

The average polyhedral volumes were read from the software Vesta at each pressure point. To determine the uncertainty for these average values, the maximum and minimum possible volumes

were calculated using the equations for regular tetrahedra and octahedra:

$$V_t = \frac{a^3}{6\sqrt{2}} \tag{3.1}$$

and

$$V_o = \frac{\sqrt{2}a^3}{3} \tag{3.2}$$

respectively, where *a* represents the length of the edge. The maximum volume of the tetrahedra $(V_{t_{max}})$ was calculated using

$$V_{t_{max}} = \frac{(a_{t_{max}} + u_V)^3}{6\sqrt{2}}$$
(3.3)

where $a_{t_{max}}$ is the maximum edge value in each polyhedron and u_a is the uncertainty for *a*. Similarly, the minimum value of the tetrahedral volume ($V_{t_{min}}$) was computed with:

$$V_{t_{min}} = \frac{(a_{t_{min}} - u_V)^3}{6\sqrt{2}}$$
(3.4)

for each pressure point. In the same fashion, the maximum (V_{omax}) and minimum $((V_{omin})$ octahedron volumes are:

$$V_{omax} = \frac{\sqrt{2}(a_{omax} + u_V)^3}{3}$$
(3.5)

$$V_{o_{min}} = \frac{\sqrt{2(a_{o_{min}} - u_V)^3}}{3}$$
(3.6)

3.4 Results and Discussion

3.4.1 High-Pressure Structure of Mg_3Pn_2 (Pn = Sb, Bi)

High-pressure powder diffraction experiments were performed to investigate the response of the Mg₃*Pn*₂ (*Pn*=Sb,Bi) structure to pressure. As shown in Figure 3.2 a - b), peaks consistent with the ambient $P\bar{3}m1$ structure persist to ~7.8 GPa for Mg₃Sb₂ and ~4.0 GPa for Mg₃Bi₂. Above these pressures, new peaks are observed, along with intensity changes of the original peaks, suggesting a 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 3.3), indicating the non-quenchability of



Figure 3.2: 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 highpressure phase. The X-ray wavelength for Mg_3Sb_2 and Mg_3Bi_2 is 0.4133 Åand 0.4340 Å, respectively. c) Mg_3Sb_2 single crystal and ruby viewed inside diamond anvil cell after gas loading. d) Precession image of Mg_3Sb_2 single-crystal at 7.8 GPa.



Figure 3.3: The reversibility of the phase transition was confirmed by decompressing the powder Mg_3Bi_2 sample. All of the original $P\bar{3}m1$ peaks re-emerged below 4.0 GPa. the high-pressure phase and confirming that the new peaks at high-pressure are not a result of decomposition.

To solve the high-pressure structure and to obtain atomic positions as a function of pressure, we turned to single crystal diffraction, using the Mg_3Sb_2 crystal shown in Figure 3.2c). Single-crystal diffraction patterns collected at pressures below and above the phase transition show a crystal-to-crystal transformation, with no signs of specimen fracture (Fig. 3.2d). The structure evolution of Mg_3Sb_2 with pressure can be further observed in the precession images shown in Figure 3.4.

A structure solution for Mg_3Sb_2 at 7.8 GPa was reached in the monoclinic C2/m space group (see Tables 3.1 and 3.2 for detailed crystallographic data from the single crystal experiments). The same C2/m structure solution provides a satisfactory fit for Mg_3Sb_2 and Mg_3Bi_2 powder data at high pressure (as shown in Figures 3.5 and 3.6), suggesting that both phases undergo the same high-pressure phase transition. Below, however, we will focus our discussion of structure to the Sb-analogue.

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				[0kl]						[h0l]			-			[h	k0]
					Т													

(c)

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				• • •		
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Figure 3.4: Precession images of Mg₃Sb₂ single crystal (same sample from Figure 3.2b)). $P\bar{3}m1$ Mg₃Sb₂ a) before gas loading and b) after gas loading (at 0.23 GPa). c) C2/m Mg₃Sb₂ after gas loading (at 7.7GPa). Blue peaks correspond to diamond peaks from the DAC.

3.4.2 Crystallographic Details from Mg₃Sb₂ Experiments

The high-pressure (HP) monoclinic structure of Mg₃Sb₂, shown in Figure 3.8b, is a highly distorted variant of the ambient-pressure (AP) trigonal CaAl₂Si₂ structure type (Figure 3.8a).

Table 3.1: Crystallographic data for the $P\bar{3}m1$ Mg₃Sb₂ structure at different pressures from single crystal XRD experiments. AP refers to ambient pressure data, i.e. outside of the diamond anvil cell.

Pressure (GPa)	AP	0.24	0.99	3.21	4.88
Space group, Z	$P\bar{3}m1, 1$	$P\bar{3}m1, 1$	$P\bar{3}m1, 1$	$P\bar{3}m1, 1$	<i>P</i> 3 <i>m</i> 1, 1
a (Å)	4.5636(11)	4.5578(4)	4.532(5)	4.4808(3)	4.4420(19)
b (Å)	4.5636(11)	4.5578(4)	4.532(5)	4.4808(3)	4.4420(19)
c (Å)	7.228(2)	7.201(6)	7.149(18)	7.066(3)	7.001(6)
Volume (Å ³)	130.37(7)	129.56(10)	127.2(4)	122.87(5)	119.63(15)
Meas.	947; 4.65	484; 4.25	585; 4.39	303; 2.62	318; 4.89
reflections; R _{int}					
No. of indep. reflections;	101	55	99	60	48
R_1 ; ωR_2 (all intensities)	1.52; 3.23	8.99; 35.8	12.4; 66.4	9.24; 33.1	8.26; 28.6
GooF	1.18	0.61	4.03	1.63	1.51

Table 3.2: Crystallographic data for the C2/m Mg₃Sb₂ structure at different pressures obtained by single crystal XRD experiments.

Pressure (GPa)	7.74	10.16
Space group, Z	C2/m, 4	C2/m, 4
a (Å)	15.118(7)	14.976(7)
b (Å)	4.2228(7)	4.1904(6)
c (Å)	7.7014(12)	7.6335(10)
$oldsymbol{eta}(^\circ)$	117.56(2)	117.611(19)
Volume (Å ³)	435.9(2)	424.5(2)
Measured reflections; Rint	912; 3.64	593; 4.06
No. of independent reflections;	353	183
R_1 ; ωR_2 (all intensities)	12.7; 56.5	14.01; 22.22
GooF	1.93	2.09

The tetrahedrally coordinated $(Mg2)_2Sb_2$ slab in AP-Mg₃Sb₂ (shown in blue/cyan) transforms at high pressure into a layer with alternating tetrahedral and square pyramidal coordination environments. In this respect, HP-Mg₃Sb₂ has structural similarities to previously reported HP-CaMn₂Bi₂ (space group $P2_1/m$)[143], which exhibits a very similar Mn₂Bi₂ slab at pressures above 2 GPa. However, HP-Mg₃Sb₂ shows key differences with HP-CaMn₂Bi₂ with respect to the octahedral Mg1 layer shown in red; in HP-Mg₃Sb₂, every other octahedron distorts to form a square-planar environment, accompanied by the breaking of two opposing Mg(1)-Sb bonds. This bond breaking

Table 3.3: 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 3.4: 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)

allows the remaining Mg1 atoms to achieve a near ideal octahedral environment. In contrast, the Ca-centered octahedra in the HP-Ca Mn_2Bi_2 structure do not undergo bond breaking. Instead, they simply distort such that one of the Ca-Bi bonds in each octahedra is elongated (as shown in Figure 3.7).

Density functional theory calculations confirm that the monoclinic C2/m structure of Mg₃Sb₂

Table 3.5: 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 3.6: 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)

is indeed more stable than the trigonal $P\bar{3}m1$ structure at higher pressures. The calculated energyvolume curves shown in Figure 3.9 for the ambient and high-pressure phases of Mg₃Sb₂ indicate a critical volume per formula unit of 116 Å³, which corresponds to a pressure of approximately 5.6 GPa. Above this pressure, the monoclinic structure is more stable. This prediction agrees reasonably well with our experimental transition pressure, which was found to be approximately 7.8 GPa for Mg₃Sb₂ powder. In addition, we calculated the energy of Mg₃Sb₂ with the $P2_1/m$ space group, and found that it was significantly higher than that of either $P\bar{3}m1$ or C2/m, which supports the current findings.



Figure 3.5: The Rietveld refinement for the C2/m phase of powder Mg₃Sb₂ at 8.4 GPa. The cif file for the refinement is from single crystal analysis. The lattice parameters, peak shape parameters, preferred orientation of (3 1 -3), and z are refined.

3.4.3 Compressibility of Mg₃Sb₂ and Mg₃Bi₂

The pressure response of the ambient- and high-pressure structures of Mg_3Sb_2 and Mg_3Bi_2 can be used to provide a deeper understanding of the chemical bonding, and in turn thermal transport. The pressure dependence of the unit cell volume for Mg_3Bi_2 and Mg_3Sb_2 is shown in Figure 3.10. The Mg_3Sb_2 single crystal data collected as a function of pressure (shown as the asterisk symbols in Figure 3.10) agree well with the powder data (circle symbols). 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 the data collected at 7.8 GPa, which can be seen in Figure 3.2, is not included here, as the lattice parameters could not be accurately refined, possibly because the phase transition was already in progress. The bulk modulus, K_o , at P=0 GPa of the ambient- and high-pressure phase of each compound was fit using the powder diffraction data



Figure 3.6: The Rietveld refinement of the C2/m phase of powder Mg₃Bi₂ at 4.5 GPa. The cif file is obtained by manually adjusting the atoms of the cif file for Mg₃Sb₂ to Mg₃Bi₂. The lattice parameters, peak shape parameters, z and x are refined.



Figure 3.7: Octahedra in a) Mg_3Sb_2 and $CaMg_2Bi_2$ at ambient pressure $P\bar{3}m1$ structure, b) in the $P2_1/m$ structure of $CaMg_2Bi_2$ at high pressure, and in c) C2/m structure of Mg_3Sb_2 at high pressure. The red octahedra are either Mg or Ca-centered, and the blue spheres represent Sb or Bi atoms, respectively.

with the 2nd-order Birch-Murnaghan equation of state. Note that the 2nd-order and 3rd-order Birch-Murnaghan equation of state give equally good fits to the data, but the 2nd-order equation



Figure 3.8: Comparison of the a) ambient $(P\bar{3}m1)$ and b) high-pressure (C2/m) structure of Mg₃Sb₂. c) Depiction of the four Mg coordination environments in the high-pressure structure. The tetrahedral and octahedral layers of the ambient pressure structure are shown in cyan and red, respectively. These layers, though highly distorted, can still be recognized in the high-pressure structure. The black box in both images illustrates the distortion of the original trigonal unit cell.



Figure 3.9: Energy-volume relation for Mg₃Sb₂ calculated by DFT. The solid curve corresponds to the high-pressure structure (C2/m), and the dashed line corresponds to the ambient structure $(P\bar{3}m1)$. The curves indicate a critical transition at approximately 5.6 GPa, which is slightly lower than experiment. Note that the unit cell volume is per formula unit (1/4 of the high-pressure unit cell).

gives more reasonable K_p parameters (see Figure 3.11). The fits are displayed as the solid curves. In the case of the high-pressure phases, the zero-pressure volume, V_o , was treated as a fitting parameter. The uncertainties of the pressure and lattice parameters is shown in Tables 3.3-3.6 and the parameters of the 2nd-order and 3rd order Birch-Murnaghan fit can be found in Table 3.7. 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



Figure 3.10: The pressure dependence of the volume per formula unit for Mg_3Sb_2 and Mg_3Bi_2 from powder (circles) or single crystal (asterisks) samples. The zero-pressure bulk modulus, K_o , 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.

HP structures of both compounds are slightly stiffer than the AP structures, similar to the behavior reported for CaMn₂Bi₂ [143]. 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) [48] and DFT (42 GPa and 37 GPa, respectively) [157].

The question of whether or not Mg_3Pn_2 (Pn = Sb, Bi) are layered structures has been under debate [50]. Anisotropic compressibility is a key feature of layered structures, in particular those characterized by weak interlayer van der Waals bonding. In such materials, the out-of-plane axis is significantly more compressible than the in-plane axis [158–160]. In contrast, 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, in the sense that both bonds can be described as primary ionic bonds. A prior computational study of the pressure dependence of AP-Mg_3Sb_2 by Zhang et al. [137] predicted nearly isotropic compressibility of the *a*- and *c*-axes. As shown in Figure 3.12a, our experimental powder diffraction data (circle and square symbols) is consistent with Zhang's predictions (dashed lines) up to 8 GPa. Further, powder data for Mg_3Bi_2 up to 4 GPa (3.12b) reveals that the *a*-axis and *c*-axis of AP-Mg_3Bi_2 compress at nearly identical rates, suggesting its compressibility is even more isotropic than AP-Mg_3Sb_2. The



Figure 3.11: A Comparison of the 2nd and 3rd-order Birch-Murnaghan EOS fits in a) AP-Mg₃Sb₂, b) HP-Mg₃Sb₂, c) AP-Mg₃Bi₂, and d) HP-Mg₃Bi₂.

compressibility along each direction, defined as $K_o(a)$ and $K_o(c)$ here, were fitted with the 2nd-order Birch-Murnaghan equation using a^3 and c^3 vs. pressure. For AP-Mg₃Sb₂, $K_o(a)$ and $K_o(c)$ are 43 GPa and 38 GPa respectively, and for AP-Mg₃Bi₂, $K_o(a)$ and $K_o(c)$ are 40 GPa and 37 GPa, respectively. The exact values and uncertainties of each data point in Figure 3.12 can be found in the Tables 3.3-3.6.

It is important to emphasize that the nearly-isotropic in-plane and out-of-plane compressibility

Table 3.7: The parameters from the 2nd-order Birch–Murnaghan EOS fit for Mg₃Sb₂ and Mg₃Bi₂ corresponding to Figure 3.10. The V₀ for the $P\bar{3}m1$ structures were obtained via Rietveld refinement of the corresponding room temperature XRD pattern. For the C2/m phase, V₀ is unknown, so it was treated as an open fitting parameter in the Birch–Murnaghan EOS fit.

	AP - Mg_3Sb_2	$C2/m \operatorname{Mg_3Sb_2}$	AP - Mg ₃ Bi 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 3.8: The parameters from the 3rd-order Birch–Murnaghan EOS fit for Mg_3Sb_2 and Mg_3Bi_2 . The V_0 for AP phases are obtained via Rietveld refinement of the corresponding room temperature XRD pattern. For C2/m phase, V_0 is unknown, so it was treated as a fitting parameter in the Birch–Murnaghan EOS fit.

	AP - Mg_3Sb_2	$HP - Mg_3Sb_2$	AP - Mg ₃ Bi ₂	HP - Mg ₃ Bi ₂
V_0 (Å ³)	130.44	119	138.79	130
K ₀ (GPa)	33.4	72	36.6	40
K_p (GPa)	7.1	2.2	4.8	6

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. Previous ab-initio calculations of the partial phonon density of states of Mg₃Sb₂ predict significantly lower frequency phonon modes associated with the octahedral Mg(1) compared with the tetrahedrally-bonded Mg(2), indicating that the former has weaker bonding [48]. To test that prediction, we used the single crystal data collected in the present study to investigate bond length as a function of pressure (see Figures 3.14, 3.15 and 3.16), revealing that the octahedral bonds compress more rapidly than the tetrahedral bonds. The values of the polyhedral volume and its corresponding pressures are summarized in Table 3.9. As shown in Figure 3.13, the total volume of the octahedral Mg1 environment decreases more rapidly than the tetrahedral Mg2 volume. Here we show polyhedral volume instead of individual bond length to minimize the influence of significant uncertainty in the Mg2 z position. The As a result, the following values are obtained: This is the first direct experimental evidence that the Mg(1)-Pn bonds are softer than the Mg(2)-Pn bonds. We note that the octahedral Mg1-Sb bonds are significantly longer than the tetrahedral Mg2-Sb bonds, which likely explain much of the disparity in their compressibility. The relatively weak octahedral Mg(1)-Pn bonds help to explain the anomalously



Figure 3.12: 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. c) - d) A comparison of the lattice constants and interatomic distance, *x*, of powder Mg₃Sb₂ and Mg₃Bi₂, normalized to their respective values at P = 0 GPa. The dashed lines in panel c) show the results of a prior computational study by Zhang et. al.[137].

weak shear modulus and soft transverse phonon modes reported in Mg_3Pn_2 compounds. These instabilities are in turn responsible for the low thermal conductivity and excellent thermoelectric performance of Mg_3Pn_2 compounds [48].

When the AP-Mg₃Pn₂ structure ($P\bar{3}m1$) transforms to the HP-Mg₃Pn₂ structure (C2/m), the

Pressure (GPa)	Octahedron volume (Å ³)	Tetrahedron volume (Å ³)
0	39.71 ± 0.48	11.80 ± 0.23
0.24	39.21 ± 0.75	11.79 ± 0.22
0.99	38.89 ± 0.44	11.47 ± 0.13
3.25	36.69 ± 0.71	11.30 ± 0.21
4.94	35.40 ± 0.73	11.08 ± 0.22

Table 3.9: Summary of uncertainties for polyhedral volume calculation for Mg_3Sb_2 below phase transition pressure.

volume collapse is highly anisotropic with respect to the relative compression of the *a*- and *c*-axes. Figure 3.12a-b) illustrates the relationship between trigonal $P\bar{3}m1$ and monoclinic C2/m unit cells, with the sub-cell corresponding to the original trigonal unit cell represented *inside* of the larger monoclinic cell. At pressures above the phase transition, we have employed a re-defined set of axes (a', b', c', and angles α' and γ') to represent the ambient-pressure sub-cell after it has lost its trigonal symmetry. Note that these parameters do not correspond to the principle axes of the monoclinic C2/m unit cell. We have also defined the distance, x and x' within the sub-cell. The distance x is equivalent to the length of the a = b axis, so long as $\gamma=120^{\circ}$.

As can be seen in Figure 3.12c-d), the *c*-axes (grey square symbols) of Mg₃Sb₂ and Mg₃Bi₂ exhibit a sudden collapse at the phase transition pressure, while the a = b axes (blue circle/triangle symbols) remain largely unaffected and show no discontinuity. The drastic collapse of the out-of-plane *c*-axis can be attributed to the distortion of the half of the [Mg-Sb₆] octahedra to a square planar coordination environment (see Figure 3.8a-c). In the high-pressure C2/m structure, the c' direction is tilted slightly relative to the a'-b' plane (i.e., $\alpha=90^{\circ}$ becomes $\alpha' \sim 92.5^{\circ}$). Meanwhile, the in-plane angle $\gamma=120^{\circ}$ increases to $\gamma' \sim 122.5^{\circ}$ at the phase transition, leading to the sudden collapse of the distance defined by x' to (cyan circle symbols).

3.4.4 Bond-Length Change as a Function of Pressure

We define the octahedral bond (Mg1-Sb) as d1, the vertical tetrahedral bond as d2, and the three-fold tetrahedral bond as d3. This is depicted in Figure 3.14:

Using the naming convention in Figure 3.14, we have plotted the individual bond lengths as a



Figure 3.13: Pressure dependence of tetrahedral and octahedral volumes obtained from Mg_3Sb_2 single crystal data at pressures below the phase transition. Dashed lines correspond to DFT simulations from the present study. Uncertainties are based on error propagation calculations, described in Section 3.3.4.



Figure 3.14: The trigonal unit cell of Mg_3Sb_2 ($P\bar{3}m1$) contains three unique bonds: the octahedral Mg1-Sb bond (d1), the vertical Mg2-Sb tetrahedral bond as (d2), and the 3-fold Mg2-Sb tetrahedral bond (d3).

function of pressure, as shown in Figure 3.15 below. In this figure, we included the most reliable pressure points from our refinements in OLEX and corroborated the accuracy of the obtained bond lengths with DFT calculations; we excluded the pressure points at 0.23 GPa and 0.98 GPa due to the large uncertainty in the z-position of Mg2.

We included Figure 3.16 that shows the *average* tetrahedral bond length, (d2+3*d3)/4, which allowed us to include the two pressure points with higher uncertainties in the Mg2 positions (those at P= 0.23 GPa and 0.98 GPa).



Figure 3.15: Pressure dependence of individual bond lengths in trigonal $(P\bar{3}m1)$ Mg₃Sb₂ obtained from refinements of single crystal data, compared with DFT predictions.



Figure 3.16: Pressure dependence of octahedral bond length and the average tetrahedral bond lengths in trigonal ($P\bar{3}m1$) Mg₃Sb₂ obtained from refinements of single crystal data, compared with DFT predictions.

Note that there is a clear difference in bond lengths throughout the pressure range. This explains, in part, the reason why the octahedral volume is more compressible than the tetrahedral volume, as shown in Figure 3.13.

3.5 Conclusions

The present work resulted in the discovery of a new high-pressure phase above 7.8 GPa and 4 GPa for Mg_3Sb_2 and Mg_3Bi_2 respectively, and confirmed the reversibility of the phase transition in the case of Mg_3Bi_2 . The transition to the high-pressure structure was shown to involve a highly anisotropic collapse of the lattice parameters. Single crystal diffraction at high pressure was used to solve the monoclinic high-pressure structure (C2/m), which is a distorted variant of the ambient-pressure structure containing four unique Mg coordination environments. The high-pressure structure of Mg_3Sb_2 and Mg_3Bi_2 has some similarities with the previously reported HP-Ca Mn_2Bi_2 , but differs in symmetry and the coordination of the cation layer. Although the ambient-pressure structures of Mg_3Sb_2 and Mg_3Bi_2 exhibit isotropic compressibility, analysis of the single crystal data shows that the octahedral Mg-Pn bonds are more compressible than the tetrahedral Mg-Pn bonds, a conclusion that was supported by DFT calculations as a function of pressure. The results obtained here serve as a means for a deeper understanding of chemical bonding and thermal properties of this class of thermoelectric materials.

CHAPTER 4

COMPRESSIBILITY AND HIGH-PRESSURE STRUCTURE OF CaMg₂Bi₂ AND YbMg₂Bi₂

4.1 Abstract

 AM_2X_2 compounds (A are rare-earth or alkaline-earth elements, M transition metals or group-13 elements, and X group-14 or group-15 elements) in the CaAl₂Si₂ structure type have recently attracted major attention in a wide variety of solid state research, where these materials have been identified as excellent candidates in quantum topological and thermoelectric applications. Previous research has revealed high-pressure phase transitions in Mg₃Sb₂, Mg₃Bi₂, CaMn₂Bi₂, SrAl₂Si₂, among others. In the present work, the structure of CaMg₂Bi₂ and YbMg₂Bi₂ as a function of pressure was investigated. For this purpose, crystals of CaMg₂Bi₂ and YbMg₂Bi₂ were grown via the molten metal flux technique. Single crystal synchrotron X-ray diffraction was carried out on these samples at pressures up to 20 GPa for both compounds. In the trigonal phase, prior to the phase transition, both compounds show similar volume and lattice parameter compressibilities. Furthermore, both compounds show that their respective octahedrally-coordinated substructures compress at a higher rate than the tetrahedra. Additionally, a phase transformation of CaMg₂Bi₂ and YbMg₂Bi₂ was observed above 11.4 and 11.3 GPa, respectivley. The high-pressure phase was solved, which is demonstrated to be a distorted variant of the CaAl₂Si₂, with space group C2/m. This monoclinic phase shows an intriguing alteration of its coordination environment, in which the tetrahedra in the trigonal phase evolve into square pyramids at high pressures.

4.2 Introduction

At ambient pressure (AP), the CaMg₂Bi₂ and YbMg₂Bi₂ compounds crystallize in the CaAl₂Si₂ structure type, in the trigonal system with space group $P\overline{3}m1$, as depicted in Figure 4.1. The CaAl₂Si₂ structure prototype consists of two-dimensional layers of $[Al_2Si_2]^{2-}$, in which Al is tetrahedrahelly coordinated by four Si atoms to form AlSi₄ substructures. These tetrahedra share three edges with neighboring tetrahedra. The bilayers of $[Al_2Si_2]^{2-}$ are separated by the divalent cations, i.e., trigonal layers of cations (Ca²⁺) that are octahedrally coordinated by six Si atoms. The

regular octahedra possess one unique bond (d1) only. In contrast, the tetrahedra have two distinct bonds, one apical bond (d2) and three basal bonds (d3).

In recent years, compounds in the AM_2X_2 stoichiometry that crystallize in the CaAl₂Si₂ structure type have been extensively studied, for their thermoelectric performance [161–164], quantum topological states [165, 166], and magnetic properties [167, 168]. Compounds in the AM_2X_2 stoichiometry that form the CaAl₂Si₂ structure type are highly tunable, for each *A*, *M*, and *X* sites can accommodate a wide range of elements [169]. The inherent tunability of this structure has caused a great amount of research efforts to explore the stability limits of this structure as well as the transport properties. One key aspect of transport properties in the field of thermoelectrics is the lattice thermal conductivity, specifically the heat conduction inside the material due to its lattice vibrations. A family of thermoelectric materials that crystallize in the CaAl₂Si₂ and that stand out for their energy conversion efficiency are ternary pnictide materials in the AM_2Pn_2 subgroup (where *A* is an alkaline-earth element or a lanthanide, and the *Pn* is occupied by either Bi or Sb). In this regard, antimonide-based ternary Zintl phases (*A*=Ca, Eu, Yb), possess a thermoelectric figure of merit at 750 K of $0.5 \leq zT \leq 1.0$ [162, 170]. However, their Bi-based analogs have received considerably less attention [85].

The promising thermoelectric performance of *Pn*-based AM_2X_2 compounds has been attributed, partially, to their intrinsic low lattice thermal conductivity κ_L . For thermoelectric materials at temperatures well above the Debye temperature, heat transport is primarily dominated by Umklapp processes, via the relation $\kappa_L \propto v^2$ [41], where v is the velocity of collective lattice vibrations (*phonons*). To gauge the phonon transport in a solid, it is useful to approximate the phonon velocity, v, as the low-frequency wave (i.e., acoustic *phonons*) propagation speed, i.e. the *speed of sound*, v_s. At this point, it is useful to represent the solid as a mass-and-spring system, in which the atoms of mass M are interconnected by springs (chemical bonds) of stiffness constant, k. Using this representation, the speed of sound is v_s ~ $\sqrt{k/M}$ [171]. From these relations, it becomes evident that intrinsic low κ_L arises from the low v_s, which, in turn is favored by soft bonds (low k) and/or high mass M. The stiffness of the bonds can be investigated by characterizing the solid's



Figure 4.1: The trigonal structure of AMg_2Bi_2 (*A*=Ca, Yb), space group $P\bar{3}m1$ at ambient pressure. a) Unit cell has unique bonds d1, d2, and d3. b) Polyhedra in the AMg_2Pn_2 structure. *A* atoms in center of octahedra (red), Mg atoms inside tetrahedra.

compressibility, through the application of pressure. This fundamental state variable allows to access the elastic behavior of the material without the introduction of disorder [105, 172].

Previous high-pressure studies on the AM_2X_2 compounds that crystallize in the CaAl₂Si₂ structure type have shown different phase transitions, with compounds SrAl₂Si₂ [140, 142] and SrMn₂P₂ [139] morphing into the tetragonal (*I4/mmm*) crystal structure, CaMn₂Bi₂ [143] transforming to the monoclinic (*P2*₁/*m*), and MgMg₂(Sb,Bi)₂ [173] evolving also to a monoclinic phase with space group *C2/m*. However, a systematic study of the bonding nature in such compounds, that ultimately control the stability of this structure type under high pressure, is still pending. For this reason, the focus of the present work is the examination of the influence of the cation on the elastic properties on *AMg*₂Bi₂ (*A* = Ca, Yb) compounds. By studying elements that have similar ionic radii and highly distinct masses on the cation site, the bonding properties and stability of this family of thermoelectric compounds is herein presented.

4.3 Experimental Details

For both the synthesis of single- and poly-crystals, the following high-purity elements were used: Ca (dendritic pieces, 99.9%, Sigma-Aldrich), Mg (granules, Alfa Aesar 99.8%), Sb (shot, Alfa Aesar, 99.999%), Bi (shot, 99.99%, RotoMetal), and Yb (pieces, Sigma-Aldrich, 99.9%). Polycrystalline samples of CaMg₂Bi₂ and YbMg₂Bi₂ were synthesized by mixing stoichiometric

amounts of their corresponding elements followed by spark plasma sintering (SPS). For poly- and single-crystals, the elements were cut into small pieces and loaded into steel vials together with small stainless-steel spheres inside an Argon-filled glovebox. The airtight vials were then placed into a SPEX mill and ball-milled for 60 minutes.

4.3.1 Polycrystalline Synthesis

After ball-milling, the vials were returned to the glovebox and the fine powder was loaded into graphite dies for SPSing using a Dr. Sinter SPS-211LX. The sintering procedure for both compounds was the same, where the powders were subjected to a pressure of 31 MPa, heated to 700°C at a rate of 68°C /min, and held at that temperature for 10 minutes. The target SPS temperature was selected to be 80% of the melting temperatures reported in Ref. [27], while the pressure and wait time were empirically determined to yield the desired phase. After that period, the pressure was immediately released and the samples were allowed to reach ambient temperature naturally. The resulting consolidated disks were ground to fine powders and checked for phase purity using X-ray diffraction (XRD) using a Rigaku SmartLab Diffractometer with a Cu K α source. The XRD experiments revealed that the impurity content was less than 3% for both compounds.

4.3.2 Single-Crystal Synthesis

Single crystals of CaMg₂Bi₂ and YbMg₂Bi₂ were grown via the self-flux method, with a starting composition of AMg_2Bi_2 (*A*=Ca, Bi). After the ball-milling process, which was identical to the polycrystalline samples, the powders were then loaded into Canfield Al₂O₃ crucibles and subsequently sealed in quartz ampules under vacuum (< 10⁻⁴ Torr). The quartz ampules were then placed in a box furnace, where the furnace temperature was brought 900°C in 8 hr, then to 850°C in 1 hr, and cooled to 650°C in 40 hours. After soaking for 48 hours at 650°C, the ampules were centrifuged to remove the liquid flux from the desired crystallized samples. As a result, large crystal (approx. 5 mm in their longest dimension) were obtained. These samples were then easily cut into smaller pieces with surgical blades, which yielded smaller samples that showed plate-like geometry. The samples that exhibited faceted morphology, and approx. 50 μ m in their longest dimension,

were selected and screened for crystallinity and phase purity using a Rigaku XtaLAB Synergy S Diffractometer at the Chemistry Department at Michigan State University.

4.3.3 High-pressure X-ray diffraction

All diffraction experiments were conducted at the Advanced Photon Source (APS) in Argonne National Lab, using diamond anvil cells (DACs) to create hydrostatic pressure environments applied to the samples.

The diamond anvils used for powder diffraction experiments had pairs of flat, 800 μ m-culets. A precompressed powder of the desired composition was loaded into a 410- μ m hole within a pre-indented steel gasket. The gasket hole was drilled using an electron discharge machine (EDM) with a discharge energy of 2 μ J and a peak power of 0.4 W. A methanol-ethanol (4:1) mixture served as a pressure transmitting medium, and a 10- μ m ruby ball was used as the pressure indicator. The diamond anvils (custom CVD, conical Boehler-Almax design, with stainless steel (Vascomax[®]), and with an effective aperture of 80° X-ray diffraction angle) used for single crystal diffraction experiments had pairs of flat 300 μ m culets. As shown in Fig. 4.2, pre-screened single crystals of the desired compositions were loaded into a 150- μ m hole within a pre-indented Re gasket. The gasket hole was drilled using an electron discharge machine (EDM) with a discharge energy of 0.2 μ J and a peak power of 0.1 W. Ne gas or a methanol-ethanol (4:1) mixture was used as the pressure transmitting medium, and a 10- μ m ruby ball was used as the pressure indicator. Ne gas was loaded at GSECARS (Sector 13) at the Advanced Photon Source, Argonne National Laboratory. Single-crystal X-ray diffraction (SC-XRD) experiments were carried out in beamline 13-BM-C. The diffraction patterns were collected with a Dectris Pilatus3 1M Pixel Array Detector.

The diffraction data for $CaMg_2Bi_2$ and $YbMg_2Bi_2$ was collected by APEX3 [125], integrated using SAINT [174] code and corrected for absorption with the SADABS method [175]. The structure was solved by the SHELXS routine [176]. For both compositions, the structures were refined in the OLEX2 Suite [126], by the full-matrix least-square methods of SHELXL.

After the crystallographic refinements, the equations of state (EoS) for the two compounds were



Figure 4.2: Samples inside DACs after gas-loading.

calculated using the graphical user interface (GUI) EoSFit7 [149]. In said software, the volume and the lattice parameter compressibilities were calculated using a second-order Birch-Murnagham (BM) EoS [177, 178], where the volume at zero pressure was modeled as an additional fitting parameter.

4.3.4 Volume calculation of polyhedra and error estimations

The volumes of the octahedra and tetrahedra were calculated by treating them as regular polyhedra, using an average of the two distinct Bi-Bi bond distances as the edge length of the octahedron (l_{oct}) and of the tetrahedron (l_{tet}) . The octahedron (V_{oct}) and tetrahedron (V_{tet}) volumes are then calculated as:

$$V_{oct} = \frac{\sqrt{2}l_{oct}^3}{3} \tag{4.1}$$

and

$$V_{tet} = \frac{l_{tet}^3}{6\sqrt{2}} \tag{4.2}$$

respectively. To calculate the uncertainty in the polyhedral volume, an error propagation scheme was calculated that starts with the uncertainty in the bond lengths as is explained next. For the octahedron volume, the longer Bi-Bi bond length (l_{oct_I}) and the corresponding uncertainty of such
bond (u_{oct_I}) was used to determine the maximum octahedral volume $V_{oct_{max}}$ as:

$$V_{oct_{max}} = \frac{\sqrt{2} \left(l_{oct_I} + u_{oct_I} \right)^3}{3} \tag{4.3}$$

Similarly, the minimum octahedron volume $V_{oct_{max}}$ is calculated using the shorter Bi-Bi bond length ($l_{oct_{II}}$) and its associated uncertainty ($u_{oct_{II}}$):

$$V_{oct_{min}} = \frac{\sqrt{2} \left(l_{oct_{II}} - u_{oct_{II}} \right)^3}{3}$$
(4.4)

Likewise, the maximum tetrahedron volume ($V_{tet_{max}}$) is calculated as a regular polyhedron via the longer Bi-Bi bond (($l_{tet_{I}}$) and its uncertainty ($u_{tet_{I}}$), as a modification of equation 4.1. It becomes:

$$V_{tet_{max}} = \frac{\left(l_{tet_{I}} - u_{tet_{I}}\right)^{3}}{6\sqrt{2}}$$
(4.5)

Conversely, the minimum tetrahedron volume ($V_{tet_{min}}$) is based on the smaller Bi-Bi bond that spans the polyhedron ($l_{tet_{II}} = l_{oct_{I}}$) and its corresponding uncertainty ($u_{tet_{II}} = u_{oct_{I}}$), which is then:

$$V_{tet_{min}} = \frac{\left(l_{tet_{II}} - u_{tet_{II}}\right)^3}{6\sqrt{2}} = \frac{\left(l_{oct_I} - u_{oct_I}\right)^3}{6\sqrt{2}}$$
(4.6)

which, again, is a modification of equation 4.2.

Now, in order to calculate the total polyhedral volume error (e_{Vol} , the *symmetric* mean absolute percentage error is obtained with the following general relation:

$$e_{V} = \frac{1}{n} \sum_{i=1}^{n} \left| \frac{V_{avg} - V_{i}}{2\left(V_{avg} + V_{i}\right)} \right|$$
(4.7)

where V_{avg} is the average volume and V_i the extreme volumes, i.e., either V_{max} or V_{min} . Then, using equation 4.7 the octahedral $(e_{V_{oct}})$ and tetrahedral volume $(e_{V_{tet}})$ errors become:

$$e_{V_{oct}} = \frac{1}{2} \left[\left| \frac{V_{oct} - V_{oct_{max}}}{2(V_{oct} + V_{oct_{max}})} \right| + \left| \frac{V_{oct} - V_{oct_{min}}}{2(V_{oct} + V_{oct_{min}})} \right| \right]$$
(4.8)

and

$$e_{V_{tet}} = \frac{1}{2} \left[\left| \frac{V_{tet} - V_{tet_{max}}}{2(V_{tet} + V_{tet_{max}})} \right| + \left| \frac{V_{tet} - V_{tet_{min}}}{2(V_{tet} + V_{tet_{min}})} \right| \right],$$
(4.9)

respectively.



Figure 4.3: Powder XRD for a) $CaMg_2Bi_2$ and b) $YbMg_2Bi_2$ as a function of pressure show evidence of phase transition between 9.6 and 11.4 GPa and between 8.7 and 11.3 GPa, respectively. The trigonal phase $(P\bar{3}m1)$ is shown in black, and the high pressure monoclinic (C2/m) phase is shown in red.

4.4 **Results and Discussion**

The powder XRD patterns on polycrystalline samples were initially collected for $CaMg_2Bi_2$ and $YbMg_2Bi_2$ as a function of pressure up to 18 GPa and 17.5 GPa, respectively. Figure 4.3 shows the patterns at selected pressures. In both samples, the trigonal phase is shown in black. Additional peaks begin to appear in the diffraction patterns of $CaMg_2Bi_2$ and $YbMg_2Bi_2$ above 11.4 and 11.3 GPa, respectively. The trigonal phase was recovered upon pressure release, suggesting that the phase transition is fully reversible.

The Rietveld analysis was initially attempted using two reported high-pressure structures of similar compounds, namely C2/m -Mg₃Sb₂ [173] and $P2_1/m$ -CaMn₂Bi₂ [143]. However, these solutions did not provide an acceptable fit. For that reason, single-crystal XRD experiments were conducted for both compositions, which showed that CaMg₂Bi₂ and YbMg₂Bi₂ crystallize in the monoclinic crystal system, space group C2/m. In the following sections, an analysis of the compressibility of the trigonal phase is presented using the high-pressure single crystal diffraction data, followed by a description of the high-pressure structure.

4.4.1 Compressibility of the Trigonal Phase

The average bond stiffness, k, can be expressed in terms of the appropriate elastic constant, where the bulk modulus, B, is an ideal choice, for it strongly depends on crystal structure and composition [179]. This thermodynamic quantity, defined as the material's resistance to compression on all surfaces, is mathematically expressed as $B=-V\frac{dP}{dV}$. B is then calculated by fitting the pressure-volume data to the Birch-Murnaghan equation of state [177, 178, 180]:

$$P(V) = \frac{3B}{2} \left[\left(\frac{V_0}{V} \right)^{\frac{7}{3}} - \left(\frac{V_0}{V} \right)^{\frac{5}{3}} \right]$$
(4.10)

where P is the applied pressure, V the deformed unit cell volume, and V_0 the reference unit cell volume. It is worth mentioning that in Eq. 4.10, B corresponds to the bulk modulus at ambient pressure, and is treated as constant below the phase transition pressure range. This pressure-volume relation is experimentally achieved by hydrostatically compressing the sample in a diamond anvil cell (DAC) and measuring its volume change via *in-situ* X-ray diffraction. The BM fits serve to evaluate the bond stiffness of the solid, which can in turn help explain trends in lattice thermal conductivity.

For the compressibility analysis discussed in the following sections, the relevant experimental data for the BM fits (obtained from the single-crystal experiments) below the phase transition pressure for both compounds is summarized in Tables 4.1 and 4.2. The experimental volume-Table 4.1: Crystallographic data for the trigonal CaMg₂Bi₂ structure at different pressures from single crystal XRD experiments.

Pressure (GPa)	AP	3.02	4.89	7.39	10.16
Space Group; Z	<i>P3m1</i> ; 1	<i>P3m1</i> ; 1	<i>P3m1</i> ; 1	$P\bar{3}ml; 1$	$P\bar{3}ml; 1$
a (Å)	4.71886(17)	4.6483(19)	4.6223(15)	4.549(2)	4.472(2)
b (Å)	4.71886(17)	4.6483(19)	4.6223(15)	4.549(2)	4.472(2)
c (Å)	7.6412(3)	7.486(4)	7.431(3)	7.283(4)	7.135(4)
Volume ($Å^3$)	147.356(10)	140.09(11)	137.49(8)	130.54(10)	123.57(11)
Meas. Reflections; R _{int}	313; 12.98	109; 5.78	121; 5.96	144; 7.76	131; 5.18
No. of indep. reflections	28	56	71	119	80
R_1 ; w R_2 (all intensities)	10.88; 23.57	12.29; 33.32	17.38; 44.00	12.59; 30.12	14.99; 48.20
GooF	1.4147	1.8207	1.4868	1.5871	2.7204

Pressure (GPa)	AP	3.36	5.21	7.06	10.03
Space Group; Z	<i>P3m1</i> ; 1	<i>P3̄m1</i> ; 1	<i>P3m1</i> ; 1	<i>P3m1</i> ; 1	$P\bar{3}ml; 1$
a (Å)	4.7149(4)	4.6502(11)	4.6034(4)	4.5624(6)	4.5058(8)
b (Å)	4.7149(4)	4.6502(11)	4.6034(4)	4.5624(6)	4.5058(8)
c (Å)	7.6063(7)	7.474(3)	7.3782(7)	7.2937(10)	7.1702(13)
Volume (Å ³)	146.43(2)	139.98(7)	135.406(19)	131.48(3)	126.07(4)
Meas. Reflections; R _{int}	152; 6.66	65; 2.42	126; 3.18	123; 2.80	126; 3.08
No. of indep. reflections	1096	161	347	324	315
R_1 ; w R_2 (all intensities)	2.99; 7.05	3.83; 11.58	4.94; 27.52	5.71; 18.17	7.09; 20.31
GooF	1.106	1.369	1.422	1.228	1.286

Table 4.2: Crystallographic data for the trigonal YbMg₂Bi₂ structure at different pressures from single crystal XRD experiments.



Figure 4.4: Single-crystal experimental data points for a) the unit cell volume b) and normalized lattice parameters as a function of pressure in $CaMg_2Bi_2$ (magenta) and $YbMg_2Bi_2$ (green). Note that the zero-pressure volumes and lattice constants are fitting parameters. Dashed lines represent 2^{nd} order Birch-Murnaghan fits.

pressure and the 2^{nd} order BM fits for unit cell volume of both compounds are displayed in Figure 4.4. The initial volume as well as their compressibility are comparable. As shown in Table 4.3, the 2^{nd} order BM fits yielded a bulk modulus (B) for CaMg₂Bi₂ and YbMg₂Bi₂ have nearly identical bulk moduli, which is perhaps unsurprising given the similar ionic radii of Ca and Yb.

The fact that there is no distinguishable difference between the two compounds for their unit cell compressibility, motivated the study of possible differences in their lattice parameter compressibility.

Figure 4.4b shows the lattice parameters as a function of pressure, from which a linear bulk modulus is extracted, for the two independent lattice parameters (a and c) using a modified $2^{n}d$ order BM equation, given by Eq. 4.10. The trigonal system of the compounds discussed in the present study allow the linear bulk modulus, M, to be calculated as $M=-1\frac{dP}{dI}$, where 1 is the length of the crystallographic axes (either a or c for the present work), and calculated by fitting the values of M in the linearized BM-equation of state (see Eq. 4.10:

$$P(a) = \frac{3M}{2} \left[\left(\frac{a_0^3}{a^3} \right)^{\frac{7}{3}} - \left(\frac{a_0^3}{a^3} \right)^{\frac{5}{3}} \right]$$
(4.11)

where the volume has been replaced by the cube of the lattice parameter a [181]. The normalized lattice constant a and c vs. pressure are expressed as a/a_0 and c/c_0 , respectively, where the subindex 0 denotes the value at ambient pressure. Both a_0 and c_0 are treated as fitting parameters. The aforementioned plot results clearly show that c compresses faster than a for both compounds, while visually there is not enough evidence to discern the difference between CaMg₂Bi₂ and YbMg₂Bi₂ for either the a or c lattice parameter.

In order to quantitatively accounts for these differences, the linear bulk modulus (M) of the two independent lattice parameters was calculated, using once more the 2^{nd} order BM equation. The results of the linear bulk modulus (see Table 4.3) for CaMg₂Bi₂ and YbMg₂Bi₂ in the a- (M_a) and c-directions (M_c) are displayed in Figure 4.5. This plot shows the spatial dependence of the linear bulk moduli for bulk compounds.

From Figure 4.5, it is evident that M_a is larger than M_c for both compounds, i.e., the crystallographic a-b plane is less compressible than the c-direction. To understand the origin of such behavior, it is necessary to identify how the individual bond stiffness inside the material, as discussed in the following section.

Until now, the bulk modulus has been discussed as an *average* elastic property of the solid. However, often times it is necessary to understand individual bond strengths of the solid. One of these cases are Mg_3X_2 -based compounds, the high-performing thermoelectric compounds in the mid-temperature range [22, 131, 182, 183], which have been shown to possess the soft octahedral



Figure 4.5: Linear bulk modulus M comparison between a) $CaMg_2Bi_2$ and b) YbMg_2Bi_2. bonds and stiffer tetrahedral bonds. These soft bonds in Mg_3X_2 have been demonstrated to yield ultralow κ_L [173, 184]. For this reason, the concept of bulk modulus has to be expanded into a *linear* bulk modulus, M, and a *polyhedral* bulk modulus [185] (either tetrahedral, K_{tet}, or octahedral, K_{oct}, in the present study). The former gives information about the equivalent bond stiffness along crystallographic directions, while the latter is a gauge of *individual* bond strength in the solid. In the case of the specific bond strength, the octahedral bulk modulus, K_{oct}, is calculated by a modification of Eq. 4.10:

$$P(V_{oct}) = \frac{3K_{oct}}{2} \left[\left(\frac{V_{0_{oct}}}{V_{oct}} \right)^{\frac{7}{3}} - \left(\frac{V_{0_{oct}}}{V} \right)^{\frac{5}{3}} \right]$$
(4.12)

where V_{oct} is the deformed octahedron volume in the structure below the phase transition, and $V_{0_{oct}}$ the octahedral reference volume. Similarly, the tetrahedral bulk modulus, K_{tet} , is obtained by Eq. 4.12. For both the octahedral and tetrahedral bulk moduli, the initial volumes were treated as fitting parameters. The polyhedral bond strength as well as the linear bond strength are determined by the symmetry and the crystal structure of the system, which is why these properties of CaMg₂Bi₂ and YbMg₂Bi₂ will be discussed next.

The individual bond stiffness was characterized via *polyhedral compressibility* for the present study below their phase transitions. As shown in Fig. 4.1b, there are two distinct polyhedral



Figure 4.6: Normalized polyhedral volume vs. pressure below the phase transition for a) $CaMg_2Bi_2$ and b) $YbMg_2Bi_2$.

environments, i.e., a tetrahedrally-coordinated Mg atom (cyan) and an octahedrally-coordinated (red) A (A=Ca, Bi) atom. The results for the CaMg₂Bi₂ and the YbMg₂Bi₂ are presented in Figure 4.6a and b, respectively. To account for uncertainties in the results, error bars are shown using an error propagation method discussed in detail in the Supporting Information Section 4.3.4. The dashed lines represent 2nd order BM fits of a polyhedral bulk modulus for the tetrahedra (K_{tet}) and for the octahedra (K_{oct}). All the previously discussed moduli for both compounds in the trigonal phase are summarized in Table 4.3.

Table 4.3: Summary of the calculated moduli for the trigonal $CaMg_2Bi_2$ and $YbMg_2Bi_2$ compounds. Bulk modulus (B), linear moduli in a- and c-directions (M), and polyhedral moduli are included (K_{tet}, K_{oct}) are included.

	CaMg ₂ Bi ₂	YbMg ₂ Bi ₂
Moduli (GPa)		
Bulk modulus, B	37 ± 3	37.6 ± 0.4
Linear modulus along a, Ma	148.4 ± 7	129.0 ± 3
Linear modulus along c, M _c	89.7 ± 5	87.8 ± 0.8
Tetrahedron modulus, K _{tet}	48 ± 1	42.4 ± 0.25
Octahedron modulus, Koct	27.3 ± 0.15	30.4 ± 0.1

The experimental data clearly demonstrate that, for both compositions, the octahedral volume compresses faster than the tetrahedral. In other words, this means that for CaMg₂Bi₂ and YbMg₂Bi₂

the tetrahedron bulk modulus, K_{tet} , is considerably larger than the octahedron bulk K_{oct} . Quantitatively, K_{tet} of $CaMg_2Bi_2$ is approx. 75% larger than K_{oct} ; for $YbMg_2Bi_2$, this difference is around 40%.

The quality of the single-crystal diffraction data of the YbMg₂Bi₂ compound allowed to take one further step in the polyhedral compressibility, i.e., to analyze *individual* bond compressibility, which are here expressed as bond moduli (K_{di}, where i = 1, 2, or 3). The data points for the measured individual bond compressibilities, as well as the 2nd-order BM fits (dashed lines) are presented in Fig. 4.7. There, the normalized bond lengths versus pressure of the individual octahedral (d1), tetrahedral apical (d2), and tetrahedral basal (d3) bonds are depicted. Again, the uncertainties were calculated using the propagation error method presented in the SI Section 4.3.4.



Figure 4.7: Normalized bond length vs. pressure below the phase transition for $YbMg_2Bi_2$ for the octahedral (d1), tetrahedral apical (d2), and tetrahedral basal (d3) bonds. Uncertainties in d1 are quite small compared to the other two.

As expected, the fitted curves clearly show a faster compression with pressure of the octahedral bond d1 with respect to the other bonds. Additionally, the tetrahedron apical bond (d2) is stiffer than the basal (d3) bonds in the same coordination. The calculated values are summarized in Table 4.4.

The bulk modulus of the solid is not only determined by the individual bond strengths, but by two other key factors: its polyhedral linkages and how these are spatially distributed [186]. It can be seen in Fig. 4.8a, that AM_2X_2 has fully-linked, edge-sharing polyhedra in three dimensions, which constitute highly rigid linkages [187]. At the same time, these compounds exhibit some

Table 4.4: Individual bond moduli (in GPa) for $YbMg_2Bi_2$ in the trigonal phase. Bonds d1, d2, and d3 correspond to the octahedral, apical tetrahedral, and basal tetrahedral, respectively.

Linear modulus of bond (GPa)	YbMg ₂ Bi ₂
Modulus of bond d1, K _{d1}	96 ± 1.5
Modulus of bond d2, K _{d2}	168 ± 15
Modulus of bond d3, K _{d3}	119 ± 2.5

anisotropy in compressibility between the a-b plane and the c-direction, due to the difference between their linear bulk moduli M_a and M_c . The smaller compressibility of the c-direction was shown to arise partially from stiff Mg-Bi tetrahedral bonds, while the softer *A*-Bi bonds yield a larger compressibility in the a-b plane. Therefore, this behavior is attributed to the combined effect of a) the rigid linkage between the edge-sharing octahedra with other octahedra, b) the more compressible tetrahedral edge-shared linkages with other tetrahedra. As a result, in both compounds, the bulk modulus lies between that of the tetrahedral modulus, i.e., that of the least compressible polyhedron, and the octahedral modulus. Mathematically, this is: $K_{tet} < B < K_{oct}$.

4.4.2 High-Pressure Crystal Structure

As previously mentioned, a high-pressure structural transformation for both compounds was first observed in the powder samples above 11.4 and above 11.3 GPa in $CaMg_2Bi_2$ and $YbMg_2Bi_2$, respectively. The single crystal data confirmed these phase transition pressures. The high-pressure structure, which is the same for both compounds, was determined to be monoclinic, with space group *C2/m* and Z = 2. The crystallographic data is summarized in Table 4.5.

As shown in Figure 4.8, the trigonal structure $(P\bar{3}m1)$ experiences a displacive phase transformation to form a monoclinic (*C2/m*) at high pressure.

Interestingly, this displacive transformation is accompanied by a coordination change from the ambient-pressure tetrahedra to a square pyramid, schematically depicted in Fig. 4.9a and c. Additionally, the octahedral environment does not experience a change in its coordination environment.

Similar compounds at high pressure, namely $MgMg_2Pn_2$ (Pn = Sb, Bi) and $CaMn_2Bi_2$, also

	CaMg ₂ Bi ₂	YbMg ₂ Bi ₂
Pressure (GPa)	12.82	11.61
Space Group; Z	<i>C2/m</i> ; 2	<i>C2/m</i> ; 2
a (Å)	7.65(3)	7.558(7)
b (Å)	4.333(3)	4.489(6)
c (Å)	7.082(10)	7.081(6)
β (°)	94.36(4)	91.82(7)
Volume (Å ³)	234.2(9)	240.1(4)
Meas. Reflections; R _{int}	70; 1.54	128; 3.90
No. of indep. Reflections	69	290
R_1 ; w R_2 (all intensities)	9.60; 26.20	18.31; 50.16
GooF	1.525	2.043

Table 4.5: Crystallographic data for the monoclinic phase of CaMg₂Bi₂ and YbMg₂Bi₂.



Figure 4.8: Ambient-pressure $(P\bar{3}mI)$ a) and high-pressure (C2/m) b) structures for CaMg₂Bi₂ and YbMg₂Bi₂.

experience a displacive phase transformation to a monoclinic symmetry. In the case of MgMg₂Pn₂, a monoclinic symmetry (Z=4, *C2/m*) was reported above 7.8 and 4.0 GPa for MgMg₂Sb₂ and MgMg₂Sb₂, respectively [173]. This trigonal-to-monoclinic transformation is accompanied by octahedral bond-breaking, as depicted by the red polyhedra in Fig. 4.10a. This is a more dramatic distortion with respect to the phase transition of CaMg₂Bi₂ and YbMg₂Bi₂. In contrast, the phase change of CaMn₂Bi₂ at above 2 GPa (Z=2, *P2*₁/*m*)[143], appears to be a much less distorted variant, where neither the octahedral bonds break, nor the tetrahedral coordination changes. Upon the phase transformation, only a elongation of the Ca-Bi bonds and increased distortion of the Ca@Bi₆ octahedra is observed.



Figure 4.9: Polyhedral comparison: Tetrahedron at a) ambient pressure evolves to c) square pyramid at high pressure; Octahedron maintains coordination from b) ambient pressure to d) high pressure.



Figure 4.10: Structure comparison of a) $MgMg_2Pn_2$ (Pn = Sb, Bi), space group C2/m, and b) CaMn_2Bi₂ space group $P2_1/m$, at high pressure.

4.5 Conclusions

The higher compressibility of $CaMg_2Bi_2$ and $YbMg_2Bi_2$ in the c-direction arises from the soft tetrahedral bonds, while the a-direction compressibility is smaller due to stiffer octahedral bonds. The AM_2X_2 compounds studied here have 3D, edge-sharing octahedra as well as tetrahedra. For this reason, to understand the bulk modulus of them, it is necessary to study it as a combined effect of different bond strengths and edge-sharing 3D polyhedra. Additionally, a high-pressure structure (monoclinic, C2/m) was discovered above 11.4 GPa and 11.3 GPa for $CaMg_2Bi_2$ and $YbMg_2Bi_2$,

respectively. This displacive, reversible phase transition is characterized by a change in the Mg-Bi coordination environment from tetrahedral to square pyramidal coordination. The study of the elastic properties and phase stability of these compounds serve as a basis for understanding the interplay between the bonding nature and thermal transport of this class of thermoelectric materials.

CHAPTER 5

INFLUENCE OF CRYSTAL STRUCTURE AND COMPOSITION ON THERMAL CONDUCTIVITY OF GeSe-AgBiSe₂ ALLOYS

5.1 Abstract

Recently, alloys of IV-VI and I-V-VI₂ semiconductors (with IV=Ge,Sn; VI=Se,Te; I=Ag; V=Bi,Sb) have been the object of intense investigations in thermoelectrics. Indeed, they possess very low thermal conductivity attributed to a spontaneous formation of nanostructures, lone-pair anharmonicity, and ferroelectric instabilities. An interesting case is that of GeSe-AgBiSe₂ alloys. In fact, within a narrow alloying region (0-40% of AgBiSe₂), the room-temperature crystal structure progressively transitions from an orthorhombic *Pnma*, to a rhombohedral R3m, to a cubic *Fm-3m* arrangement, with marked consequences on the lattice thermal conductivity. At high temperatures, the cubic rock salt phase is the thermodynamically stable phase across the compositional range. . In this work, we investigate the elastic behavior of the $(GeSe)_{1-x}$ - $(AgBiSe_2)_x$ system to shed light on the respective contributions of chemistry and crystal structure to thermal transport. Within the same structure, alloying progressively reduces the lattice thermal conductivity due to point-defect phonon scattering. An anomalous increase is instead noticed upon temperature with the transition from the rhombohedral to the cubic phase, and is correlated with a significant increase in elastic moduli. This is connected with a reduction in the average bond length, possibly related to an increase in the ionic character, leading to a stiffening of the lattice. The improved understanding of the intrinsic properties of this system can guide the design of chalcogenide thermoelectric materials with tailored thermal properties.

5.2 Introduction

One potential route to counter the environmental impact of ever-increasing worldwide energy consumption is to recover energy from waste heat using thermoelectric devices. Thermoelectric materials are capable of transforming a temperature gradient to electricity or vice versa, and their energy conversion efficiency is expressed as the dimensionless thermoelectric figure of merit $zT = S^2 \sigma \kappa^{-1}T$ with S, σ , κ , T, as the Seebeck coefficient, the electrical conductivity, the thermal

conductivity, and the absolute temperature, respectively. In this last equation, κ , can be expressed by the contributions of the lattice thermal conductivity, κ_L , and the electronic thermal conductivity, κ_e , as $\kappa = \kappa_L + \kappa_e$. From these two equations, it becomes evident that the suppression of κ is needed to maximize *zT*, without detrimental effects on the electronic properties. For this reason, it is imperative to study the heat transport from the collective lattice vibrations (*phonons*), and therefore, isolate the effect of lattice dynamics on κ_L . It is well known [10, 188] that the frequencydependence of heat-carrying phonons can be exploited to achieve low thermal conductivity by means of phonon scattering by defect [189–192] and micro- and nano-structural manipulation [193–195] of the material. However, the intrinsic role of composition and crystal structure on κ_L is elusive, due to the complex mechanisms that determine the solid's chemical bonds and unit cell [41, 196]. Nevertheless, the understanding of the fundamental principles of the chemistry and structure represents a powerful tool towards chemical design of high-preforming thermoelectrics. For this purpose, the present study focuses on the relation between structure/composition and its effect on the intrinsic low lattice thermal conductivity in the (GeSe)_{1-x}-(AgBiSe₂)_x system.

Chalcogenide-based IV-VI compounds, particularly PbTe [197, 198], GeTe [199, 200], and SnSe [69, 201] show excellent thermoelectric efficiency ($zT\sim2$) in the mid-temperature range (275°C to 500°C). For instance, Bi-doped single crystals of SnSe have achieved a zT value of 2.2 at 460°C [202], while polycrystalline GeTe doped with Bi achieved a $zT \sim 1.9$ at 723 K [203] through vacancy manipulation in the Ge atom site. Nevertheless, the majority of them exhibit p-type behavior, which, for TE device compatibility, imposes the need of an n-type, high-efficiency IV-VI thermoelectric material. Although recent theoretical studies proposed GeSe as a highly efficient (zT>2) n-type material upon optimization of the carrier density [71], several experimental results show a p-type behavior and low zT (< 0.2) [72, 74]. The need to improve the thermoelectric performance of GeSe by tuning the carrier concentration, has led researchers to try different dopants, such as Na [204], Ag/Bi/Pb [72], and by alloying it with AgSbTe₂. More recently, GeSe was alloyed with AgBiSe₂ [74]—trigonal $P\bar{3}mI$ at ambient temperature [205]—, where the authors found that this system is particularly interesting, for it crystallizes in three different lattice systems: orthorhombic, rhombohedral, and cubic within an alloying range of 0% to 40% of AgBiSe₂ (shown in Figure 5.1). That study demonstrated that GeSe crystallizes in the orthorhombic structure (*Pnma*), while above 10% AgBiSe₂ alloying, the unit cell is rhombohedral (*R3m*), and becomes cubic (*Fm3̄m*) above 40% alloying. The formation of the cubic structure appears to be driven by entropy, since the orthorhombic and rhombohedral structures transform into the cubic unit cell at high temperatures. A crucial result of that study, as well a more recent one [76], was the observation of ultralow lattice thermal conductivity of the (GeSe)_{1-x}-(AgBiSe₂)_x system, especially for the alloys that exhibit rhombohedral symmetry. The remarkably low κ_L in the (GeSe)_{1-x}-(AgBiSe₂)_x system is responsible for the its high thermoelectric performance.

The $(GeSe)_{1-x}$ - $(AgBiSe_2)_x$ system is intriguing because, in a narrow composition and temperature range, it exhibits three important crystal structures for thermoelectrics. The study of this system provides a platform for understanding and decoupling the effect of composition and crystal structure on the lattice thermal conductivity, κ_L . In this work, an in-depth analysis of the thermal properties of the $(GeSe)_{1-x}$ - $(AgBiSe_2)_x$ system is presented, using a combination of elasticity measurements with resonant ultrasound spectroscopy, high-temperature X-ray diffraction, to reveal the fine relationship connecting crystal structure and composition to speed of sound, phonon scattering and ultimately κ_L . These results contribute to the understanding of the parameters that govern each aspect of the lattice thermal conductivity, and guide the chemical design of high-performing thermoelectric materials with ultralow κ_L .

5.3 Experimental methods

5.3.1 Sample Synthesis

Stoichiometric amounts of Ag, Bi, Ge, and Se were weighted in an Ar filled glovebox (O₂ and H₂O level below 1 ppm) to obtain the five different compositions of $(GeSe)_{1-x}$ - $(AgBiSe_2)_x$ with x=0, 0.1, 0.2, 0.3, and 0.4. These were sealed in quartz ampules under running vacuum (~ 10⁻⁴ Torr) and heated in a box furnace to 400°C over 12 hours. The ampules were soaked at said temperature for 4 hours, then brought to 900°C in 7 hours, kept at 900°C for 10 hours and finally cooled down



Figure 5.1: a) Phase diagram for the $(GeSe)_{1-x}$ - $(AgBiSe_2)_x$ system from x=0 to x=0.4 In a), \blacklozenge and \circ correspond to XRD and DSC experiments, respectively, performed for this study; \diamondsuit is an experimental XRD value from Ref. [58]. b) depicts the three ambient-temperature structures from x=0 to x=0.4: orthorhombic *Pnma*, rhombohedral *R3m*, and cubic *Fm3m*. c) shows the different coordination environments and bond lengths for the three structures at room temperature.

to room temperature in 18 hours. Then, the ingots were crushed in the glovebox using a mortar and pestle. For each composition, approximately 5 g of powder were loaded into cylindrical graphite dies of 10 mm of inner diameter, and consolidated into solid pucks via the spark plasma sintering (SPS) technique, using a Dr. Sinter LAB 211Lx (Fuji Electronic Industrial Co.) under vacuum. For all compositions the same SPS pressure (50 MPa) and temperature profile was used: heating to 500°C in 24 min., held at that temperature for 20 min., after which the pressure was decreased to 3 MPa. Then, the sample was allowed to cool to room temperature inside the SPS in 25 min. These synthesis parameters were optimized using Refs. [74, 76]. The obtained SPS samples were 10 mm in diameter and 3-5 mm in height.

5.3.2 Structural Characterization

The phase purity of the crushed ingots and of the SPS samples was checked with room temperature X-ray diffraction (XRD), using a Rigaku SmartLab, with a Cu K α radiation source ($\lambda = 1.5406$ Å). A Rietveld refinement of XRD data was performed with the software GSAS-II for crystallographic

information and with the software TOPAS 6 Academic [206] for microstructural details [207]. For high-temperature XRD (HT-XRD) experiments, pristine samples, i.e. samples that were not previously used for any experiment, of GSAB20 and GSAB40 compositions were crushed into fine powders using a mortar and pestle and then loaded onto a Rigaku HT1500 high-temperature stage. XRD patterns were collected in the temperature range 30°C to 330°C during both the heating and cooling cycles. A rate of 10°C /min was used, allowing the sample temperature to stabilize before each collection for 6 min., during which a height alignment was performed. For the heating cycle, diffraction patterns were collected every 20°C from 30 to 150°C, every 10°C from 150 to 230°C, and again every 20°C from 230 to 330°C. These steps were chosen such as to intensify the collection during the phase transition. For the cooling cycle, diffraction patterns were collected in steps of 30°C from 330 to 30°C.

5.3.3 Thermal Analyses

Differential Scanning Calorimetry (DSC) and Thermo Gravimetric Analysis (TGA) have been performed with a Netzsch 449C STA apparatus. Around 10 mg of samples in the form of fine powders were loaded in Al crucibles and measured in the temperature range 30-400°C, with a ramp rate of 5 K/min and under a 20 ml/min flow of Ar. The measurement was repeated twice to see the reversibility of processes. The complete data can be found in the Appendix, Section 6.3.

5.3.4 Resonant Ultrasound Spectroscopy

The temperature-dependent elastic moduli and speed of sound were obtained via resonant ultrasound spectroscopy (RUS) experiments, performed with an ambient- and high-temperature RUS stages (Alamo Creek Engineering, New Mexico, USA). Samples were polished to obtain cylinders of 10 mm diameter and approximately 3 mm in height, and balanced between two transducers inside a furnace under flowing Ar. RUS spectra were recorded from 30°C to 400°C in intervals of 10°C and with a frequency range of 50-400 kHz. Sufficient time was allowed between temperature steps for the sample to thermally stabilize. The RUS patterns were acquired via the open-source, LabViewTM ResonanceSpectrometer Software [96]. Subsequently, the resonant peak positions were determined

within the same software, using a Lorenztian fit. Finally, the elastic moduli were determined by fitting the experimental data in the Cyl.exe program [14].

5.3.5 Thermal and Electronic Properties

The total thermal conductivity (κ) was calculated as $\kappa = C_P \rho D$, where C_P , ρ , and D are the specific heat capacity at constant pressure, the geometric density, and the thermal diffusivity, respectively. For the thermal diffusivity experiments, the SPS pellets were cut into approximately 1 mm thick disks with 10 mm in diameter. The thermal diffusivity (D) values were recorded in heating and cooling every 10°C in a temperature interval of 30°C to 400°C using a Laser Flash Apparatus (Netzsch LFA 467). These results are summarized in Fig. 5.2.



Figure 5.2: Thermal diffusivity results for all compositions in the heating (solid circles) and cooling (hollow circles) cycles.

The total thermal conductivity κ was then obtained using the relation:

$$\kappa = \mathrm{D}\rho\mathrm{C}_{\mathrm{p}} \tag{5.1}$$

where D, ρ , and C_p are the thermal diffusivity, the geometric density, and the specific heat capacity at constant pressure, respectively. The C_P was treated as temperature-independent and calculated using the Dulong-Petit approximation. The obtained values for C_P and ρ are summarized in Table 5.1. The Seebeck coefficient was measured in an uni-axial four-probe arrangement using the slope

Composition (GeSe) _{1-x} -(AgBiSe ₂) _x	$C_P\left[\frac{J}{g\cdot K}\right]$	$\rho\left[\frac{g}{\mathrm{cm}^3}\right]$
x=0	0.330	5.53
x=0.1	0.310	5.90
x=0.2	0.295	5.98
x=0.3	0.285	6.31
x=0.4	0.277	6.87

Table 5.1: Dulong-Petit heat capacity (C_P) and geometric density (ρ) for the synthesized samples in the (GeSe)_{1-x}-(AgBiSe₂)_x system.

method [208], with 60-minute sinusoidal temperature oscillations with maximum temperature difference of 5 K. Measurements were performed in the temperature range 50-275°C, with a step of 50 K and a heating rate of 120 K/min. The electrical resistivity and Hall effect were measured in Van der Pauw configuration in the temperature range 30-400°C, with a heating rate of 1.5 K/min and a current of 100 mA.

5.4 **Results and Discussion**

5.4.1 Crystal Structure Evolution

Room temperature XRD (Figure 5.3) confirmed that all the samples in the $(GeSe)_{1-x}$ - $(AgBiSe_2)_x$ series are single phase and reached the target literature phases [74]. A Rietveld refinement of XRD data was performed to confirm the structural arrangement and to obtain crystallographic and microstructural parameters for the samples, which can be found in Table 5.2.

The XRD experiments on the $(GeSe)_{1-x}$ - $(AgBiSe_2)_x$ system of the present study confirmed the reported data. The x = 0 sample displays an orthorhombic structure (space group *Pnma*, Figure 5.1b, as extensively reported for pure GeSe [209–212]. The literature data at 10% (x=0.1)[76] and 20% (x=0.2)[73] alloying, was also confirmed to be, instead, rhombohedral (*R3m*, Figure 5.1b). The orthorhombic structure of GeSe can be considered to have highly distorted octahedra of Ge atoms coordinated by six Se atoms. Such environment, as shown in Figure 5.1c displays four bond lengths. Such configuration becomes a less distorted octahedron in the rhombohedral phase, where only two distinct bonds are present. These two bonds, eventually evolve into one unique

bond length for the cubic symmetry. The other end-member of the present research, i.e., at 40% alloying, displays a rock-salt cubic structure (space group $Fm\bar{3}m$, Figure5.1b, as described in previous studies [74]. Interestingly, the Rietveld refinement of the XRD data collected for the x=0.3 sample, points to a coexistence of the R3m and $Fm\bar{3}m$ phases. This can indicate that the composition is at the phase boundary. The increase in alloying within the rhombohedral system (see Table 5.2) is accompanied by a slight increase in lattice parameters. This is expected due to the larger ionic radii of Ag and Bi with respect to Ge. The observed evolution towards higher-symmetry structural arrangements with the incorporation of AgBiSe₂ has been attributed to the increase in entropy associated with alloying [74]. Coherently, with increasing temperature all the compositions are reported to eventually transition to a $Fm\bar{3}m$ cubic structure, as happens for both the end members of GeSe [58, 73] and AgBiSe₂ [77]. With the aid of DSC, the phase transition temperature for each Table 5.2: Lattice parameters for the three crystal structures of (GeSe)_{1-x}-(AgBiSe₂)_x (x = 0, 0.1, 0.2, 0.3, 0.4), where the abbreviations ortho and rhombo correspond to orthorhombic and rhombohedral, respectively.

Composition	Lattice System	Space Group	a (Å)	b (Å)	c (Å)	Angles (°) α, β, γ	$V(Å^3)$
GSAB0	Ortho	Pnma	10.92084	3.87080	4.40750	90, 90, 90	186.3155
GSAB10	Rhombo	R3m	3.97261	3.9726	10.1368	90, 90, 120	138.5426
GSAB20	Rhombo	R3m	4.01373	4.01373	10.0847	90, 90, 120	140.6986
GSAB30	Rhombo	R3m	4.03480	4.03480	10.1143	90, 90, 120	142.5970
GSAB30	Cubic	Fm3̄m	5.74910	5.74910	5.74910	90, 90, 90	190.0201
GSAB40	Cubic	Fm3̄m	5.75991	5.75991	5.75991	90, 90, 90	191.0940

composition was determined, as this is expected to depend on the alloying fraction. Results from XRD and thermal analyses are arranged in the phase diagram reported in Figure 5.1a, where the symbols \blacklozenge and \circ depict XRD and DSC values, respectively, from experiments performed for this study; is from Ref. [58]. The reported literature value of 925 K for the phase transition of GeSe from orthorhombic to cubic is included (\diamondsuit symbol in Fig. 5.1a) [58], whereas the *liquidus* line was linearly extrapolated from the reported melting temperatures of the GeSe [58] and AgBiSe₂ [213] end members. Additionally, the AgBiSe₂ phase transformation temperatures were taken from [205].



Figure 5.3: XRD patterns of the $(GeSe)_{1-x}$ - $(AgBiSe_2)_x$ system at room temperature.

5.4.2 Transport Properties

The thermoelectric transport properties for (x = 0, 0.1, 0.2, 0.3, and 0.4) in the (GeSe)_{1-x}-(AgBiSe₂)_x system are presented in Figure 5.4, including a) Seebeck coefficient S, electrical conductivity σ , total thermal conductivity κ , and thermoelectric figure of merit *zT*. Note that the goal of this study was to study the thermal properties, not to optimize performance. As expected, all of the samples studied exhibit low *zT* values

Pristine GeSe shows quite high Seebeck coefficient and low electrical conductivity. Values are in accordance with other literature reports ([72, 74]) and are indicative of an intrinsic semiconductor behavior with low carrier concentration (in the order of 10^{14} cm⁻³ at RT, see Appendix, Section 6.3). The p-type nature in GeSe has been attributed to the low formation energy of Ge vacancies [214]. The carrier density increases in the alloyed samples (to RT values in the order of $10^{18} - 10^{19}$ cm⁻³, see data in Appendix, Section 6.3), as also noticeable from the comparatively higher σ and lower absolute values of Seebeck coefficient. The increasing trend of σ with temperature points to a classical semiconducting behavior. Interestingly, the electronic character passes from p- (x=0.1)



Figure 5.4: Thermoelectric characterization for the samples within the studied $(GeSe)_{1-x}$ - $(AgBiSe_2)_x$ series, including thermal conductivity κ , electrical conductivity σ , Seebeck coefficient S and thermoelectric figure of merit zT. Filled and empty markers represents heating and cooling data, respectively.

and 0.2 samples) to n-type (x=0.3 and 0.4) with the progressive incorporation of AgBiSe₂. Cubic $(GeSe)_{1-x}$ -(AgBiSe₂)_x with with x = 0.3-0.5 alloying has been reported in the literature to display n-type conduction [74]. This was attributed to the partial substitution of Ge with Bi, acting as a donor defect (Bi³⁺ in place of Ge²⁺), and leading to a larger density of states at the conduction band minimum owing to Bi p-orbitals.

5.4.3 Lattice Thermal Conductivity

The lattice component of thermal conductivity, κ_L , (Figure 5.5) was calculated as $\kappa_L = \kappa - \kappa_E$, where κ_E is the electronic component. This was estimated with the Wiedemann-Franz Law as κ_E = L σ T, where L is the Lorenz number, calculated according to ref. [215] (data in the Appendix, 6.3), and T is the absolute temperature. κ_E shows a negligible contribution for all the compositions. The κ_L of pristine GeSe shows a T^{-1.4} behavior, indicative of a temperature trend dominated by



Figure 5.5: Lattice thermal conductivity of $(GeSe)_{1-x}$ - $(AgBiSe_2)_x$. Only GeSe shows Umklappdominated κ_L . Within the *R3m*-phase at low temperature, alloying effect shows high κ_L suppression (from x=0.1 to x=0.2), followed by small drop (x=0.2 to x=0.3). The x=0.4 (*Fm3m*) sample at room temperature breaks this trend.

phonon-phonon scattering, or Umklapp, processes. For samples of compositions of x=0.1, 0.2, and 0.3, the first evident feature is the step increase in κ_L (visible also in κ) at approximately 525 K, 425 K, and 380 K. This seems to be more pronounced for lower the AgBiSe₂ content. These discontinuities are believed to be the hallmark of the phase transition from the rhombohedral to the cubic arrangement. The alloyed compositions exhibit generally flatter trends than GeSe, pointing to other mechanism as main phonon scattering source. For the three rhombohedral samples (x=0.1, 0.2, 0.3) below their phase transition temperatures, the progressive incorporation of Ag and Bi on Ge sites suppresses κ_L in the (GeSe)_{1-x}-(AgBiSe₂)_x system. The decay in the near room temperature κ_L is rapid from the x=0.1 to x=0.2 composition, followed by a much smaller drop from the x=0.2 to the x=0.3 sample. Interestingly, this downwards trend seems to be broken with the cubic polymorph (x=0.4), showing room temperature κ_L slightly higher than for x=0.2. At temperatures above the phase transition to the cubic arrangement, all the alloyed samples "recover" the trend of suppressed κ_L with increasing alloying. These observations point to a possible predominant role of structural and bonding features, and will be discussed in detail in the next sections.

Another interesting feature is that, above 450-500 K, the x = 0.2, 0.3, and 0.4 samples show

an increasing trend of κ_L with temperature. This can be due to non negligible bipolar effects. Thus, the plotted κ_L is likely a sum of the real κ_L and the bipolar contribution, κ_B . The bipolar effect is due to the thermal excitation of carriers of different type in a material. This is observed in those circumstances when more than one electronic band contributes to transport: for small bandgap E_g semiconductors at high temperature ($k_B T \sim E_g$, with k_B the Boltzmann constant), or for intrinsic, undoped, semiconductors with minimal difference in carrier density between majority and minority carriers. The bipolar effect is normally observed in the Seebeck coefficient as a decline from the linear trend with temperature, due to the compensating effects of different carrier types. Nevertheless, it can also be observed in κ : at high temperature carrier of opposite sign tend to form at the hotter side of the sample with the absorption of heat, and recombine at the colder end with heat release, overall causing an apparent increase of thermal conductivity. The presence of bipolar effects is also supported by the curved shaped of the Seebeck coefficient (Figure 5.4a) and from the high temperature rise of the Hall carrier concentration (explained in the Appendix, in Section 6.3).

In order to study the behavior of κ_L in the (GeSe)_{1-x}-(AgBiSe₂)_x system, the influence of lattice softening and phonon scattering effects need to be decoupled. Both of these are a function of composition and structure type. Using the Debye model on the kinetic theory of gases, the lattice contribution to the heat transport inside the material can be approximated via the following relation:

$$\kappa_{\rm L} = \frac{1}{3} C_{\rm v} v^2 \tau \tag{5.2}$$

where C_v is the heat capacity at constant volume, v the phonon velocity, and τ the phonon relaxation time. The phonon velocity in Eq. 5.2 is approximated to the low frequency phonon velocity, i.e., to the speed of sound v_s , and treated as frequency-independent. Furthermore, the approximation of the phonon velocity to the speed of sound, allows to relate the elastic properties of the bulk material with the relation:

$$v_s \propto \sqrt{\frac{K}{\rho}}$$
 (5.3)

with K and ρ as the appropriate elastic constant and the solid's density, respectively. This last equation gives crucial information about the bonding features of the bulk material in relation to its

phonon transport. By investigating the bond stiffness of the solid, the influence of the structure on κ_L is isolated from its composition. Using resonant ultrasound spectroscopy (RUS), high-temperature X-ray diffraction, and transport measurements, the underlying mechanisms that determine κ_L in the $(GeSe)_{1-x}$ - $(AgBiSe_2)_x$ system are hereby elucidated.

5.4.4 Speed of Sound and Bonding Evolution

5.4.4.1 Elastic Moduli

In order to measure the speed of sound for the different compositions and gain insights on their bonding behavior, resonant ultrasound spectroscopy (RUS) measurements were performed. RUS is a laboratory technique to measure the elastic properties of a solid based on its mechanical response, i.e. the resonance peaks arising from vibrational excitations [14]. It is a bench-top, non-destructive technique, and consists of two piezoelectric transducers, where one acts as frequency emitter (constant amplitude, varying frequency), and the other as detector. The recorded resonance peaks depend on the shape of the sample and on the materials' elastic moduli. The latter are then used to calculate bulk mechanical properties, as well as the longitudinal (v_1), transverse (v_t), and average (v_s) speed of sound inside the material, where these three are related via the following relation:

$$\mathbf{v}_{s} = \left(\frac{1}{3} \left[\frac{1}{\mathbf{v}_{1}^{3}} + \frac{2}{\mathbf{v}_{t}^{3}}\right]\right)^{-\frac{1}{3}}.$$
(5.4)

Using the experimental data from RUS experiments, i.e., C_{11} and C_{44} , the constitutive relation for elastic constants of isotropic material were obtained. This means, using the elastic tensor elements in the isotropic approximation C_{11} , C_{44} , and C_{12} (as $C_{12}=C_{11} - 2C_{44}$), the shear modulus (G), the bulk modulus (B), the Young's modulus (Y), and the Poisson ratio (μ) were calculated. The following equations were used: Y = 9 G B/(3 B+G), G = C_{44}, B = $C_{12} + 2/3 C_{44}$, and $\mu =$ Y/(2G) – 1. The results are shown in Figure 5.6 —additional calculated moduli can be found in the Appendix, Section 6.3.

The observed trends in the elastic moduli (Figures 5.6a and b) resemble κ_L behavior, in which the phase transition from rhombohedral to cubic exhibits a significant increase, where the stiffening



Figure 5.6: Temperature dependence of a) Young's modulus, b) shear modulus, c) speed of sound, and d) speed of sound. Note the dramatic stiffening after the phase transition to the cubic structure for samples the x=0.1, x=0.2, and x=0.3 compositions. Additionally, there is a substantial softening with increasing Ag/Bi substitution.

is more pronounced the lower the alloying is. Moreover, within the same crystal structure, an increase in alloying leads to a softening. Furthermore, this trend holds true for the speed of sound (v_s) , as shown in Figure 5.6c. Interestingly, the same behavior as for the elastic constants is observed, despite the inclusion of density for the speed of sound calculation (where the relation $v_s \propto \sqrt{K/\rho}$ is evoked). As the elastic properties are deeply rooted in the bonding nature of the solid, the bond evolution as a function of temperature was investigated via HT-XRD and discussed in the following sections.

5.4.4.2 High-Temperature X-ray Diffraction and Bond Length Considerations

Room-temperature experiments in the $(GeSe)_{1-x}$ - $(AgBiSe_2)_x$ system were conducted on all samples (x=0, 0.1, 0.2, 0.3, 0.4), while HT-XRD patterns were collected on the (x=0.2 and x=0.4) samples.

The results are summarized in Figure 5.7.



Figure 5.7: XRD patterns with increasing temperature for a) $(GeSe)_{0.8}$ - $(AgBiSe_2)_{0.2}$ and b) $(GeSe)_{0.6}$ - $(AgBiSe_2)_{0.4}$. Note phase transition for the 20% alloying sample from rhombohedral (in black) to cubic (red) above 457 K. Peak at $2\theta = 38^{\circ}$ (denoted by *) corresponds to instrument contamination. c) Unit cell volume vs. temperature for all compositions. Samples x=0.2 and x=0.4 have high-temperature data, while the others have ambient-temperature data only. Note that the trend follows as expected, i.e., more alloying increases the unit cell volume. e) Lattice parameter ratio evolution with temperature for the sample with 20% alloying of AgBiSe₂.

As demonstrated in Figure 5.7a, the high-temperature experiment on the x=0.2 composition revealed a phase transition from the rhombohedral to the cubic structure at appox. 457 K, which is consistent with the reported literature value [74]. For the x=0.4 sample, as shown in Figure 5.7b, no phase transition up to 563 K. The Rietveld refinements on the (GeSe)_{1-x}-(AgBiSe₂)_x unit

cell volume (Figure 5.7c), shows, as expected, an increase of the unit cell volume with increasing alloying of AgBiSe₂. Furthermore, the rhombohedral phase in the x=0.2 composition, shows a shallower slope when compared to the one of the cubic phase of both the x=0.2 and the x=0.4compositions—additional crystallographic information is reported in the Appendix, Section 6.3. In order to accurately track down the evolution of the x=0.2 sample from the rhombohedral to the cubic phase, Figure 5.7e shows the c/a ratio vs. T. When $c/a = 2\sqrt{3/2}$, the cubic symmetry forms-details of the calculation are included in the Appendix, Section 6.3. Moreover, the relatively larger size of the rhombohedral with respect to the cubic unit cell is both evidenced by the shrinkage after the phase transition, and in the room-temperature unit cell volume trend with respect to composition—the x=0.4 composition appears to defy this trend. This same behavior has been also observed in other similar compounds, for instance SnTe, [216], GeTe [217], SnTe-GeTe alloys [218], among others [219]. Furthermore, Figure 5.7c shows that at room temperature, the unit cell volume increases as a function of alloying. These XRD experiments allow to understand the trends observed in the elastic properties of this system, for the material's bonding nature is closely related to its elastic behavior. It now becomes clear that in the $(GeSe)_{1-x}$ - $(AgBiSe_2)_x$ system, a larger unit cell volume (achieved with increasing alloying) yields a suppression of its elastic constants. Furthermore, the cubic unit cell possesses a smaller volume and, consequently, higher values in its elastic constants. The lattice softening (stiffening) is a consequence of weaker (stronger) bonds, as they become longer (shorter). The trend of bond lengths is presented in Table 5.3.

	d1 (Å)	d2 (Å)	d3 / d4 (Å)
x=0	2.5365	2.57591	3.29862 /3.41082
x=0.1	2.69376	3.02101	n/a
x=0.2	2.71023	3.03254	n/a
x=0.3	2.7201	3.0398	n/a
x=0.4	2.88043	n/a	n/a

Table 5.3: Bond lengths at room temperatures in the $(GeSe)_{1-x}$ - $(AgBiSe_2)_x$ system, obtained from Rietveld refinements.

5.4.5 Contributions to phonon relaxation time

The scattering rate, τ^{-1} , i.e. the average number of phonon scattering events per unit time, was estimated using the measured κ_L and v_s as a function of temperature using Equation 5.2, where C_V was approximated by the Dulong-Petit limit and the experimental values of v_s as the phonon velocities. The results are shown in Figure 5.8, where the calculations were limited to the temperature range in which the bipolar contribution does not play an important role. Additionally, the slight discrepancies of the phase transition temperatures between the RUS and the LFA measurements, as well as the inherit anomalous scattering rate around the phase transition temperatures, may give false results of the scattering rate in the (GeSe)_{1-x}-(AgBiSe₂)_x system. For this reason, the data points in the vicinity of the phase transition temperatures (labeled by hollow circles) are not considered from the following discussion.



Figure 5.8: Scattering rate τ^{-1} of the (GeSe)_{1-x}-(AgBiSe₂)_x system. Hollow circles denote the scattering rate anomaly characteristic of the phase transition region. There is a clear increase in scattering rate after the rhombohedral-to-cubic phase transition, i.e., for the compositions of x=0.1, 0.2, and 0.3.

The phonon scattering rate in a material is modeled as a summation of contributions from different scattering mechanisms, and expressed as $\tau^{-1} = \sum_i \tau_i^{-1}$ [220, 221]. In order to include the most relevant terms only, this last equation is reduced to $\tau = \tau_{GB}^{-1} + \tau_U^{-1} + \tau_{AS}^{-1}$ where the τ_U , τ_{GB} , and τ_{AS} are the phonon relaxation times due to Umklapp, grain boundaries, and alloy scattering, respectively. From the Rietveld refinements performed on all samples , there are no significant

differences of the average grain size among all compositions. For this reason, the grain boundary scattering rate difference is considered to be similar for all compositions. The following discussion will, therefore, focus on the Umklapp, $\tau_{\rm U}$, and alloy $\tau_{\rm AS}$ scattering mechanisms.

5.4.5.1 Phonon-Phonon Scattering

Umklapp scattering is a three (or more) phonon process, in which two phonons of wave vectors $\mathbf{k_1}$ and $\mathbf{k_2}$ interact to create third one with wave vector $\mathbf{k_3}$ (of allowed value), such that $\mathbf{k_3} \neq \mathbf{k_1} + \mathbf{k_2}$. Umklapp scattering is an important mechanism that results in thermal resistance [222], and is often dominant at temperatures above the Debye temperature, θ_D [188]. Umklapp processes are closely related to the anharmonic bonding features of the material and, therefore with the Grüneisen parameter, γ , [223]. The Umklapp scattering rate, τ_U^{-1} , is usually approximated by the equation [17, 224]:

$$\tau_U \propto \frac{\bar{M} v_s^3}{V^{1/3} \omega^2 \gamma^2 T}$$
(5.5)

with \overline{M} as the compound's average atomic mass, and ω the phonon frequency. The only unknown of this last equation is the Grüneisen parameter, which will be calculated in the following section to estimate the effect of crystal structure and/or composition on the anharmonicity of the (GeSe)_{1-x}-(AgBiSe₂)_x system.

To determine the anharmonicity of the different systems, γ was calculated via three methods, representing thermodynamic averages. The first method, based on the Poisson's ratio (μ), was used to estimate the Grüneisen parameter (γ_{μ}) as:

$$\gamma_{\mu} = \frac{3+3\mu}{4-6\mu} \tag{5.6}$$

where μ was calculated from RUS experiments. The second method, known as γ_L after Ledbetter, Yuen, and coworkers [19, 225], relates the change of the elastic properties with respect to temperature as follows:

$$\frac{\partial \mathbf{K}}{\partial \mathbf{T}} = -\frac{3\mathbf{k}_{\mathbf{B}}}{\mathbf{V}_{a}}\gamma_{\mathbf{L}}(\gamma_{\mathbf{L}}+1)$$
(5.7)

where k_B , V_a , and T are the Boltzmann constant, volume per atom, and temperature, respectively. K can be any elastic modulus, and for the present study, the shear modulus G (obtained from the RUS experiments) was used. Equation 5.7 is used for the current research, since the temperature range of the experiments is well above the material's Debye temperature, θ_D . For the (GeSe)_{1-x}-(AgBiSe₂)_x system, the Debye temperature was calculated for all compositions (x=0, ..., x=0.4) with the equation:

$$\theta_{\rm D} = \frac{\hbar}{k_{\rm B}} \left(\frac{6\pi^2}{V_{\rm a}} \right)^{1/3} v_{\rm D} \tag{5.8}$$

where \hbar is the reduced Planck constant, and v_D the Debye velocity in an elastic isotropic medium, and calculated as: $v_D^{-3} = 1/3(v_L^{-3} + 2v_T^{-3})$ [226]. Two different slopes, sufficiently far from the phase transition, were used for the x=0.1, 0.2, and 0.3 samples in order to assess the change in γ with different structural arrangements.

The third, and most commonly employed, estimate of Grüneisen parameter is based on the volumetric coefficient of thermal expansion, α_V , and was obtained using the following relation:

$$\gamma_{\alpha} = \frac{\alpha_{\rm V} B}{C_{\rm V} \rho} \tag{5.9}$$

where B and ρ are the bulk modulus, and density, respectively. B was determined from RUS experiments and C_V was calculated with the Dulong-Petit approximation. The values for ρ and α_V were determined by the HT-XRD scans.

Method 1, i.e., the calculation of γ_{μ} , were performed on all samples from x=0 to x=0.4 in the $(GeSe)_{1-x}$ - $(AgBiSe_2)_x$ system, while method 2 and 3 (γ_L and γ_{α} were calculated for the x=0, x=0.2, and x=0.4 compositions only, since they require experimental values of α_V . The coefficients of thermal expansion were obtained from the HT-XRD scans of the present study, while α_V for the pure GeSe composition was used from Ref. [58]. The results are presented in Figure 5.9.

Although the values γ_{μ} for all compositions (left panel of Figure 5.9) show little variation among them, the anharmonicity of the system appears to increase with more alloying. This trend becomes evident when the samples with rhombohedral symmetry, i.e., x=0.1, x=0.2, and x=0.3, transform to the cubic structure. Additionally, the results from γ_{α} seem to support the hypothesis that a cubic structure (one with higher symmetry than the rhombohedral or orthorhombic) appears to exhibit higher anharmonic behavior. This is further evidenced by the increase in γ_{α} when the



Figure 5.9: Grüneisen parameter as a function of temperature in $(GeSe)_{1-x}$ - $(AgBiSe_2)_x$ (from x=0 to x=0.4), calculated with the Poisson ratio (left) and temperature dependence of the Grüneisen parameter, γ , for the $(GeSe)_{1-x}$ - $(AgBiSe_2)_x$ system for the x=0.2 (left) and the x=0.4 (right) compositions. The three curves were obtained via the Ledbetter method (γ_L), the thermal expansion coefficient (γ_α), and the Poisson ratio (γ_μ). The shear modulus was chosen for the Ledbetter method. Note substantial increase of γ_L and γ_α after the phase transition for the sample with 20% alloying.

x=0.2 composition undergoes the phase transformation from the rhombohedral to the cubic structure. However, the estimate based on the softening rate, γ_L , does not support this conclusion, showing almost no change between rhombohedral and cubic phases.

5.4.5.2 Alloy Scattering

From Equation 5.5), it is possible to see that the Umklapp-dominated κ_L will show a T⁻¹ dependence. In the case of pure GeSe, as shown in Figure 5.5, $\kappa_L \sim T^{-1.4}$, which indicates that Umklapp scattering is the determining contribution to κ_L . For all others, there is clearly no T⁻¹ proportionality, which indicates a substantial contribution from alloy scattering.

As shown in Figure 5.5, the progressive addition of $AgBiSe_2$ to GeSe suppresses the near room temperature κ_L . This phenomenon can be regarded as point-defect or alloy scattering, and is controlled by the mass and radius contrast between the intrinsic (Ge) and alloyed (Ag/Bi) species. This scattering mechanism is rooted in the variations of a crystal's kinetic and potential energy upon alloying. One of the most commonly used models for alloy scattering is the Klemens Model [190, 227–229]. This accounts for the effect of variation in mass and ionic radius through the parameter Γ , calculated as:

$$\Gamma = \Gamma_M + \varepsilon \Gamma_R = \frac{\langle \overline{\Delta M^2} \rangle}{\langle \overline{M} \rangle^2} + \varepsilon \frac{\langle \overline{\Delta R^2} \rangle}{\langle \overline{R} \rangle^2}$$
(5.10)

where the squared mass $(\langle \overline{\Delta M} \rangle)$ and ionic radius $(\langle \overline{\Delta R} \rangle)$ variances are divided by the system's average mass $(\langle \overline{M} \rangle)$ and ionic radius $(\langle \overline{R} \rangle)$ squared—detailed calculations can be found in the Appendix, Section 6.3; ε serves as a scaling parameter to fit the experimental data to include lattice strain effects. This scattering parameter Γ is then used in the disorder parameter u, which is expressed as:

$$u^{2} = \frac{\left(6\pi^{5}V^{2}\right)^{\frac{1}{3}}}{2k_{B}v_{s}}\kappa_{P}\Gamma$$
(5.11)

where V_a , k_B , v_s , and κ_P , are the volume per atom, the Boltzmann constant, the speed of sound, and the lattice thermal conductivity, respectively; V_a , v_s , and κ_P are composition-dependent calculation parameters, obtained for the different compositions through a linear extrapolation of experimental properties of the end members, i.e. GeSe (values from experiments of this study) and AgBiSe₂ (from Ref.[205]). Finally, κ_L is calculated using the equation:

$$\kappa_L = \frac{\arctan u}{u} \kappa_P \tag{5.12}$$

Using equations 5.10,5.11, and 5.12, the expected effect of alloy scattering on the lattice thermal conductivity κ_L for the (GeSe)_{1-x}-(AgBiSe₂)_x system is calculated and displayed in Figure 5.10. The room temperature experimental data of κ_L are plotted in black circles. For the compositions from x=0 through x=0.4, the data come from the present study (see Figure 5.5) while the end member data point of κ_L for x=1 (AgBiSe₂) is from ref.[205].



Figure 5.10: Klemens model fit (blue line) and experimental values (black dots) for x=0, 0.1, 0.2, 0.3, 0.4, and x=1 (AgBiSe₂) from ref. [205].

It is evident that the current model (black line) underestimates the κ_L for all the alloyed compositions, in particular for those in a cubic arrangement. This points to a possible effect of the crystal structure, normally not accounted for in the model. Indeed, the Klemens model was developed for systems that form a complete solid solution, keeping the same crystal structure throughout the compositions. The (GeSe)_{1-x}-(AgBiSe₂)_x system, instead, possesses 4 different structural arrangements (orthorhombic *Pnma* for GeSe, rhombohedral *R3m* for $x \ge 0.05$ up to $x \sim 0.25$, cubic *Fm3m* for $x \ge 0.30$, and *P3m1* for AgBiSe₂ at room temperature). In order to account for the observed discrepancy between experimental and expected κ_L , the data point at 0% alloying (GeSe) was adjusted (blue circle) until the model matched the *R3m* compositions. This is to be regarded as an hypothetical κ_L for GeSe, if it were arranged in a *R3m* symmetry. The newly calculated Klemens model (blue curve) would represent the expected κ_L trend upon alloying, if all the compositions preserved the *R3m* structure. This model demonstrates that the

 $\kappa_{\rm L}$ of the cubic systems, i.e., for the 30% and 40% alloying compositions, is larger than predicted by the *R3m* Klemens model, while that of experimental *Pnma* GeSe is significantly lower. In the complex superposition of effects influencing $\kappa_{\rm L}$ in this system, the observed discrepancies can help elucidate the structural contribution to $\kappa_{\rm L}$, independent of alloy scattering mechanisms. The observed trend can be correlated with the progressive loss in lattice distortion passing from the *Pnma*, to the *R3m*, to the *Fm3m* structure. For what concerns phonon scattering mechanisms, it has been herein demonstrated that Umklapp processes in the (GeSe)_{1-x}-(AgBiSe₂)_x system seem not to be greatly affected by composition, nor by crystal structure. Indeed, γ shows small variations among all samples and before/after phase transitions (see Figure 5.9). A large effect is instead attributed to alloy scattering, which is modeled by a structure-independent $\kappa_{\rm L}$, implemented via the Klemens model. Therefore, the observed variation in τ is to be attributed for the most part to composition, and originates from alloy scattering.

5.5 Conclusions

In conclusion, by using a combination of resonant ultrasound spectroscopy and high-temperature XRD experiments, the influence of crystal structure and composition on the lattice thermal of the $(GeSe)_{1-x}$ - $(AgBiSe_2)_x$ system. Elasticity measurements show that the temperature-induced phase transformation from the rhombohedral to the cubic symmetry is accompanied by a lattice stiffening. Interestingly, the increasing of alloying should be accompanied by a volume expansion due to the presence of the larger atoms Ag and Bi. However, the rhombohedral-to-cubic transformation results in a volume contraction, and therefore, higher κ_L . The present study highlights the decoupled role of alloy scattering and structural features towards a fundamental understanding of thermal conductivity in this important class of thermoelectrics.

CHAPTER 6

CONCLUSIONS AND FUTURE WORK

The focus of the present work was the elastic characterization of two classes of materials relevant to thermoelectrics, namely AM_2X_2 Zintl phases and the $(GeSe)_{1-x}$ - $(AgBiSe_2)_x$ alloys. Using a combination of high-pressure synchrotron X-ray diffraction and high-temperature resonant ultrasound spectroscopy, the bonding nature for the two classes of materials were investigated. For this purpose, a series of poly- and single- crystals using spark plasma sintering and self-flux growth techniques. In this regard, a novel technique for single-crystal synthesis was developed, that is based on the directional single crystal growth method, and driven by chemical vapor. The results for the corresponding results for each system will be briefly summarized in the next sections.

6.1 Elastic Properties of Mg₃Sb₂, Mg₃Bi₂, CaMg₂Bi₂, and YbMg₂Bi₂ at High Pressure

The present study has shown the compressibility behavior and stability of 122 Zintl phases. The four compounds investigated here, Mg_3Pn_2 (Pn = Sb, Bi) and AMg_2Bi_2 (A = Ca, Yb) were characterized in terms of their compressibilities of unit cells, lattice parameters, and individual bonds. By studying these materials under high-pressure, their bond evolution was investigated, which shows a clear discrepancy between the octahedral (more compressible) and tetrahedral (less compressible) bonds for all compounds, regardless of the cation size. Additionally, by studying the individual bond evolution with increasing pressure, the change of bonding environments as a function of pressure shed light onto the bond strength as well as the ambient-pressure phase stability of these compounds. This evolution of bonding with pressure was evident in the bond-breaking of octahedra, as well as the tetrahedra-to-pyramid transformation in the Mg_3Pn_2 compositions. For the other two compounds, there is no observation of octahedral bonds that break, however, the tetrahedra do evolve into the same pyramidal coordination. In addition, the high-pressure structures for all compounds were solved and identified as monoclinic, with space group C2/m.
6.2 Lattice Thermal Conductivity in the (GeSe)_{1-x}-(AgBiSe₂)_x System

The lattice thermal conductivity, κ_L , of the (GeSe)_{1-x}-(AgBiSe₂)_x system was studied in the composition range from x=0.1 through x=0.4. Using high-temperature resonance ultrasound spectroscopy and high-temperature X-ray diffraction, the elastic behavior and the scattering mechanisms present in these alloys were characterized. From these experiments, it was shown that the compositions that have a rhombohedral (*R3m*) at room temperature (x=0.1, x=0.2, x=0.3 — the sample with 30% alloying shows presence of the rhombohedral and cubic symmetries), undergo a phase transition to the cubic (*Fm3m*) structure at high temperatures, which is accompanied by a unit cell volume reduction. The cubic structure at room (x=0.4) was found to possess stiffer bonds than the rhombohedral and orthorhombic symmetries. Additionally, the increase in alloying was observed to suppress κ_L due to a decrease in the phonon relaxation time due to an increase in alloy scattering rates.

6.3 Future Work

The literature lattice thermal conductivity values, κ_L , of the Mg₃*Pn*₂ (*Pn* = Sb, Bi) are lower than those of AMg_2Bi_2 (*A* = Ca, Yb). However, the results presented here show little difference between the compressiblities among all of them. One possible explanation is that κ_L is strongly dependent on the shear modulus of the compound which, unfortunately, cannot be probed by the hydrostatic-pressure experiments of this research. For this reason, one possible route would be the investigation of these materials via in-situ static shear strain, e.g., inside a rotational diamond anvil cell (RDAC).

Another area of research that is opened by this study is the study of the effect of the bonding between the anion and the cation within the materials studied here. For this purpose, the compounds CaMg₂Sb₂ and YbMg₂Sb₂ would need to be studied. By adding these two compounds, the current research could potentially reveal the bond strength and stability as a function of the cation-anion interactions.

In this study, the $(GeSe)_{1-x}$ - $(AgBiSe_2)_x$ system was investigated from compositions ranging from pure GeSe to x=0.4. Interestingly, at room temperature, the other end member of the $(GeSe)_{1-x}$

-(AgBiSe₂)_x system, i.e., AgBiSe₂, is trigonal with space group $P\bar{3}m1$. Furthermore, this trigonal phase becomes rhombohedral ($R\bar{3}m$) and eventually cubic ($Fm\bar{3}m$) at ~ 460 K, and ~ 580 K, respectively. All the phases present in the (GeSe)_{1-x}-(AgBiSe₂)_x system, in such a small temperature range, make it intriguing and offer the platform to study the phase diagram and its relation with $\kappa_{\rm L}$ for compositions above x=0.4, to complete the overview of the phase space. This information could potentially offer complete the picture of the whole composition range of this system, and offer insights into the influence of composition, structure, and alloy scattering for the design and manipulation of high-performance thermoelectrics with intrinsically low $\kappa_{\rm L}$.

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APPENDIX A: MASS AND RADIUS VARIANCE CALCULATIONS FOR THE KLEMENS MODEL OF THE (GeSe)_{1-x}-(AgBiSe₂)_x ALLOY

The Γ parameter, that accounts for mass and radius variances of the system as a consequence of alloying, is calculated by dividing the system's mass variance by the average mass, as shown in equation 5.10. The detailed procedure to calculate Γ is presented in the following section. The average mass of each site s of the structure is given by:

$$\overline{M_s} = \sum_i f_{s,i} M_{s,i} \tag{A1}$$

where $f_{s,i}$ is the site fraction of species i in site s and $M_{s,i}$ the mass of atomic species i in site s. Then, the average mass of the material $(\langle \overline{M} \rangle)$ is calculated by taking the stoichiometric amount of each site s (a_s) as follows:

$$\langle \overline{M} \rangle = \frac{\sum_{s} a_{s} M_{s}}{\sum_{s} a_{s}} \tag{A2}$$

There are two distinct sites in the $(GeSe)_{1-x}$ - $(AgBiSe_2)_x$ system, site 1 which can be occupied by either Ge, Ag, or Bi, and site 2 which is only populated by Se atoms. The average mass of site 1 $(\overline{M_1})$ results in:

$$\overline{M_1} = \frac{(1-x)M_{Ge} + xM_{Ag} + xM_{Bi}}{(1+x)}$$
(A3)

where M_{Ge} , M_{Ag} , and M_{Bi} are the molar masses of Ge, Ag, and Bi, respectively. The average mass of site 2 ($\overline{M_2}$) is the mass of Se (M_{Se}). Therefore, the average mass in the GSAB system becomes:

$$\langle \overline{M} \rangle = \frac{\overline{M_1} + M_{Se}}{2} \tag{A4}$$

Analogous to equation A1, the mass variance $\left(\overline{\Delta M_s^2}\right)$ of site s is:

$$\overline{\Delta M_s^2} = \sum_i f_{s,i} (M_{s,i} - \overline{M_s})^2 \tag{A5}$$

which yields a mass variance of the site 1 $\left(\overline{\Delta M_1^2}\right)$ for the (GeSe)_{1-x}-(AgBiSe₂)_x system:

$$\overline{\Delta M_1^2} = \frac{(1-x)(M_{Ge} - \overline{M_1})^2 + x(M_{Ag} - \overline{M_1})^2 + x(M_{Bi} - \overline{M_1})^2}{(1+x)}$$
(A6)

Similar to equation A2, the total mass variance $\left(\langle \overline{\Delta M^2} \rangle\right)$ for any given system is:

$$\langle \overline{\Delta M^2} \rangle = \frac{\sum_s a_s \overline{\Delta M_s^2}}{\sum_s a_s} \tag{A7}$$

which is used to obtain the total average mass variance of the $(GeSe)_{1-x}$ - $(AgBiSe_2)_x$ system. Again, since there is no mass variance of site 2, Equations A5 and A7 yield:

$$\langle \overline{\Delta M^2} \rangle = \frac{\overline{\Delta M_1^2}}{2} \tag{A8}$$

APPENDIX B: ELECTRONIC CHARACTERIZATION OF THE $(GeSe)_{1-x}$ - $(AgBiSe_2)_x$ SYSTEM

The electronic part of thermal conductivity κ_E has been calculated with the Wiedemann-Franz law, as $\kappa_E = L\sigma T$, where L is the Lorenz number, estimated from the Seebeck coefficient S (in μV K⁻¹) as $L = (1.5 + \exp\left\{-\frac{|S|}{116}\right\})10^{-8}W\Omega K^{-2}$ [230]



Figure B1: Electronic properties.

APPENDIX C: DIFFERENTIAL SCANNING CALORIMETRY AND THERMOGRAVIMETRIC ANALYSIS OF (GeSe)_{1-x}-(AgBiSe₂)_x

Figure C1 shows the differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA) data collected for the different alloyed compositions. From the TGA signal, no significant mass evolution can be noticed for any of the samples. The rhombohedral R3m to cubic Fm-3m phase transition can be observed as a reversible endothermic peak for the GSAB10 and GSAB20 samples. From the onset of the peak, we retrieve the critical temperature of the transition T_C , reported in Table C1. Values are in reasonable agreement with the critical temperatures observed in the thermal diffusivity, and somewhat in the elastic constant measurements.

Although the GSAB30 sample presented a clear transition signal in the thermal diffusivity and resonant ultrasound spectroscopy measurements, no apparent peak is visible in the DSC curve.

For the GSAB0, GSAB30 and GSAB40 samples, some non-identified irreversible peaks can be noticed in the heating ramp. For GSAB0, the temperature coincides with the melting point of Se and might be connected with some Se impurities. For GSAB30 and GSAB40, XRD indicates a minor fraction of AgBiSe2 secondary phases. As this is known to undergo two consecutive phase transitions at and (to be please completed), we tentatively attribute these peaks to possible transitions from AgBiSe₂ impurities.

Table C1: Estimation of semiconducting bandgap Eg from the Seebeck coefficient data for the $(GeSe)_{1-x}$ - $(AgBiSe_2)_x$ system (x = 0, 0.1, 0.2, 0.3, 0.4). The crystal structure to be considered for the estimation is based on the expected arrangement that a particular composition would assume at the temperature used for the calculation.

	DSC	LFA	RUS
GSAB10	490K	510K	560K
GSAB20	430K	420K	470K
GSAB30	410	390K	410K



Figure C1: Differential Scanning Calorimetry (DSC) and Thermal Gravimetric Analysis (TGA) for the GSAB system.

Table D1: Lattice parameters for the two crystal structures of GSAB20 as a function of tempera	l-
ture.	

Temperature (°C)	Lattice System	Space Group	a (Å)	c (Å)	Angles (°) α, β, γ	$V(\text{\AA}^3)$
30	Rhombo	R3m	4.01747	10.10506	90, 90, 120	141.246
59	Rhombo	R3m	4.01924	10.10628	90, 90, 120	141.387
76	Rhombo	R3m	4.02213	10.09697	90, 90, 120	141.46
98	Rhombo	R3m	4.02553	10.09001	90, 90, 120	141.602
118	Rhombo	R3m	4.02918	10.07722	90, 90, 120	141.679
120	Rhombo	R3m	4.03426	10.05707	90, 90, 120	141.752
157	Rhombo	R3m	4.04012	10.03225	90, 90, 120	141.814
163	Rhombo	R3m	4.04921	10.00513	90, 90, 120	142.067
174	Rhombo/cubic	R3m/Fm3m	4.0511	9.99569	90, 90, 120	142.066
174	Rhombo/cubic	R3m/Fm3m	5.74068	5.74068	90, 90, 120	189.187
194	Cubic	$Fm\overline{3}m$	5.74159	5.74159	90, 90, 120	189.277
204	Cubic	$Fm\overline{3}m$	5.74264	5.74264	90, 90, 120	189.381
212	Cubic	$Fm\overline{3}m$	5.74343	5.74343	90, 90, 120	189.458
220	Cubic	$Fm\overline{3}m$	5.74512	5.74512	90, 90, 120	189.625
231	Cubic	$Fm\overline{3}m$	5.74634	5.74634	90, 90, 120	189.747
241	Cubic	$Fm\overline{3}m$	5.74758	5.74758	90, 90, 120	189.87
251	Cubic	Fm3m	5.74901	5.74901	90, 90, 120	190.011
270	Cubic	Fm3m	5.75135	5.75135	90, 90, 120	190.244
290	Cubic	Fm3m	5.75404	5.75404	90, 90, 138	190.511
310	Cubic	$Fm\overline{3}m$	5.75696	5.75696	90, 90, 120	190.801
330	Cubic	$Fm\overline{3}m$	5.75982	5.75982	90, 90, 120	191.085

APPENDIX E: LATTICE PARAMETER CONVERSION FROM RHOMBOHEDRAL R3M TO CUBIC FM3M

Note that hexagonal axes are used.

- Rhombohedral volume: V_R
- Cubic volume: V_C
- Lattice parameters a and c in rhombohedral structure: a_R, c_R
- Lattice parameter a in cubic structure: a_C

The rhombohedral volume is given by:

$$V_{\rm R} = \frac{\sqrt{3}}{2} a_{\rm R}^2 c_{\rm R} \tag{E1}$$

and the cubic unit cell volume is

$$V_{\rm C} = a_{\rm C}^3 \tag{E2}$$

When the following equation applies,

$$\frac{c_{\rm R}}{a_{\rm R}} = \frac{2\sqrt{3}}{\sqrt{2}} \tag{E3}$$

the rhombohedral structure transforms to cubic. Then, it follows that the cubic lattice parameter a_C can be transformed to an *equivalent* rhombohedral cell by:

$$a_{\rm C} = a_{\rm R}\sqrt{2} \tag{E4}$$

and c_R is obtained using E3



Figure F1: Elastic properties of the GSAB system.