NEW CHALCOGENIDE-BASED PHASE-CHANGE MATERIALS FOR POTENTIAL DATA STORAGE APPLICATIONS

By

Joseph B. Wachter

A THESIS

Submitted to Michigan State University in partial fulfillment of the requirements for the degree of

> MASTER OF SCIENCE Chemistry 2010

ABSTRACT

NEW CHALCOGENIDE-BASED PHASE-CHANGE MATERIALS FOR POTENTIAL DATA STORAGE APPLICATIONS

By

Joseph B. Wachter

Phase-change materials are defined here as materials that undergo reversible, thermallyactivated glass-to-crystal transformations. These materials are utilized commercially in data storage media such as rewriteable CDs and DVDs as a way to reversibly encode binary data. The current industry standards for these materials are $Ge_2Sb_2Te_5$ and several nonstochiometric alloys of Ag, Sn, Sb, Ge, In, and Te. The next generation of data storage devices calls for faster switching rates, higher storage density, and better cyclability, for which the currently used materials may not be sufficient. This thesis will present several new chalcogenidebased phase-change materials that contain alkali metals and the lighter chalcogenides S and Se. These materials, including $K_{1-x}Rb_xSb_5S_8$, $K_2Sb_8Se_{13}$, and $K_2Bi_8S_{13}$, can be reversibly, thermally interconverted between glassy and crystalline phases. They are semiconductors and have optical band gaps in the range of 0.9-1.8 eV, which permits encoding by visible or ultraviolet laser irradiation. The $_{1-x}Rb_xSb_5S_8$ family of solid solutions shows the ability to tune the thermal and optical properties of these materials by changing the value of x. $K_2Sb_8Se_{13}$ shows the extremely rare behavior of polyamorphism wherein there exists two distinct amorphous phases as well as a crystalline phase, and each is stable and can be isolated at room temperature. Formed as a thin film on glass and silicon substrates, $K_2Bi_8S_{13}$ was shown by kinetic measurements to have the potential to switch faster than existing materials. These compounds were characterized by thermal and optical analysis (DTA, DSC, UV-Vis), X-ray diffraction (XRPD, PDF), and electron microscopy (TEM, SEM).

To Nora and Ethan.

ACKNOWLEDGMENTS

The author would like to acknowledge the National Science Foundation, Grant DMR-0443785, for funding this project. Additionally, collaborators on this project are acknowledged for their invaluable contributions.

TABLE OF CONTENTS

\mathbf{LI}	ST (OF TA	BLES v	ii
LI	ST (OF FIC	GURES vi	ii
1	Intr Refe	oducti erences a	on and Notes	$\frac{1}{5}$
2	Loc	al stru	cture and influence of bonding on the phase-change behavior of	
	the	chalco	genide compounds $K_{1-x}M_xSb_5S_8$ (M= Rb, Tl)	6
	2.1	Introd	uction	6
	2.2	Experi	imental section	9
		2.2.1	Synthesis	9
		2.2.2	Electron microscopy 1	10
		2.2.3	Powder X-ray diffraction	10
		2.2.4	Synchrotron radiation diffraction experiments	0
		2.2.5	Thermal analysis	10
		2.2.6	Raman scattering	1
		2.2.7	Thermal conductivity measurements	1
		2.2.8	Electronic structure calculations	12
	2.3	Result	s and discussion	12
		2.3.1	Phase-change behavior	12
		2.3.2	Glass-forming ability (GFA)	15
		2.3.3	Local structure: crystal versus glass	20
		2.3.4	Electronic absorption and Raman spectroscopy	24
		2.3.5	Thermal conductivity	31
	2.4	Conclu	isions	32
	Refe	erences	and Notes	35
3	K ₂ S	Sb ₈ Se1	3: a phase-change material exhibiting polyamorphism 3	8
	3.1	Introd	uction	38
	3.2	Experi	imental section	39
	0	3.2.1	Synthesis	39
		3.2.2	Differential Scanning Calorimetry (DSC)	39
		3.2.3	X-ray powder diffraction	10

		3.2.4	Synchrotron radiation diffraction experiments
		3.2.5	Optical energy band gaps 40
		3.2.6	Pyncnometry
	3.3	Result	s and discussion
		3.3.1	Structural analysis
		3.3.2	Optical properties
		3.3.3	Density measurements
	3.4	Conclu	48
	Refe	rences a	and Notes
4	Inve	estigati	ion into the switching mechanisms of the polyamorphic chalco-
	geni	ide K_2	Sb_8Se_{13} 52
	4.1	Introd	uction $\ldots \ldots \ldots$
	4.2	Experi	imental section
		4.2.1	Synthesis
		4.2.2	Differential Scanning Calorimetry (DSC)
	4.3	Result	s and Discussion
		4.3.1	Kissinger analysis
		4.3.2	Ozawa-Flynn-Wall analysis
	4.4	Conclu	sions $\ldots \ldots 59$
	Refe	rences a	and Notes
5	Syn	thosis	and phase-change behavior of KaBiaSta thin films 65
0	5 1	Introd	uction 65
	5.2	Evperi	imental section 66
	0.2	5.2.1	Synthesis of crystalline KaBioSta
		5.2.1 5.2.2	Synthesis of amorphous K ₂ Bi ₂ S ₁₂ thin films 66
		5.2.2	Differential Scapping Calorimetry (DSC)
		5.2.5	Transmission electron microscopy (TEM)
		525	Sepanning electron microscopy (SEM) 67
	53	Bosult	s and discussion 67
	0.0	5 2 1	Structural analyzia
		520	Analysis of films
		5.3.4 5.2.2	Flectron microscopy
		0.0.0 5.9.4	Thermal analysis
	F 4	0.5.4	
	3.4	Conch	ISIONS
	Df		
	Refe	rences a	and Notes
A	Refe P PE I	rences a	and Notes

LIST OF TABLES

2.1	Dependence on the reduced glass transition temperature T_{rg} , the supercooled liquid region ΔT_{xg} and Hruby parameters K_{gl} and K'_{gl} from Rb content for $K_{1-x}Rb_xSb_5S_8$ at a heating rate of 10°C/min	15
3.1	Energy gaps and density of the three states of $K_2Sb_8Se_{13}$	48
4.1	Comparison of crystallization energy, E_c , and rate constant, $k(T)$, of $K_2Sb_8Se_{13}$ with KSb_5S_8 and $Ge_2Sb_2Te_5$ at 20 K/min heating rate	57
5.1	Comparison of crystallization energy, E_c , and reduced glass transition temper- ature, $T_{rg} = T_g/T_m$ (3), of K ₂ Bi ₈ S ₁₃ with KSb ₅ S ₈ , K ₂ Sb ₈ Se ₁₃ and Ge ₂ Sb ₂ Te ₅ .	72
A.2	Connections from Atmega128 to AD5206	85
A.3	Connections from Atmega128 to MAX9483.	85

LIST OF FIGURES

2.1	Powder X-ray diffraction patterns of as-synthesized glasses of $K_{1-x}Rb_xSb_5S_8$ (a-c, $x = 0.25, 0.5, 0.75$, respectively) and $TlSb_5S_8$ (d), showing their amorphous nature.	8
2.2	X-ray diffraction patterns of: (a) $K_{0.25}Rb_{0.75}Sb_5S_8$ glass, as-synthesized. (b) $K_{1-x}Rb_xSb_5S_8$ after annealing for 2 h at 300°C. (c) KSb ₅ S ₈ calculated from crystal structure (monoclinic Pn ; $a = 8.1374$ Å; $b = 19.5013$ Å; $c = 9.0620$ Å) (11). The difference in low-angle peak ((020) reflection) between the pure K structure and the 75% Rb structure is 0.402° in 2θ .	14
2.3	DSC thermograms of $K_{1-x}Rb_xSb_5S_8$ amorphous alloys with heating rate $10^{\circ}C/min$. (a) $x = 0.0$, (b) $x = 0.25$, (c) $x = 0.5$, and (d) $x = 0.75$. The glass transition (T_g) was determined by the intersection of the curve and the halfway line between the two base lines.	16
2.4	Dependence of the glass transition (T_g) , crystallization peak (T_p) and the onset of melting point (T_m) on the Rb content (x) in $_{1-x}Rb_xSb_5S_8$	17
2.5	DSC thermograms with heating rate 10° C/min: (a) RbSb ₅ S ₈ , (b) TlSb ₅ S ₈ , first heating and (c) TlSb ₅ S ₈ , second heating.	19
2.6	Experimental structure functions of crystalline and glassy $\mathrm{KSb}_5\mathrm{S}_8.$	21
2.7	(a) PDF plot of crystalline KSb_5S_8 , experimental, (b) PDF plot of glassy KSb_5S_8 , (c) Sb coordination environment of KSb_5S_8 .	22
2.8	Solid state UV-Vis reflectance spectra of $K_{0.75}Rb_{0.25}Sb_5S_8$ converted to absorption via the Kubelka-Monk procedure. The spectra for $K_{0.5}Rb_{0.5}Sb_5S_8$ and $K_{0.25}Rb_{0.75}Sb_5S_8$ glasses are similar. Band gaps extrapolated linearly to 0 are 1.50, 1.47, and 1.51 eV respectively.	25

2.9	Raman scattering data on crystalline (a) and glassy (b) KSb_5S_8 at room temperature.	26
2.10	Raman scattering data of glassy KSb_5S_8 at various temperatures along the heating curve, The crystallization event is shown by the sharpening of peaks between 210 and $335^{\circ}C.$	27
2.11	Raman scattering data of KSb_5S_8 cooled from the molten state. Crystallization is evidenced by the sharpened features near 338, 321, 310, 298, and 280 cm ⁻¹ .	28
2.12	Temperature dependence of thermal conductivity of the crystalline and glassy KSb_5S_8 (4-300K)	30
3.1	The crystal structure of $K_2Sb_8Se_{13}$	42
3.2	(A) crystalline $K_2Sb_8Se_{13}$. (B) material obtained by quenching molten $K_2Sb_8Se_{13}$ (glass- β). (C) X-ray powder diffraction patterns from the three phases of $K_2Sb_8Se_{13}$: i) as-synthesized glass- β ; (ii) glass- α after heating to 225°C and (iii) crystalline phase after heating above 263°C. (Cu K α radiation).	43
3.3	DSC thermogram of $K_2Sb_8Se_{13}$ ribbon. Three phase changes are observed from glass- β to glass- α (227°C), from glass- α to crystal (263°C), and melting (443°C).	45
3.4	(A) Pair-distribution function analysis of the three phases of $K_2Sb_8Se_{13}$: as- synthesized glass- β ; glass- α after heating to 220°C and crystalline phase after heating to 270°C. (B) Optical absorption spectra showing energy gaps for crystalline and glass- α K ₂ Sb ₈ Se ₁₃ .	46
4.1	Baseline-corrected, nonisothermal DSC traces of $K_2Sb_8Se_{13}$ at heating rates β of 5, 10, 15, and 20 K/min	56
4.2	Kissinger plot of K ₂ Sb ₈ Se ₁₃ glass β to glass α , $\ln(\beta/T_p)$ vs. $1000/T$ and the straight regression line (β in K s ⁻¹)	58
4.3	Kissinger plot of K ₂ Sb ₈ Se ₁₃ glass α to crystal, $\ln(\beta/T_p)$ vs. $1000/T$ and the straight regression line (β in K s ⁻¹)	58

4.4	OFW plot of $\ln(\beta)$ vs. $1/T$ for different values of α during the first phase transition (glass β -to-glass α) of K ₂ Sb ₈ Se ₁₃	60
4.5	OFW plot of $\ln(\beta)$ vs. $1/T$ for different values of α during the first phase transition (glass β -to-glass α) of K ₂ Sb ₈ Se ₁₃	61
5.1	XRPD of $K_2Bi_8S_{13}$ film after annealing at temperatures (from top) of 350, 325, 275, 250, 150, and 100°C, showing the glass-to-crystal phase change and stability of the crystal up to 350°C.	69
5.2	TEM image of $K_2Bi_8S_{13}$ film after annealing. Crystalline Bi_2S_3 domains are visible.	70
5.3	SEM image of as-synthesized $K_2Bi_8S_{13}$ glass film	71
5.4	DSC trace of $K_2Bi_8S_{13}$ glass film at a heating rate of 15 K/min. The exotherm at 181°C shows crystallization of the glass, confirmed by XRPD after the scan.	73
5.5	Kissinger plot of K ₂ Bi ₈ S ₁₃ film for heating rates of 5, 10, and 15 K/min. Regression line has the equation $\ln(\beta/T_p^2) = 14.48/T_p - 12756.88.$	74
5.6	Ozawa-Flynn-Wall plots, $\ln\beta$ vs. $1/T$ for α =0.2-0.85, of K ₂ Bi ₈ S ₁₃ film	75
5.7	Activation energy of crystallization E_c vs. extent of reaction α for K ₂ Bi ₈ S ₁₃ film.	76
5.8	JMA-Matusita plot of $K_2Bi_8S_{13}$ films at heating rates of 5, 10, and 15 K/min.	77
A.9	Schematic of data flow in the laser device.	83
A.10	The extracted laser diode module	84
A.11	The user input module (Olimex AVR-MT-128)	85
A.12	The MAX9483 laser driver mounted to a printed circuit board. Extension pins are spaced 0.001" apart	86

CHAPTER 1

Introduction

With the volume of data carried and processed by the world increasing at a substantial rate, the need for ultra-high-density data storage becomes more prevalent. Conventional non-volatile storage media, such as magnetic hard disks, will run into a spot size barrier well before the predicted need of 20 nm spots because of inherent limitations such as supermagnetic effects (1). Phase-change materials are promising in this area since they allow for extremely small spots that are thermally stable in a large temperature range and unaffected by electric or magnetic fields. (2-5)

Most conventional phase-change materials, such as the widely used $Ge_2Sb_2Te_5$, exhibit glassy and crystalline phases that can be interconverted with heat. The glass forms upon cooling from the melt. Reheating the glass causes it to go through a glass transition and then a glass-crystal transition below the melting point. After this point, the material is cooled and maintains its crystallinity, where re-melting can again afford the glass. A useful material should exhibit excellent cyclability without significant degradation. (6, 7)

The methods for heating the material vary greatly, leading to an assortment of promising devices for non-volatile data storage. Currently in wide use are the laser-activated rewriteable compact discs (CD) and digital versatile discs (DVD). In these devices, a polycarbonate disc is coated with a thin film of phase-change material in the glass form. The data are written by focusing a laser with frequency above the band gap of the material on a spot and heating just beyond the crystallization temperature. The disc is read by a less powerful laser measuring the difference in refraction between glassy and crystalline spots as binary data.

Because of the limitations of laser-written, disc-based media, new methods of data storage have been investigated, many utilizing phase-change materials. Current-induced phase changes, heating the material with an electrical current rather than a laser (Joule heating), have become attractive for their fast access times, potentially smaller spot sizes, and, in some cases, no moving parts. Phase-Change Random Access Memory (PC-RAM), also called Ovonic Unified Memory (OUM), seeks to replace the current RAM-hard drive tandem used in virtually all computers with a single device. The capacitance-driven RAM currently used in computers can be accessed extremely fast, but the data must eventually be written to a hard drive as the RAM is volatile and will degrade after a short period of time. PC-RAM solves this problem by storing the data in a way that is thermally and electrically stable. The spots are read in this case by measuring the difference in resistance between the crystalline and glassy phases as binary data. Simulations using conductive transparent probes have achieved spot sizes as low as 20 nm, leading to nearly 1 terabit/inch2 storage density, hundreds of times greater than today's best materials. (2)

For all the research and development going into new technology based on phase-change materials, there is little research into new materials. New PC-based devices, from the latest in high-density DVD's to the current-based systems mentioned above, all utilize either a Ge/Sb/Te phase (most often Ge₂Sb₂Te₅) or the non-stoichiometric Ag/In/Sb/Te phases (\mathcal{S}). Progress in the area of new materials exhibiting phase-change properties could positively impact whichever technology becomes the industry standard, and advances in the properties of the materials stand to benefit the efficacy of the device from the most basic level; therefore, research into the most fundamental materials is crucial to the success of the format.

In order to synthesize new phase-change materials with the desirable properties of high interconversion speed, good cyclability and stability, the underlying chemistry should be examined. For a fast interconversion time, there should be a large driving force, such as a large energy difference between the amorphous and crystalline structure, and the atoms should not need to travel a long distance. For good cyclability, the composition of the structure should be stoichiometric so as to avoid phase separation. The material should also be a semiconductor, allowing it to be interconverted by lasers and used in optical data storage devices. (9)

The alkali (or pseudoalkali) antimony sulfides are a promising system to explore for new phase-change materials. They are semiconductors with a range of band gaps. Most compounds have well-defined stoichiometries and are charge-balanced. The variety in the coordination environment of antimony can also be a factor in its ability to form phase-change materials. The mostly inert lone pair in Sb^{3+} is expressed by distorting the coordination away from octahedral. This may contribute to the phase-change behavior exhibited in several antimony chalcogenides.

Currently, there are no known bismuth-based phase-change materials in the literature. Antimony seems to occupy a "sweet spot" between As and Bi with regard to its ability to vary its coordination, leading to phase-change behavior. Many phosphorus and arsenic compounds vitrify easily (10); indeed, they may be more difficult to crystallize, while Bi compounds are often more symmetric and more difficult to vitrify. This does, however, make Bi a likely target for exceptionally fast PCMs, as the quenching rate needed to form the glass has been implicated in the speed of the glass-to-crystal phase transition. **References and Notes**

References and Notes

- [1] Lee, K. M.; Polycarpou, A. A. **2006**, 20, 1322 1337.
- [2] Murashita, T. Mat. Res. Soc. Symp. Proc. 2004, 803, HH1 3 1.
- [3] Kado, H.; Tohda, T. Appl. Phys. Lett. 1995, 6, 296.
- [4] Peng, C.; Cheng, C.; Mansuripur, M. J. Appl. Phys. 1997, 82, 4183.
- [5] Gotoh, T.; Sugawara, K.; Tanaka, K. J. Non-Cryst. Solids 2002, 299-302, 968.
- [6] Yamada, N.; Ohno, E.; Nishiuchi, K.; Akahira, N.; Takao, M. Journal Of Applied Physics 1991, 69, 2849 – 2856.
- [7] Yamada, N.; Matsunaga, T. Journal Of Applied Physics **2000**, 88, 7020 7028.
- [8] Wright, C. D.; Armand, M.; Aziz, M. M.; Senkader, S.; Yu, W. Mat. Res. Soc. Symp. Proc. 2004, 803, HH1 – 2 – 1.
- [9] Feringa, B.; Jager, W.; Delange, B. Tetrahedron 1993, 49, 8267 8310.
- [10] Chung, I.; Jang, J. I.; Gave, M. A.; Weliky, D. P.; Kanatzidis, M. G. Chem. Commun. 2007, 4998 – 5000.

CHAPTER 2

Local structure and influence of bonding on the phase-change behavior of the chalcogenide compounds $K_{1-x}M_xSb_5S_8$ (M= Rb,

Tl)

2.1 Introduction

Phase-change materials are gaining increasing interest because of their use in the data storage media crucial to the information technology industry. (1, 2) These materials exhibit reversible glass-to-crystal phase transitions and can be used in applications as diverse as non-volatile memory (3), digital video disks (4), polarized holograms (5), opto-mechanical actuators (6) and infrared optical waveguides (7). There are two major classes of phasechange materials: stoichiometric and non-stoichiometric. Stoichiometric phase-change materials, such as the industry standard Ge₂Sb₂Te₅ (8), consist of a single crystallographically distinct structure, which is recovered in pure form upon recrystallization. Non-stoichiometric glasses tend to crystallize into a mixture of two or more structures. An example of this is the (Li₂S)_x(Sb₂S₃)_{1-x}, x=0-0.17 system, which crystallizes into a mixture of LiSbS₂ and Sb₂S₃ (9). The stoichiometric materials are more advantageous due to faster crystallization rates, better cyclability and long lifetimes.

The compound KSb_5S_8 is isostructural to TlSb_5S_8 , the mineral parapierrotite, and is a stoichiometric phase-change material that exhibits a rapid and reversible glass-to-crystal transition (10). The crystalline phase melts at 441°C and does not recrystallize on rapid cooling. Upon subsequent heating, there is a glass transition at 223°C followed by a rapid crystallization at 287°C. Its structure is made of undulating $[Sb_5S_8]^-$ layers with K⁺ ions seated in between the layers. The layers however interact strongly with one another forming essentially a three-dimensional $[Sb_5S_8]^-$ network, Figure 2.1(a) (11). This system is an interesting study case because it presents a combination of covalent bonding (i.e. Sb–S bonds) and ionic K—S bonding both of which can influence the phase-change behavior. Almost all materials that have been studied so far possess exclusively covalent bond frameworks. KSb₅S₈ is a semiconductor with a band gap of 1.82 eV for the crystalline phase and 1.67 eV for the glass. The activation energy of crystallization for KSb₅S₈ is 167 ± 3.1 kJ/mol and the rate constant for the peak temperature was found to be comparable to that of Ge₂Sb₂Te₅ (12). The crystallization process appears to proceed via a bulk multi-step crystallization mechanism, where the nucleation rate increases with time. (13)

To further understand the KSb₅S₈ system we investigated the isostructural solid solutions of the type $K_{1-x}Rb_xSb_5S_8$. By partially substituting K for Rb the properties can be subtly altered while preserving the structure and the phase-change capacity. For example, the same ASb₅S₈ structure forms with K⁺, Rb⁺ and Tl⁺ and thus it is possible to prepare solid solutions of the type $K_{1-x}Rb_xSb_5S_8$ and $K_{1-x}Tl_xSb_5S_8$ (11, 14). These represent small but significant perturbations on the parent phase that could allow a better assessment of how changes in ionic bonding affect the phase-change and other properties of KSb₅S₈. Such studies could lead to a deeper understanding of the relationship of ionic vs. covalent bonding and crystallization kinetics in phase-change materials. Here we report on the evolution of physical, thermal and phase-change properties of a representative set of $K_{1-x}Rb_xSb_5S_8$ solid solutions. We discuss structure-property relationships though local structure studies using pair distribution function analysis (PDF), electronic structure and bonding analysis using density functional theory (DFT) band structure calculations. We also performed Raman and optical spectroscopic studies recorded during a phase-change event. In addition we report thermal conductivity measurements for KSb₅S₈. The thermal conductivity is a key property



Figure 2.1. Powder X-ray diffraction patterns of as-synthesized glasses of $K_{1-x}Rb_xSb_5S_8$ (a-c, x = 0.25, 0.5, 0.75, respectively) and TlSb₅S₈ (d), showing their amorphous nature.

in phase-change switching materials and it is highly favorable in this case as it is one of the lowest known for solid-state materials.

2.2 Experimental section

2.2.1 Synthesis

 K_2S and Rb_2S were prepared by the reaction of a stoichiometric mixture of potassium or rubidium metal and sulfur in liquid ammonia at -78°C until no trace of the metal was left (approx. 12 h). The ammonia was then allowed to evaporate and the resulting pale yellow powder was dried under vacuum for 24 h. Sb_2S_3 was prepared by reacting a stoichiometric mixture of Sb and S powders in a silica tube at 750°C for 24 h, then quenched in air to room temperature. $K_{1-x}Rb_xSb_5S_8$ solid solutions were prepared by a stoichiometric combination of potassium sulfide, rubidium sulfide, and antimony sulfide, where the potassium sulfide to rubidium sulfide ratio was allowed to vary. A mixture of K_2S (1-x mmol, 0 < x < 1), Rb_2S (x mmol), and 1.698 g Sb₂S₃ (5.00 mmol) was loaded in a silica tube under a dry nitrogen atmosphere in a Vacuum Atmospheres Dri-Lab glovebox and flame-sealed under reduced pressure ($< 10^{-4}$ mbar). The mixture was heated in a flame until a homogeneous, orange melt was achieved, which was then quenched in air to form a silver, glassy ingot. The yield was quantitative. Crystalline $K_{1-x}Rb_xSb_5S_8$ was formed by annealing the glassy ingot above the crystallization point, which ranged from 278 to 314°C depending on composition. Glassy $TlSb_5S_8$ was prepared by the reaction of a stoichiometric combination of Tl metal, Sb_2S_3 , and sulfur powder. The reactants were loaded into in a silica tube under a dry nitrogen atmosphere in a Vacuum Atmospheres Dri-Lab glovebox and flame-sealed under reduced pressure (< 10^{-4} mbar). The mixture was heated in a furnace at 800°C for 1 d, then quickly removed and quenched in ice water to afford the $TlSb_5S_8$ glass.

2.2.2 Electron microscopy

Quantitative microprobe analyses of the compounds were performed with a JEOL JSM-35C scanning electron microscope (SEM) equipped with a Tracor Northern energy-dispersive spectroscopy (EDS) detector. Data were acquired using an accelerating voltage of 25 kV and a 1-min acquisition time.

2.2.3 Powder X-ray diffraction

The samples were examined by X-ray powder diffraction for identification and to assess phase purity. Powder patterns were obtained using a CPS 120 INEL X-ray powder diffractometer with Ni-filtered Cu K α radiation operating at 40 kV and 20mA and equipped with a positionsensitive detector. The purity of phases was confirmed by comparison of the X-ray powder diffraction patterns to ones calculated from single crystal data using the NIST Visualize 1.0.1.2 software.

2.2.4 Synchrotron radiation diffraction experiments

Synchrotron radiation scattering experiments were carried out at the beamline 11-ID-C at the Advanced Photon Source at Argonne National Laboratory using X-rays of energy 115.68 keV ($\lambda = 0.1072$ Å). The higher energy X-rays were used to obtain diffraction data to higher values of the wave vector, Q, which is important for the success of atomic PDF analysis. The measurements were carried out in symmetric transmission geometry and scattered radiation was collected with an intrinsic germanium detector connected to a multi-channel analyzer.

2.2.5 Thermal analysis

Differential thermal analysis (DTA) was performed with a computer-controlled Shimadzu DTA-50 thermal analyzer. The crushed powders (~ 25 mg total mass) were sealed in silica ampoules under reduced pressure ($< 10^4$ mbar). A silica ampoule of equal mass was sealed and placed on the reference side of the detector. The samples were heated to 850° C at a rate

of 10° C/min where they were isothermed for 5 min followed by cooling at 10° C/min to room temperature. The differential scanning calorimetric (DSC) measurements were carried out with a Setaram DSC141 calorimeter. Temperature and energy calibrations of the instrument were performed, for different heating rates, using the well-known melting temperatures and melting enthalpies of high-purity zinc and indium supplied with the instrument. Bulk-shaped specimens weighing about 7 mg were crimped in aluminum crucibles; an empty aluminum crucible was used as reference. A constant flow of nitrogen was maintained to provide a constant thermal blanket within the DSC cell, thus eliminating thermal gradients and ensuring the validity of the applied calibration standard from sample to sample. In the DSC measurements, the heating rate was 10° C/min.

2.2.6 Raman scattering

Raman spectra were measured on a Jobin-Yvon LABRAM 28 spectrometer equipped with a LINKAM high-temperature cell. To eliminate artifacts from oxidative sample decomposition, all the experiments were repeated with the samples sealed in silica ampules. A solid-state diode laser was used for all measurements, generating 10mW power at an excitation wavelength of 785 nm. Scattered radiation was collected with a CCD. For each run, two scans were accumulated at a scanning time of 60 s, generating a spectrum with a resolution of 0.7 cm⁻¹. Raman spectra were also obtained with a Holoprobe Raman spectrograph equipped with a CCD camera detector using 633nm radiation from a HeNe laser for excitation and a resolution of cm⁻¹.

2.2.7 Thermal conductivity measurements

The thermal conductivity was determined with a longitudinal steady-state method over the temperature range 4-300 K. In this case, samples were attached (using either a low melting point solder or silver-loaded epoxy) to the cold tip of the cryostat, while the other end of the sample was provided with a small strain gauge resistor (thin film), which serves as a

heater. Temperature difference across the sample was measured using differential chromelconstantant hermocouple. Both crystalline and glassy KSb_5S_8 materials were measured. The polycrystalline samples were cylindrical in shape with diameter 4 mm and length about 5 mm. Radiation loss is an unavoidable error in all thermal conductivity measurements made using a longitudinal steady-state technique manifested in deviations from the true value that increase with temperature above about 200 K. In order to determine the radiation loss experimentally, we made a subsequent measurement with the sample detached from the heat sink (sample hangs by thin connecting wires). We determined the amount of heat needed to supply to the heater that raises the temperature of the entire sample to the same average temperature as during the actual measurement of the thermal conductivity. The values of the thermal conductivity were then corrected for this radiation loss.

2.2.8 Electronic structure calculations

Electronic structure calculations were performed using the self-consistent full-potential linearized augmented plane wave (LAPW) method (15) within DFT (16), using the generalized gradient approximation (GGA) of Perdew *et al.* (17) for the exchange and correlation potential. Convergence of the self-consistent iterations was performed for 20 k points inside the irreducible Brillouin zone to within 0.0001 Ry with a cutoff of -6.0 Ry between the valence and the core states. Scalar relativistic corrections were included and a spin-orbit interaction was incorporated using a second variational procedure (18). The calculations were performed using the WIEN2K program (19).

2.3 Results and discussion

2.3.1 Phase-change behavior

Solid solutions of the form $K_{1-x}Rb_xSb_5S_8$ were synthesized with x = 0, 0.25, 0.5 and 0.75 by quenching the corresponding melts in air or water. They were obtained as shiny, gray metallic-like glasses, which are red-purple in fine powdered form and are amorphous by powder X-ray diffraction (Figure 2.1(b)). The crystalline phases exhibit the same color difference between bulk and powder, though the crystalline form is a dull, silver ingot rather than mirror-like. Powder X-ray diffraction of these samples obtained after annealing above the crystallization temperature showed them to be isostructural to the parent KSb₅S₈ (20). The increasing incorporation of the larger Rb atom in $K_{1-x}Rb_xSb_5S_8$ is confirmed by the shift of the (200) reflection in the X-ray diffraction pattern from 9.031 to 8.601 in 2 θ (Figure 2.2).

The effect of this substitution on the thermal properties of the materials was measured with DTA and DSC experiments. We observed systematic evolution of the crystallization as a function of temperature, and in some cases incongruent melting as indicated by the two melting endotherms. The thermograms of the four different samples with x = 0, 0.25, 0.50and 0.75 are presented in Figure 2.3 where the glass transition (T_g) , the crystallization peak (T_p) and the melting point (T_m) , considered as the onset of melting peak, temperatures are shown. There is a pronounced differentiation in phase-change behavior as the Rb fraction increases in the compound. As shown by the sharp exothermic crystallization peaks in the range 280 - 310°C, each of these glasses is a phase-change material with a well-defined crystallization process.

The melting point decreases with enrichment (Figure 2.4), which is most probably due to the larger size of Rb⁺ as compared to K⁺ (1.60 Å vs. 1.51 Å) giving rise to longer and weaker Rb₂S bonds thereby softening the lattice. This follows the general trend in alkali metal chalcogenides of a decrease in melting point with increasing alkali metal size (21). This trend is followed until x = 0.50 (eutectic point) and then it reverses as we move towards pure RbSb₅S₈. A similar trend is observed in the crystallization peaks. The increase of x (Rb content) up to 0.25 results in quite a small shift of the crystallization peak to lower temperatures, and then for x = 0.25 is observed a shift to higher temperatures, indicating a minimum value at about x = 0.25. The shifts in crystallization temperature could be attributed to a destabilization of the glass up to a minimum between x = 0.25 and 0.50 (melting point temperature trend), and then a locking in of the structure nearing total K



Figure 2.2. X-ray diffraction patterns of: (a) $K_{0.25}Rb_{0.75}Sb_5S_8$ glass, as-synthesized. (b) $K_{1-x}Rb_xSb_5S_8$ after annealing for 2 h at 300°C. (c) KSb₅S₈ calculated from crystal structure (monoclinic Pn; a = 8.1374 Å; b = 19.5013 Å; c = 9.0620 Å) (11). The difference in low-angle peak ((020) reflection) between the pure K structure and the 75% Rb structure is 0.402° in 2θ .

$K_{1-x}Rb_xSb_5S_8 x(Rb)$	T_{rg}	$\Delta T_{xg}(K)$	K_{gl}	K'_{gl}
0.00	0.68	52.7	0.31	0.29
0.25	0.69	58.5	0.48	0.37
0.50	0.71	65.9	0.58	0.48
0.75	0.72	69.9	0.61	0.56

Table 2.1. Dependence on the reduced glass transition temperature T_{rg} , the supercooled liquid region ΔT_{xg} and Hruby parameters K_{gl} and K'_{gl} from Rb content for K_{1-x}Rb_xSb₅S₈ at a heating rate of 10^oC/min.

occupancy leading to the increase in the crystallization temperature.

The compounds $TlSb_5S_8$ and $RbSb_5S_8$ were not examined in-depth because of their propensity to phase separate when undergoing transitions, both in melting and crystallization. The glass formed by melting a stoichiometric mixture of Rb_2S and Sb_2S_3 and quenching it in water was found to recrystallize at 311 and 391°C, respectively, before melting at $421^{\circ}C$ (Figure 2.5(a)). Annealing the Rb-containing glass at $320^{\circ}C$ showed crystallization to $RbSb_5S_8$, $RbSbS_2$, and Sb_2S_3 , as determined with X-ray diffraction.

The initial glass of TlSb₅S₈ crystallizes at 294 °C and melts rather congruently at 417°C (Figures 2.5(b) and 2.5(c)). Upon cooling, however, a mixture of the crystalline phases TlSbS₂, Sb₂S₃, and TlSb₅S₈ were identified. This is consistent with the phase diagram of the Tl₂S/Sb₂S₃ system reported previously (22).

2.3.2 Glass-forming ability (GFA)

GFA as related to the ease of devitrification is a crucial property for understanding the origins of glass formation and also important for designing and developing new bulk glasses (23). In $K_{1-x}Rb_xSb_5S_8$, following the initial heating treatment, the samples were cooled from 500°C to RT at rates of 10 and 25°C/min. It was observed that the parent KSb₅S₈ phase (x = 0) crystallizes completely upon slow cooling (10 or 25°C/min) from 500°C, whereas for x = 0.25 and 0.50 the compound crystallizes partially under these conditions and complete vitrification was observed for x = 0.75. Thus, the incorporation of Rb tends to enhance GFA.



Figure 2.3. DSC thermograms of $K_{1-x}Rb_xSb_5S_8$ amorphous alloys with heating rate $10^{\circ}C/min$. (a) x = 0.0, (b) x = 0.25, (c) x = 0.5, and (d) x = 0.75. The glass transition (T_g) was determined by the intersection of the curve and the halfway line between the two base lines.



Figure 2.4. Dependence of the glass transition (T_g) , crystallization peak (T_p) and the onset of melting point (T_m) on the Rb content (x) in $_{1-x}Rb_xSb_5S_8$.

The GFA of a melt is evaluated in terms of critical cooling rate (R_c) for glass formation, which is the minimum cooling rate necessary to keep the melt amorphous without precipitation of crystals during solidification. The smaller the R_c , the higher the GFA of a system; however, R_c is a parameter that is difficult to measure precisely. As a result, many criteria have been proposed to reflect the relative GFA on the basis of the characteristic temperatures measured by DTA (24). The most extensively used criteria are the reduced glass transition temperature T_{rg} (glass transition temperature T_g over liquidus temperature T_l or melting temperature T_m) and the supercooled liquid region ΔT_{xg} (the temperature difference between the onset crystallization temperature T_x and the glass transition temperature T_g). Generally, the larger the temperature interval ΔT_{xg} the higher the GFA. Another parameter K_{gl} suggested by Hruby (25) is also used as a measure of the glass-forming tendency of materials:

$$K_{gl} = (T_x - T_g)/(T_m - T_x)$$
(2.1)

or K'_{gl} where T_l instead of T_m is used (26). According to Hruby, the higher the value of K_{gl} in a glass, the higher is its stability against crystallization on heating and, presumably the higher its vitrifiability on cooling.

In Table 2.1, we present the values of all the characteristic parameters $(T_{rg}, \Delta T_{xg}, K_{gl}, K'_{gl})$ for the K_{1-x}Rb_xSb₅S₈ system. All the calculated parameters increase with the decrease in the K⁺ ion fraction, indicating that glass stability and GFA increase with an increase in x. This stabilization means that the melt need not be cooled as quickly to afford the glass and implies a much higher energy barrier of atomic realignment towards the crystal resulting in a slower crystallization speed. This effect is believed to be caused by the greater polarizability and larger size of the Rb atom as compared to K, which results in lower mobility in the lattice and slows down the conversion process to the ordered crystalline phase. Furthermore, the longer Rb₂S bonds and increased structural disorder of the solid solution result in a decreased absolute lattice energy compared to the pristine KSb₅S₈. This diminishes the thermodynamic driving force to transform from the higher energy glass state to the lower



Figure 2.5. DSC thermograms with heating rate 10° C/min: (a) RbSb₅S₈, (b) TlSb₅S₈, first heating and (c) TlSb₅S₈, second heating.

lying crystalline state.

2.3.3 Local structure: crystal versus glass

The structures of crystalline and glassy KSb₅S₈ and several $K_{1-x}Rb_xSb_5S_8$ compositions were probed with X-ray scattering using PDF analysis (27). Deeper structural clues were sought as to the nature of glass vis-a-vis crystal by investigating similarities and differences in the structure of both forms at the atomic level. The atomic PDF technique has emerged recently as a powerful tool for the characterization and structure refinement of materials with intrinsic disorder. The utility of the technique stems from the fact that it takes into account the total diffraction, that is Bragg as well as diffuse scattering, and so it can be applied to both crystalline (28) and amorphous materials (29). Therefore, the technique is both a local and an extended structure probe and thus a powerful tool that can be used to identify differences in structural features between the crystalline and glassy versions of these materials (30).

The PDF, G(r), is obtained from the experimentally determined total-scattering structure function, S(Q), by a sine Fourier transform

$$G(r) = \frac{2}{\pi} \int_0^\infty Q[S(Q) - 1] \sin(Qr) dQ$$
 (2.2)

$$= 4\pi r [\rho(r) - \rho_0]$$
 (2.3)

where ρ is the distance between two atoms and Q the magnitude of the scattering vector, and S(Q) is the corrected and properly normalized powder diffraction pattern of the material (also called the structure function). $\rho(r)$ and ρ_0 are the local and average atomic number densities, respectively, and ρ is the radial distance. Experimental structure functions S(Q)for crystalline and glassy KSb₅S₈ are shown in Figure 2.6 on an absolute scale. The structure of crystalline KSb₅S₈ was analyzed and refined based on the PDF data to obtain a basis for the structural comparisons of the glass forms and the results were in excellent agreement with those of the single crystal refinement (11). In the glass, the Bragg peaks are lacking and



Figure 2.6. Experimental structure functions of crystalline and glassy KSb_5S_8 .



Figure 2.7. (a) PDF plot of crystalline KSb_5S_8 , experimental, (b) PDF plot of glassy KSb_5S_8 , (c) Sb coordination environment of KSb_5S_8 .

only diffuse scattering is observed; however, the scattering profile tracks closely the profile of the crystalline form. Beyond 8 Å⁻¹, both scattering patterns merge into a slowly oscillating diffuse component.

The experimental PDFs for both forms of KSb_5S_8 are shown in Figures 2.7(a) and (b), respectively. They were obtained from the synchrotron radiation diffraction data following the usual data reduction procedures described previously (28). As can be seen in Figure 2.7 the experimental PDFs peak at characteristic distances separating pairs of atoms and thus reflect the local atomic-scale structure. In the crystalline phase, these molecular units are arranged into a 3D periodic structure and the corresponding experimental PDF oscillates out to high interatomic vectors (see Figure 2.7(a)). In particular, the first peak in both PDFs is located between 2.4 and 2.8 Å, reflecting the Sb-S bonds in the sample. As determined from the crystal structure of KSb_5S_8 , there are several SbS_6 and SbS_7 coordination polyhedra with a spread of Sb-S bond lengths. One typical such fragment is shown in Figure 2.7(d). The second and third PDF peaks occur at approximately 4 and 6 Å and reflect mostly the nearest Sb-Sb and S-S atomic neighbor distances and possibly some longer Sb-S distances. The three PDF peaks, which occur within the first 7 Å, correspond to a well-defined and compact structural fragment of SbS_7 shown in Figure 2.7(d). The calculated PDF of the molecular SbS_7 fragment is shown for comparison in Figure 2.7(c). It is clear that the three correlation peaks due to Sb-S bond and S-S second neighbor distances are very similar to those observed experimentally (Figures 2.7(a) and (b)). The PDFs of the $K_{1-x}Rb_xSb_5S_8$ members (not shown) were similar to that of the parent compound suggesting they possess the same local structure.

In the glass, the experimental PDF is seen to decay to zero at ~15 Å. Obviously, its structural coherence length is much shorter than that observed in the crystal. This coherence length, however, is much longer than those of more conventional glasses such as SiO_2 and underscores a much more organized and well-defined local structure in the amorphous $[Sb_5S_8]^-$ framework. Based on the strong similarity of the G(r) of the two forms up to 7 Å,

see Figures 2.7(a) and (b), we surmise that this structural fragment is essentially invariant in both the glass and the crystal. The glass structure consists essentially of the same rigid SbS_n fragments as the crystalline KSb_5S_8 structure except that they are connected in a disordered fashion. If the basic building units that define the structure of KSb_5S_8 are intact in the glass, only a small reorganization would be required to regain the periodic crystalline state. This is consistent with the rapid and facile crystallization processes in this system.

2.3.4 Electronic absorption and Raman spectroscopy

The effect of the substitution of Rb^+ into the structure on the electronic properties was probed with optical reflectance spectroscopy in the glasses (Figure 2.8). Each glass member showed a band gap $\mathrm{E_g} \sim 1.50$ eV, which is slightly lower than that of the parent KSb₅S₈ glass of 1.67 eV. There was no significant variation in the experimentally measured band gaps of the solid solutions as a function of x which may be due to the competing effects of the larger, more polarizable nature of the Rb⁺ ion, which should decrease the band gap, and the increased ionicity of the more electropositive Rb⁺ ion, which should increase it. This is consistent with the bonding insights obtained by the electronic band structure calculations on KSb₅S₈ (14)

Figure 2.8 compares the Raman spectra of glassy and crystalline KSb_5S_8 measured at room temperature. While the crystalline material shows five well-defined peaks between 280 and 345 cm⁻¹, which can be attributed to vibrations involving the $[Sb_5S_8]^-$ framework, the spectrum observed in the glass is extremely broad, suggesting a wide distribution of bond angles. Nevertheless, the centers of gravity of both spectra roughly coincide, supporting the close structural resemblance of both phases inferred from the PDF study discussed above. The amorphous KSb_5S_8 phase at room temperature shows Raman shifts on top of a broad feature centered at 100-150 cm⁻¹ and a characteristic broad peak in the 250-350 cm⁻¹ range. Essentially identical room temperature spectra were observed for the mixedalkali $K_{1-x}Rb_xSb_5S_8$ glasses, further supporting the interpretation that all of these spectral



Figure 2.8. Solid state UV-Vis reflectance spectra of $K_{0.75}Rb_{0.25}Sb_5S_8$ converted to absorption via the Kubelka-Monk procedure. The spectra for $K_{0.5}Rb_{0.5}Sb_5S_8$ and $K_{0.25}Rb_{0.75}Sb_5S_8$ glasses are similar. Band gaps extrapolated linearly to 0 are 1.50, 1.47, and 1.51 eV respectively.



Figure 2.9. Raman scattering data on crystalline (a) and glassy (b) $\rm KSb_5S_8$ at room temperature.


Figure 2.10. Raman scattering data of glassy KSb_5S_8 at various temperatures along the heating curve, The crystallization event is shown by the sharpening of peaks between 210 and 335°C .



Figure 2.11. Raman scattering data of KSb_5S_8 cooled from the molten state. Crystallization is evidenced by the sharpened features near 338, 321, 310, 298, and 280 cm⁻¹.

features can be attributed to vibrations involving only the framework atoms of antimony and sulfur.

To obtain further insight into the local structure of the glass and the phase-change process, we conducted temperature-dependent Raman scattering experiments in an attempt to observe the crystallization process in situ. The Raman spectra as a function of temperature of a KSb_5S_8 glass sample are shown in Figure 2.10. As long as the temperature remained below the glass transition temperature of 220°C, no significant changes were observed in the Raman spectra of the glass. Above T_g , well-defined features are observable, which are successively developed above 240°C. The new features include intense peaks at 81 and 150 cm^{-1} , as well as features near 230 and 305 cm^{-1} with a shoulder near 330 cm^{-1} . When the temperature exceeded the compound's melting point, this spectrum disappeared giving rise to a similar one observed for the glass at room temperature. While the nucleation of crystals above T_p is easily detected in the Raman spectra, the comparison of the spectra above 240°C (Figure 2.10) with that of the fully crystallized material (Figure 2.8(a)) reveals that the sharpening of these Raman peaks is only gradual. That the Raman peaks do not entirely sharpen in this temperature region indicates that the nucleated material is still strongly disordered above T_p , and extra energy is needed to fully crystallize and lock the atoms into their crystallographic coordinates. DTA studies conducted on KSb₅S₈ during melt cooling reveal no crystallization exotherms, suggesting the formation of glassy material under these conditions (10). Nevertheless, Raman spectra obtained during melt cooling (Figure 2.11) reveal the same features as those obtained above Tp during the heating cycle, indicating that small crystalline nuclei have formed under these (relatively slow) cooling conditions. This is most clearly seen by the appearance of peaks near 338, 321, 310, 298, and 280 cm⁻¹ (reflecting peak positions observed in crystalline KSb_5S_8) which become increasingly well-defined with decreasing temperature. The sizes of the nuclei generally depend on the cooling rate and in the case of the Raman experiments the cooling rate was considerably slower that those used in the DTA experiments $(10^{\circ}C/min)$.



Figure 2.12. Temperature dependence of thermal conductivity of the crystalline and glassy KSb_5S_8 (4-300K).

2.3.5 Thermal conductivity

In phase-change materials, besides optical response, the thermal behavior is important for reasons involving heating, quenching and switching speeds, cyclability and suppression of thermal cross talk (31). A low thermal conductivity is necessary to ensure fast, localized heating over a minimum area. Optimization for thermal performance requires accurate knowledge of the thermal conductivity of both glass and crystalline states and it is therefore imperative to have an accurate estimation of the thermal transport properties of these materials. The thermal conductivity of bulk crystalline and glassy KSb₅S₈ was measured with a steady-state technique over the temperature range of 4-300K (Figure 2.12). Because both forms of KSb₅S₈ have a very low electrical conductivity (e.g. < 10^{-8} S/cm) the data shown essentially represent the lattice thermal conductivity.

The thermal conductivity of crystalline KSb_5S_8 exhibits the expected Umklapp peak at low temperatures (about 8K) and is characteristic of crystalline materials (32). It is caused by the competition between the phonon-boundary scattering and Umklapp phonon-phonon interactions. On the other hand, glassy KSb_5S_8 shows no such peak at low temperatures, which is a typical behavior for amorphous materials and presents significantly lower values as expected due to the structural disorder (33).

At higher temperatures, the thermal conductivity for both samples is similar regarding both magnitude and trend. The thermal conductivity of crystalline KSb_5S_8 at room temperature is an amazingly low 0.4 W/mK. This value in fact represents an upper bound in this family of materials as we expect the solid solutions $K_{1-x}Rb_xSb_5S_8$ to be even less thermally conducting.

The thermal conductivity of KSb_5S_8 is lower than that of $Ge_2Sb_2Te_5$, which is 0.55 W/mK (34). This may appear surprising since KSb_5S_8 consists of lighter elements than $Ge_2Sb_2Te_5$ and is generally expected to have higher lattice thermal conductivity (35). The lower values in the sulfide compound can be attributed to the characteristically lower crystal symmetry, the relatively large unit cell, and the presence of weakly bound K atoms (i.e. K —

S ionic bonding). All of these are absent in $Ge_2Sb_2Te_5$. This finding implies that in certain cases KSb_5S_8 may have an advantage over $Ge_2Sb_2Te_5$ in sustaining smaller spot sizes and higher packing densities without thermal cross talk.

2.4 Conclusions

 $\mathrm{KSb}_5\mathrm{S}_8$ is a good example of a phase-change material with a mixed ionic/covalent bonding. The K site in the structure can be used to modulate the glass-forming properties and crystallization rates of the system via isomorphic substitution with Rb. In this work we introduced perturbations on the ionic bonding, i.e. K(Rb) — S, which affects the phase change properties of the system significantly. The members of the $K_{1-x}Rb_xSb_5S_8$ series exhibit phase-change properties with greater GFA than KSb_5S_8 . The GFA increases with increasing Rb content. In this case, the random alloy disorder in the alkali metal sublattice seems to predominate over the increased degree of ionicity in going from $\rm K-S$ to $\rm Rb-S$ bonding and works to stabilize the glass forms in $K_{1-x}Rb_xSb_5S_8$ and slow the crystallization process compared to pure KSb_5S_8 . Tl ions also substitute for K but the Tl analog itself is not stable on melting and therefore its phase change behavior is relatively complicated. Property modification could not be accomplished with neither Sb nor S site substitution in the structure of KSb_5S_8 as these sites do not lend themselves for similar substitutions with e.g. Bi, Se, respectively. Band structure calculations on KSb₅S₈ and TlSb₅S₈ suggest a wide indirect energy gap with the Tl - S interactions being slightly stronger than those of K -S (14).

In-depth studies are needed in chalcogenide systems in which the ionic/covalent bonding ratio can be varied. In this regard, KSb_5S_8 and related A/Sb/Q (A = alkali metal, Q = S, Se) phases could be excellent study cases. Of particular interest would be to compare the behavior of K/ Sb/S systems to that of K/Sb/Se counterparts and some of these results are reported in Chapters 3 and 4 of this thesis. The glass possesses relatively long-range order (up to 7 Å) compared to most known glasses. The glassy and the crystalline states share large, well-defined local coordination polyhedral SbS_7 fragments of an approximate length scale of 7 Å. This represents a substantial degree of built-in pre-organization in the amorphous form that sets the stage for facile crystallization. Finally, the thermal conductivity of both glass and crystalline KSb_5S_8 is among the lowest known for any dense inorganic solid-state material.

References and Notes

References and Notes

- (a) Hesselink, L.; Mijiritskii, A. E. Advanced data storage materials and characterization techniques. MRS Proceedings, 2003; p 803, references therein; (b) Borg, H. J.; van woudenberg, R. Journal Of Magnetism And Magnetic Materials 1999, 193, 519 525;
 (c) Popescu, M.; Sava, F.; Anghel, A.; Lorinczi, A.; Kaban, I.; Hoyer, W. Journal Of Optoelectronics And Advanced Materials 2005, 7, 1743 1748; (d) Gidon, S.; Lemonnier, O.; Rolland, B.; Bichet, O.; Dressler, C.; Samson, Y. Applied Physics Letters 2004, 85, 6392 6394.
- [2] (a) Lankhorst, M. H. R.; Ketelaars, B. W. S. M. M.; Wolters, R. A. M. Nature Materials 2005, 4, 347 352; (b) Teteris, J.; Reinfelde, M. Journal Of Optoelectronics And Advanced Materials 2003, 5, 1355 1360; (c) Hisakuni, H.; Tanaka, K. Science 1995, 270, 974 975.
- [3] (a) Edwards, A. H.; Pineda, A. C.; Schultz, P. A.; Martin, M. G.; Thompson, A. P.; Hjalmarson, H. P. Journal Of Physics-Condensed Matter 2005, 17, L329 L335; (b) Ahn, D. H.; Kang, D. H.; Cheong, B. K.; Kwon, H. S.; Kwon, M. H.; Lee, T. Y.; Jeong, J. H.; Lee, T. S.; Kim, I. H.; Kim, K. B. IEEE Electron Device Letters 2005, 26, 286 288.
- [4] Ohta, T. Journal Of Optoelectronics And Advanced Materials **2001**, *3*, 609 626.
- [5] Spektor, B.; Lisiansky, M.; Shamir, J.; Klebanov, M.; Lyubin, V. Applied Physics Letters 2000, 76, 798 – 800.
- [6] Tikhomirov, V. K.; Elliott, S. R. Physical Review B 1994, 49, 17476 17479.
- [7] Lucas, J. Current Opinion In Solid State and Materials Science 1999, 4, 181 187.
- [8] (a) Yamada, N.; Ohno, E.; Nishiuchi, K.; Akahira, N.; Takao, M. Journal Of Applied Physics 1991, 69, 2849 – 2856; (b) Yamada, N.; Matsunaga, T. Journal Of Applied Physics 2000, 88, 7020 – 7028.
- [9] de la Parra, S.; Torres-Gonzalez, L. C.; Torres-Martinez, L. M.; Sanchez, E. Journal Of Non-Crystalline Solids 2003, 329, 104 – 107.

- [10] Kyratsi, T.; Chrissafis, K.; Wachter, J.; Paraskevopoulos, K. M.; Kanatzidis, M. G. Advanced Materials 2003, 15, 1428 – 1431.
- [11] Berlepsch, P.; Miletich, R.; Armbruster, T. Zeitschrift Fur Kristallographie 1999, 214, 57 – 63.
- [12] Park, J.; Kim, M. R.; Choi, W. S.; Seo, H.; Yeon, C. Japanese Journal Of Applied Physics Part 1-Regular Papers Short Notes and Review Papers 1999, 38, 4775 – 4779.
- [13] Chrissafis, K.; Kyratsi, T.; Paraskevopoulos, K. M.; Kanatzidis, M. G. Chemistry Of Materials 2004, 16, 1932 – 1937.
- [14] Wachter, J. B.; Chrissafis, K.; Petkov, V.; Malliakas, C. D.; Bilc, D.; Kyratsi, T.; Paraskevopoulos, K. M.; Mahanti, S. D.; Torbrügge, T.; Eckert, H.; Kanatzidis, M. G. J. Solid State Chem. 2007, 180, 425 – 436.
- [15] Singh, D. Pseudopotential and the LAPW method; Kluwer Academic, Boston, MA, 1994.
- [16] (a) Hohenberg, P.; Kohn, W. Physical Review 1964, 136, B864 B871; (b) Kohn, W.;
 Sham, L. J. Physical Review 1965, 140, A1133 A1138.
- [17] Perdew, J. P.; Burke, K.; Ernzerhof, M. Physical Review Letters **1996**, 77, 3865 3868.
- [18] Koelling, D. D.; Harmon, B. N. Journal Of Physics C-Solid State Physics 1977, 10, 3107 – 3114.
- [19] Blaha, P.; Schwarz, K.; Madsen, G.; Kvasnicka, D.; Luitz, J. WIEN2K, An Augmented Plane Wave+Local Orbitals Program for calculating Crystal Properties; Karlheinz Schwarz Technical University, Wien, 2001.
- [20] Attempts to prepare solid solutions of KSb₅S₈ with respective Bi and Se substitutions were not successful.
- [21] TB. Massalski (Ed.), ASM International (Corporate Author), H. Okamoto (Ed.), Compare Melting Points of A₂Q Systems (A = alkali metal, Q = S, Se, Te): Binary Alloy Phase Diagrams, 1986.
- [22] Jumas, J. C.; Olivierfourcade, J.; Rey, N.; Philippot, E. Revue De Chimie Minerale 1985, 22, 651 – 665.
- [23] Turnbull, D. Contemporary Physics **1969**, 10, 473 and.
- [24] Li, Y.; Ng, S. C.; Ong, C. K.; Hng, H. H.; Goh, T. T. Scripta Materialia 1997, 36, 783 - 787.
- [25] Hruby, A. Czechoslovak Journal of Physics 1972, 78, 1187.

- [26] Zhang, Z.; Wang, W. H.; Hirotsu, Y. Materials Science And Engineering A-Structural Materials Properties Microstructure And Processing 2004, 385, 38 – 43.
- [27] (a) Toby, B. H.; Egami, T. Acta Crystallographica Section A 1992, 48, 336 346; (b)
 Egami, T. Journal Of Physics And Chemistry Of Solids 1995, 56, 1407 1413.
- [28] Petkov, V.; Jeong, I. K.; Chung, J. S.; Thorpe, M. F.; Kycia, S.; Billinge, S. J. L. *Physical Review Letters* **1999**, *83*, 4089 – 4092.
- [29] Waseda, Y. The Structure of Non-crystalline Materials; McGraw Hill, New York, 1980.
- [30] Billinge, S. J. L.; Kanatzidis, M. G. Chemical Communications 2004, 749 760.
- [31] Ohta, T.; Inoue, K.; Uchida, M.; Yoshioka, K.; Akiyama, T.; Furukawa, S.; Nagata, K.; Nakamura, S. Japanese Journal Of Applied Physics Part 1-Regular Papers Short Notes and Review Papers 1989, 28, 123 – 128.
- [32] Berman, R. Thermal Conduction in Solids; Clarendon, Oxford, 1976.
- [33] (a) Kittel, C. Physical Review 1949, 75, 972 974; (b) Zeller, R. C.; Pohl, R. O. Physical Review B 1971, 4, 2029 and.
- [34] Konstantinov, P. P.; Shelimova, L. E.; Avilov, E. S.; Kretova, M. A.; Zemskov, V. S. Inorganic Materials 2001, 37, 662 – 668.
- [35] Spitzer, D. P. Journal Of Physics And Chemistry Of Solids 1970, 31, 19 and.

CHAPTER 3

$K_2Sb_8Se_{13}$: a phase-change material exhibiting polyamorphism

3.1 Introduction

Phase-change materials have been widely studied over the past two decades, most notably for their utility as data storage media. (1-4) The ability for a material to exist in two stable states at room temperature distinguishable by a simple measurement, usually optical reflectance or electronic resistance, makes it a perfect fit for the binary system ubiquitous in the computing world. Additionally, the ability for the material to be rapidly switched from one state to another, generally using heat, allows for the facile writing and erasing of data. Because of the permanent nature of written data in PC materials and the relative ease of rewriting, it is postulated that further advancement of these materials could lead to their replacing the conventional 3-step computer memory process of electrical memory→magnetic memory \rightarrow optical memory with a single memory device. (2, 5, 6) The utility of most PC materials is based upon their ability to exist as both crystalline and amorphous structures at room temperature, and all currently-used materials have this property. Here we report the remarkable behavior of potassium antimony selenide $K_2Sb_8Se_{13}$ (PASE: potassium-antimonyselenide), a material that shows a glass \rightarrow glass, polyamorphic phase change as well as a glass→crystal phase change, making it a three-state PC system. Polyamorphism is a phenomenon that is well-studied in several binary compounds (e.g. SiO_2 , GeO_2 , H_2O , BeF_2) and some pure elements (C, Si, Ge, Bi, Se, Te, I), often under high pressures, but is, in general, quite rare. (7-9) Recent discoveries of polyamorphism in liquid phosphorus (10)

and Al_2O_3 - Y_2O_3 (11, 12) have further proven the existence of these systems, but represents the first example of a stoichiometric, chalcogenide-based polyamorphic material functioning at ambient pressure. Unlike these examples, $K_2Sb_8Se_{13}$ is a single phase with a well-defined crystal structure and contains both ionic and covalent bonds.

3.2 Experimental section

3.2.1 Synthesis

Crystalline PASE was synthesized by combining 0.345 g K₂Se, 0.122 g Sb, and 0.079 g Se powders under a nitrogen atmosphere in a 13 mm diameter, fused silica tube, which was then sealed under reduced pressure ($<10^{-4}$ torr) and heated at 850°C for 24 h, when heating was ceased and the tube was allowed to cool in the furnace. The resulting ingot was proven to have the K₂Sb₈Se₁₃ stoichiometry by energy dispersive X-ray elemental analysis. The ingot was then crushed and loaded into a 9 mm fused silica tube whose bottom had been drawn out to a sharp point and ground to reveal a hole <0.5 mm in diameter. This tube was loaded into a nitrogen atmosphere glove box and suspended ~2 cm over two copper cylinders, each 2 in. in diameter, rotating in opposite directions. The powder in the bottom of the tube was heated by a small heating element until molten, where it was held in the tube by surface tension until the tube was lightly pressurized by nitrogen, immediately forcing the molten K₂Sb₈Se₁₃ through the hole to be flattened and rapidly cooled by the rotating copper cylinders. The resulting thin glassy ribbon was ~150 μ m thick.

3.2.2 Differential Scanning Calorimetry (DSC)

The differential scanning calorimetric (DSC) measurements were carried out with a Shimadzu DSC-50 calorimeter. Temperature and energy calibrations of the instrument were performed, for different heating rates, using the well-known melting temperatures and melting enthalpies of high-purity zinc, indium and tin. Bulk-shaped foil specimens weighing about 5 mg were crimped in aluminum crucibles; an empty aluminum crucible was used as reference. A

constant flow of nitrogen was maintained to provide a constant thermal blanket within the DSC cell, thus eliminating thermal gradients and ensuring the validity of the applied calibration standard from sample to sample.

3.2.3 X-ray powder diffraction

The samples were examined by X-ray powder diffraction for confirmation of their amorphous nature and evidence of crystallization. Powder patterns were obtained using a CPS 120 INEL X-ray powder diffractometer with Ni-filtered Cu K α radiation operating at 40 kV and 20 mA and equipped with a position-sensitive detector.

3.2.4 Synchrotron radiation diffraction experiments

The local structure was solved using atomic pair distribution function (PDF) analysis. Powder of crystalline and glass K₂Sb₈Se₁₃ was packed in a flat aluminum plate with thickness of 1.0 mm sealed with kapton tape. Diffraction data were collected at 300 K using the rapid acquisition pair distribution function (RA-PDF) technique (13). Data were collected using an MAR345 image plate detector and ~100 keV energy X-rays ($\lambda = 0.123515$ Å) at the 6-IDD beam line at the Advanced Photon Source (APS). Measurements were repeated 4-5 times per sample to improve counting statistics. The data were combined and integrated using the program FIT2D (14). Various corrections were made to the data, such as subtraction of background, Compton and fluorescence scattering, geometric corrections, absorption, and so on, as described in reference. Corrections were made using the program PDFgetX2 (15). Finally, S(Q) was truncated at Q_{max} of 25 Å⁻¹ before the PDF was calculated (16). Structural models are fit to the data using the program PDFFIT (17).

3.2.5 Optical energy band gaps

Optical band gaps were determined at room temperature using Kubelka-Munk theory (18) on data collected by diffuse reflectance UV/Vis spectroscopy on finely ground sample portions of the foil. A background was collected before each scan using BaSO₄. A spectrum was collected for the region of 200-2500 nm with a Shimadzu UV-3101 PC double-beam, double-monochromator spectrophotometer.

3.2.6 Pyncnometry

Density was calculated from the sample mass (~40mg) and the volume determined from a Micromeritics AccuPyc 1340 gas pycnometer at 293 K. Samples of glass α were obtained by heating glass β to 230°C in a Shimadzu DSC-50 and rapidly cooling to obtain the desired glassy phase.

3.3 Results and discussion

3.3.1 Structural analysis

The structure of K₂Sb₈Se₁₃ is a three-dimensional, dense array of octahedral blocks. The structure is similar to that of β -K₂Bi₈Se₁₃ (19) and includes two different interconnected types of Sb/Se rod-shaped building blocks forming a framework with parallel tunnels filled with K⁺ atoms (Figure 3.1). The triclinic structure is an ordered variant of the monoclinic structure of K₂Bi₈Se₁₃ with two types of blocks designated as NaCl⁽¹¹¹⁾- and NaCl⁽¹⁰⁰⁾- because they represent excised fragments of the NaCl structure with cuts along the (111) and (100) plane respectively. The blocks are connected to each other by shared Sb atoms. Figures 3.2A and 3.2B show typical sample fragments of crystalline and glass- β PASE. The as-synthesized PASE foil (glass- β) was found to be amorphous by X-ray powder diffraction (Figure 3.2c).

The three broad features visible at 13-17°, 23-35°, and 42-58°2 θ angle indicate a high degree of order in the glass, though it clearly has no periodic structure. Upon heating, the material undergoes two well defined exothermic transitions, as evidenced by differential scanning calorimetry (DSC, Figure 3.3 and XRPD, Figure 3.2C. The first transition, beginning at 220°C, represents reorganization to another amorphous structure (glass- α). The powder



Figure 3.1. The crystal structure of $K_2Sb_8Se_{13}$.



Figure 3.2. (A) crystalline $K_2Sb_8Se_{13}$. (B) material obtained by quenching molten $K_2Sb_8Se_{13}$ (glass- β). (C) X-ray powder diffraction patterns from the three phases of $K_2Sb_8Se_{13}$: i) as-synthesized glass- β ; (ii) glass- α after heating to 225°C and (iii) crystalline phase after heating above 263°C. (Cu K α radiation).

diffraction data confirm the amorphous nature of this product (Figure 3.2C); however, there is clearly some change in structure as suggested by the fact that the broad peak at 23-35°has sharpened, and the other peaks are starting to show definition beyond their counterparts in the β glass. Upon further heating to 263°C, the structure undergoes another exothermic reorganization, this time to a crystalline product, as shown by XRPD (Figure 3.2). In this XRPD pattern, all peaks corresponding to the K₂Sb₈Se₁₃ structure are present, and no amorphous background is observed. The exothermic nature of the two transitions suggests the metastable nature of glass- α and glass- β .

To examine the consequences of these transitions on the local structure of the materials, the pair-distribution function (PDF) was examined for each structure (Figure 3.4A). The PDF was determined from the processing of X-ray diffraction data of a Synchrotron source and validates the existence of three distinct phases. In the as-synthesized glass- β (Figure 3.4A), the presence of atomic pair correlations indicate ordering to nearly 10 Å, a considerable distance for a glass. There are clear peaks at 2.6 Å, showing Sb–S bonds and at ~4 Å & 6.5 Å, showing 2nd- (Se···Se and Sb···Sb) and 3rd-nearest neighbor distances. On conversion to glass- α , more order is observed (Figure 3.4A). Peaks have developed at 4.9 Å, 7.1 Å, 10.7 Å, 12.4 Å, showing that the transition from glass- β to α has indeed resulted in a change in the local structure, and that this new structure is more ordered than glass- β . The PDF of the crystallized compound (Figure 3.4A) shows a further sharpening of the peaks, as well as new features at much longer radial distances, demonstrating full crystallization of the material.

3.3.2 Optical properties

The other unusual property in this material is the shifting of the band gap from 1.43 eV to 1.3 eV to 0.74 eV as the material is switched from $\beta\alpha$ crystal. All other PC materials show the canonical behavior: a slight increase (usually 0.1-0.2 eV) in the band gap as the material is switched from glass-crystal, attributed to the removal of "band tailing"



Figure 3.3. DSC thermogram of $K_2Sb_8Se_{13}$ ribbon. Three phase changes are observed from glass- β to glass- α (227°C), from glass- α to crystal (263°C), and melting (443°C).



Figure 3.4. (A) Pair-distribution function analysis of the three phases of $K_2Sb_8Se_{13}$: assynthesized glass- β ; glass- α after heating to 220°C and crystalline phase after heating to 270°C. (B) Optical absorption spectra showing energy gaps for crystalline and glass- α $K_2Sb_8Se_{13}$.

effects in the glass. A change of nearly double in energy in the opposite direction must be attributed to a major change in electronic structure. One way to account for this is that the coordination number of antimony has changed. Several systems are known in which an increase of chalcogenide atoms coordinated to a central metal leads to a sharp decrease in band gap. CdS undergoes a pressure-induced phase transition from a wurtzite structure to a rock salt structure around 3 GPa (20) As it moves from tetrahedral coordination in the wurtzite structure to octahedral coordination in the rock salt structure, the band gap decreases from 2.5 eV to 1.5-1.7 eV (21) A similar effect is seen in HgS, which transitions from the two-coordinate cinnabar structure (band gap = 2.3 eV) to the four-coordinate zinc blende structure, where the band gap collapses and the material becomes metallic (22)Though it is not a phase transition, we can also draw similarities to $K_2Bi_8S_{13}$. $K_2Bi_8S_{13}$ has a band gap of 0.06-0.25 eV (19, 23) and contains primarily octahedral Bi atoms. This can be compared with the trigonal pyramidal Bi atoms in Bi_2S_3 , which has a larger band gap of 1.1 eV (24). The contribution of potassium can be ignored here because, in general, increased ionicity will afford a wider band gap (25). These examples support the hypothesis that the glass of PASE contains a greater number of 3-coordinate Sb sites, while the crystal, as shown by X-ray crystallography, contains primarily 6-coordinate Sb.

3.3.3 Density measurements

Moving from a structure with 3-coordinate Sb to the known crystal structure of PASE with 6-coordinate Sb should lead to an increase in density, which we probed using a pycnometer. Density values are reported in Table 3.1 for each phase. Consistent with the PDF and X-ray data, the density data show a slight increase in density upon transition from glass $\beta \rightarrow \alpha$ and then a more pronounced change to the crystalline form. This lends further proof to the increase in coordination and clear evidence of a polyamorphic transition. (11)

Phase	glass β	glass α	$\operatorname{crystal}$
Density (g/cm^3)	4.949(1)	5.060(1)	5.278(1)
Energy gap (eV)	1.43(1)	1.30(1)	0.74(1)

Table 3.1. Energy gaps and density of the three states of $K_2Sb_8Se_{13}$.

3.4 Conclusions

The glass→glass transition discovered in K₂Sb₈Se₁₃ is unique in that this is both the first example of a true ternary polyamorphic system as well as the first ambient pressure chalcogenide-based polyamorphic system. The suitability of chalcogenides for use as functional materials in phase-change memories (PCMs) has been well-documented (26), so the new tri-state system described here could see application in data storage and novel computing devices utilizing ternary logic mechanisms (27) rather than the current binary systems (28). The tri-stability property found in PASE raises the prospect of additional systems yet to be discovered with similar properties. If tri-stability is more common than we currently imagine, then materials with ideal three-state behavior may soon emerge as new platforms for a variety of experimentation relevant to higher than binary logic. Additionally, the PASE system should be ideal for fundamental studies of the rare polyamorphic phenomenon, as both glasses α and β are stable at standard temperature and pressure, and are not reactive with air or water.

References and Notes

References and Notes

- [1] Wuttig, M.; Yamada, N. Nature Materials **2007**, *6*, 824 832.
- [2] Lankhorst, M. H. R.; Ketelaars, B.; Wolters, R. A. M. Nature Materials 2005, 4, 347 352.
- [3] Welnic, W.; Pamungkas, A.; Detemple, R.; Steimer, C.; Blugel, S.; Wuttig, M. Nature Materials 2006, 5, 56 – 62.
- [4] Hamann, H. F.; O'Boyle, M.; Martin, Y. C.; Rooks, M.; Wickramasinghe, K. Nature Materials 2006, 5, 383 – 387.
- [5] Pirovano, A.; Lacaita, A. L.; Benvenuti, A.; Pellizzer, F.; Bez, R. IEEE Transactions on Electron Devices 2004, 51, 452 – 459.
- [6] Cho, W. Y. et al. *Ieee Journal of Solid-State Circuits* **2005**, *40*, 293 300.
- [7] Poole, P. H.; Grande, T.; Angell, C. A.; McMillan, P. F. Science **1997**, 275, 322 323.
- [8] Angell, C. A. Science **1995**, 267, 1924 1935.
- [9] Sheng, H. W.; Liu, H. Z.; Cheng, Y. Q.; Wen, J.; Lee, P. L.; Luo, W. K.; Shastri, S. D.; Ma, E. Nature Materials 2007, 6, 192 – 197.
- [10] Katayama, Y.; Mizutani, T.; Utsumi, W.; Shimomura, O.; Yamakata, M.; Funakoshi, K. *Nature* **2000**, 403, 170 – 173.
- [11] Aasland, S.; McMillan, P. F. *Nature* **1994**, *369*, 633 636.
- [12] McMillan, P. F.; Wilding, M. C. J. Non-Cryst. Solids 2008, 354, 1015 1025.
- [13] Chupas, P. J.; Qiu, X.; Hanson, J. C.; Lee, P. L.; Grey, C. P.; Billinge, S. J. L. J. Appl. Crystallogr. 2003, 36, 1342 – 1347.
- [14] Hammersley, A. P.; Svensson, S. O.; Manfland, M.; Fitch, A. N.; Hausermann, D. High Pressure Res. 1996, 14, 235 – 248.
- [15] Egami, T.; Billinge, S. J. L. Underneath the Bragg peaks: structural analysis of complex materials; Pergamon Press, Elsevier, Oxford, England, 2003.

- [16] Qiu, X.; Thompson, J. W.; Billinge, S. J. L. J. Appl. Crystallogr. 2004, 37, 678.
- [17] Proffen, T.; Billinge, S. J. L. J. Appl. Crystallogr. 1999, 32, 572 575.
- [18] (a) Wendlandt, W. W.; Hecht, H. G. Reflectance spectroscopy; Interscience Publishers: New York, NY, 1966; (b) Kortüm, G. Reflectance spectroscopy. Principles, methods, applications; Springer: Berlin, Germany, 1969.
- [19] Kanatzidis, M. G.; McCarthy, T. J.; Tanzer, T. A.; Chen, L. H.; Iordanidis, L.; Hogan, T.; Kannewurf, C. R.; Uher, C.; Chen, B. X. Chem. Mater. 1996, 8, 1465 – 1474.
- [20] Batlogg, B.; Jayaraman, A.; Vancleve, J. E.; Maines, R. G. Physical Review B 1983, 27, 3920 – 3923.
- [21] Cervantes, P.; Williams, Q.; Cote, M.; Zakharov, O.; Cohen, M. L. Physical Review B 1996, 54, 17585 – 17590.
- [22] Yoffe, A. D. Advances in Physics **2001**, 50, 1 208.
- [23] Chung, D. Y.; Choi, K. S.; Iordanidis, L.; Schindler, J. L.; Brazis, P. W.; Kannewurf, C. R.; Chen, B. X.; Hu, S. Q.; Uher, C.; Kanatzidis, M. G. Chem. Mater. 1997, 9, 3060 – 3071.
- [24] Nkum, R. K.; Adimado, A. A.; Totoe, H. Mater. Sci. Eng., B 1998, 55, 102 108.
- [25] Axtell, E. A.; Park, Y.; Chondroudis, K.; Kanatzidis, M. G. J. Amer. Chem. Soc. 1998, 120, 124 – 136.
- [26] (a) Yamada, N.; Ohno, E.; Nishiuchi, K.; Akahira, N.; Takao, M. Journal Of Applied Physics 1991, 69, 2849 – 2856; (b) Kolobov, A. V.; Fons, P.; Frenkel, A. I.; Ankudinov, A. L.; Tominaga, J.; Uruga, T. Nature Materials 2004, 3, 703 – 708.
- [27] (a) Rusu, M. I.; Miclos, S.; Savastru, D.; Popescu, M. New phase-change materials to achieve cognitive computing Overview and future trends. In Icton 2007: Proceedings of the 9th International Conference on Transparent Optical Networks, 2007; pp 287 289; (b) Ovshinsky, S. R.; Pashmakov, B. In Innovation providing new multiple functions in phase-change materials to achieve cognitive computing.; Ahner, J. W., Levy, J., Hesselink, L., Mijiritskii, A., Eds.; 2004; Vol. 803, pp 49 60.
- [28] (a) Bogdanov, Y. I.; Chekhova, M. V.; Krivitsky, L. A.; Kulik, S. P.; Penin, A. N.; Zhukov, A. A.; Kwek, L. C.; Oh, C. H.; Tey, M. K. *Physical Review A* 2004, 70, year; (b) Bechmann-Pasquinucci, H.; Peres, A. *Phys. Rev. Lett.* 2000, 85, 3313 – 3316; (c) Ghosh, P.; Das, P. P.; Mukhopadhyay, S. In *An alternative proposal of arithmetic* and image operations in optical parallel computation.; Marsh, J. H., Bhattacharya, P., Wada, O., Eds.; 2001; Vol. 4598, pp 175 – 181.

CHAPTER 4

Investigation into the switching mechanisms of the polyamorphic chalcogenide K₂Sb₈Se₁₃

4.1 Introduction

 $K_2Sb_8Se_{13}$ was the first phase-change material to show both glass-to-glass and crystal-tocrystal transitions (1). Several techniques have been developed to probe the kinetic and thermodynamic properties of solid state phase changes (2, 3), but few studies have been done on stoichiometric materials akin to $K_2Sb_8Se_{13}$. Chrissafis et. al. have studied the stoichiometric KSb₅S₈ system, which is similar to the $K_2Sb_8Se_{13}$ described here (4). Several kinetic and thermodynamic factors must be calculated to determine the nature and underlying mechanisms of these transformations. Analysis of these transformations is often based upon the single-step kinetic equation

$$\frac{\mathrm{d}\alpha}{\mathrm{d}t} = k(T)f(\alpha) \tag{4.1}$$

where α is the extent of reaction, t is the time, T is the temperature (in Kelvin), k(T) is the rate constant, and $f(\alpha)$ is the reaction model. This equation shows that dependence of the reaction on time is proportional to the reaction model $f(\alpha)$, and that the rate constant depends upon temperature. If the rate constant is replaced by the Arrhenius equation, the explicit temperature dependence is revealed:

$$\frac{\mathrm{d}\alpha}{\mathrm{d}t} = A \exp\left(\frac{-E}{RT}\right) f(\alpha) \tag{4.2}$$

where A is the Arrhenius preexponential factor, E is the crystallization energy (also from the Arrhenius equation), and R is the gas constant. Since the measurements here will be nonisothermal, it is more appropriate to replace $d\alpha/dt$ in Equation 4.2 with the heating rate, β .

$$\beta(\mathrm{d}\alpha/\mathrm{d}T) = \frac{\mathrm{d}T}{\mathrm{d}t} \tag{4.3}$$

The rate of change of fractional extent of reaction with respect to time $(d\alpha/dt)$ is proportional to the measured specific heat flow ϕ , normalized to sample mass, so these measurements are well suited to differential scanning calorimetry (DSC), where α can be calculated from the normalized integration of heating curves.

Crystallization kinetics can be interpreted in terms of the standard nucleation-growth model first developed by Johnson and Mehl (5) and later refined by Avrami (2) (JMA). Their model shows the time dependence of α and is often written thusly:

$$\alpha = 1 - \exp[-(kt)^n] \tag{4.4}$$

where k, the rate constant, depends on temperature, crystal growth rate, and nucleation frequency. The exponent n depends on the phase change mechanism and can reflect the nucleation frequency and/or the growth morphology. Differentiation of Equation 4.4 with respect to time gives

$$\frac{\mathrm{d}\alpha}{\mathrm{d}t} = kn(1-\alpha)[-\ln(1-\alpha)]^{1-1/n} \tag{4.5}$$

Equation 4.5, referred to as "the JMA equation," is frequently used to describe thermal crystallization data; however, there are several assumptions upon which its validity depends. First, the phase change occurs under isothermal conditions; second, crystal growth is highly isotropic; third, the nucleation occurs at randomly dispersed phase-changed particles; fourth, the growth rate of the new phase is controlled by temperature and completely independent of time. Since the validity of these assumptions is not usually known *a priori* for a new phase-change material, several methods have been developed for testing a given system's adherence to the JMA model.

The most popular method for testing the applicability of the JMA model to a new, nonisothermal system is to test the linearity of the JMA plot. Matusita et al. have suggested an equation applicable to nonisothermal crystallization given by

$$\ln[-\ln(1-\alpha)] = -n\ln(\beta) - 1.052\frac{mE_a}{RT} + \text{constant}$$
(4.6)

where β is the heating rate, m and n depend on the nucleation and growth of the new phase, and E_a is the crystallization energy (6, 7). It was suggested that n = (m+1) for a perfectly quenched glass with no nuclei and $n = m^2 0$ for a glass with a large number of nuclei (6). The value of m is given by the dimensionality of crystal growth (1,2, or 3). The plot of $\ln[-\ln(1-\alpha)]$ vs. reciprocal temperature should be linear to show the applicability of the JMA model; however, any double logarithmic function is not very sensitive to changes in its arguments, so substantial linearity in these plots is often observed even when the JMA model is not the strongest model of the system under investigation. Ultimately, more realtime methods, such as time-resolved electron microscopy, will need to be developed to gain a more complete understanding of the complex and varied mechanisms at work in phase-change systems, especially with regard to nucleation and growth.

4.2 Experimental section

4.2.1 Synthesis

Crystalline K₂Sb₈Se₁₃ was synthesized by combining 0.345 g K₂Se, 0.122 g Sb, and 0.079 g Se powders under a nitrogen atmosphere in a 13 mm diameter, fused silica tube, which was then sealed under reduced pressure ($<10^{-4}$ torr) and heated at 850°C for 24 h, when heating was ceased and the tube was allowed to cool in the furnace. The resulting ingot was proven to have the K₂Sb₈Se₁₃ stoichiometry by energy dispersive X-ray elemental analysis. The ingot was then crushed and loaded into a 9 mm fused silica tube whose bottom had been drawn out to a sharp point and ground to reveal a hole <0.5 mm in diameter. This tube was loaded into a nitrogen atmosphere glove box and suspended ~2 cm over two copper

cylinders, each 2 in. in diameter, rotating in opposite directions. The powder in the bottom of the tube was heated by a small heating element until molten, where it was held in the tube by surface tension until the tube was lightly pressurized by nitrogen, immediately forcing the molten $K_2Sb_8Se_{13}$ through the hole to be flattened and rapidly cooled by the rotating copper cylinders. The resulting thin glassy ribbon was ~150 m thick.

4.2.2 Differential Scanning Calorimetry (DSC)

The differential scanning calorimetric (DSC) measurements were carried out with a Shimadzu DSC-50 calorimeter. Temperature and energy calibrations of the instrument were performed, for different heating rates, using the well-known melting temperatures and melting enthalpies of high-purity zinc, indium and tin. Bulk-shaped foil specimens weighing about 5 mg were crimped in aluminum crucibles; an empty aluminum crucible was used as reference. A constant flow of nitrogen was maintained to provide a constant thermal blanket within the DSC cell, thus eliminating thermal gradients and ensuring the validity of the applied calibration standard from sample to sample. DSC data were analyzed with OriginPro 7.0 software.

4.3 Results and Discussion

 $K_2Sb_8Se_{13}$ shows a rare glass-to-glass transition at 227°C and glass-to-crystal transition at 263°C. To better understand the nature of these transitions, quantitative kinetic analyses were performed on the DSC data (Figure 4.1). Each thermogram shows two exothermic events: the first, broad peak arises from the glass-to-glass transition and the second, sharp peak from the glass-to-crystal transition.

4.3.1 Kissinger analysis

Calculating the activation energy E_c of each phase transition can give insight into their mechanisms and relative speeds. The dependence of peak temperature, T_p , on heating rate



Figure 4.1. Baseline-corrected, nonisothermal DSC traces of $K_2Sb_8Se_{13}$ at heating rates β of 5, 10, 15, and 20 K/min.

Material	Transition	$E_c \; (kJ/mol)$	$k(T) \ (s^{-1})$
$K_2Sb_8Se_{13}$	glass 1 - glass 2	245	2.4×10^{-3}
$K_2Sb_8Se_{13}$	glass 2 - crystal	316	$2.6 imes 10^{-3}$
$\mathrm{KSb}_5\mathrm{S}_8$	glass - crystal	167	2.1×10^{-2}
$\mathrm{Ge}_2\mathrm{Sb}_2\mathrm{Te}_5$	glass - crystal	215	2.45×10^{-2}

Table 4.1. Comparison of crystallization energy, E_c , and rate constant, k(T), of K₂Sb₈Se₁₃ with KSb₅S₈ and Ge₂Sb₂Te₅ at 20 K/min heating rate.

 β is given by Equation 4.7 (8)

$$T_p = A + B \log \beta \tag{4.7}$$

where A and B are constants for a given composition. Kissinger analysis (9), which combines the single-step mechanism with the Arrhenius equation, can give a rough estimation of the activation energy of a solid-solid phase transition from the slope of a $\ln(\beta/T_p^2)$ vs. $1/T_p$ plot (see Equation 4.8, where R is the universal gas constant).

$$\ln(\beta/T_p^2) = -E_c/RT_p + \ln(A \cdot R/E_c) \tag{4.8}$$

Kissinger plots for both peaks are shown in Figures 4.2 and 4.3. The data show good linearity, though this is not surprising considering the logarithmic relationship. The values of the activation energies E_{c1} and E_{c2} were found to be 245 kJ/mol and 316 kJ/mol respectively, and preexponential factors A_1 and A_2 were calculated as 1.05×10^{23} s⁻¹ and 2.10×10^{28} s⁻¹ from the intercept. By substituting the Arrhenius equation into the single-step kinetic equation (Equation 4.9), the rate constants k(T) were calculated (Equation 4.10) to be 2.4×10^{-3} s⁻¹ for peak 1 and 2.6×10^{-3} s⁻¹ for peak 2 at $\beta = 20$ K/min.

$$d\alpha/dt = Ae^{-E/RT}f(\alpha) \tag{4.9}$$

$$k(T) = Ae^{-E_c/RT_p} \tag{4.10}$$

Table 4.1 shows the comparison of these kinetic parameters with previously studied phasechange materials KSb_5S_8 and $Ge_2Sb_2Te_5$. These data seem to indicate that the transitions in $K_2Sb_8Se_{13}$ are slower than those in comparable materials, but the assumption of the



Figure 4.2. Kissinger plot of K₂Sb₈Se₁₃ glass β to glass α , $\ln(\beta/T_p)$ vs. 1000/T and the straight regression line (β in K s⁻¹)



Figure 4.3. Kissinger plot of K₂Sb₈Se₁₃ glass α to crystal, $\ln(\beta/T_p)$ vs. 1000/T and the straight regression line (β in K s⁻¹)

Kissinger method, that the phase transitions are single-step, may not be applicable in this case. This is not surprising, as the unusual nature of the glass \rightarrow glass polyamorphic transition may require more sophisticated kinetic analysis.

4.3.2 Ozawa-Flynn-Wall analysis

The isoconversional method first developed by Ozawa, Flynn and Wall (3) uses a model-free approach by measuring the temperatures at each value of α (extent of reaction) and plotting them at different heating rates (Equation 4.11).

$$\ln(\beta) = \ln[Af(\alpha)/d\alpha/dT] - E_c/RT$$
(4.11)

The plots of $\ln(\beta)$ vs. 1/T are shown in Figure 4.4. According to the OFW equation (Equation 4.11), the slopes are proportional to the activation energy $(-E_c/R)$. If the activation energy is calculated to be similar for different values of α , it can be reasonably concluded that the transition proceeds via a single-step mechanism; however, if there is a substantial change in slope with increasing degree of conversion, then the separation of variables involved in the OFW analysis is no longer appropriate, indicating a more complex reaction mechanism. Figure 4.4 shows the OFW plots for the glass β -to-glass α transition of K₂Sb₈Se₁₃ and Figure 4.5 shows the relationship of activation energy with extent of conversion α . The inconsistency of activation energy calculations for each α show that there are likely variations in mechanism throughout the phase change, showing the polyamorphic transition to be of a complex mechanism and most likely multi-step. Since this is a unique example of polymorphism at ambient pressure, it is reasonable to expect that the phase transition mechanisms will be significantly different from previously studied systems (10-12).

4.4 Conclusions

Kinetic studies on $K_2Sb_8Se_{13}$ glass showed great variability in mechanism and form, its nonadherence to classical models underscoring the novelty of this system. Kissinger analysis of



Figure 4.4. OFW plot of $\ln(\beta)$ vs. 1/T for different values of α during the first phase transition (glass β -to-glass α) of K₂Sb₈Se₁₃.



Figure 4.5. OFW plot of $\ln(\beta)$ vs. 1/T for different values of α during the first phase transition (glass β -to-glass α) of K₂Sb₈Se₁₃.

DSC data showed linearity, but the isoconversional OFW method showed a clear deviation from the model. As this represents the first example of a polyamorphic material stable in both glass forms at ambient temperature and pressure, it may be an excellent candidate for developing new models to describe the kinetics of polyamorphic phase transitions.
References and Notes

References and Notes

- Wachter, J. B.; Chung, D.-Y.; Kyratsi, T.; Malliakas, C.; Chrissafis, K.; Sootsman, J. R.; Kanatzidis, M. G. Science 2010, submitted, .
- [2] Avrami, M. J. Chem. Phys. 1941, 9, 177.
- [3] Ozawa, T. J. Therm. Anal. **1970**, 2, 301.
- [4] Chrissafis, K.; Kyratsi, T.; Paraskevopoulos, K. M.; Kanatzidis, M. G. Chemistry Of Materials 2004, 16, 1932 – 1937.
- [5] Johnson, W. A.; Mehl, R. F. Trans. Am. Inst. Min. (Metall.) Eng 1939, 135, 416.
- [6] Matusita, K.; Sakka, S. Phys. Chem. Glasses 1979, 20, 81.
- [7] Matusita, K.; Konatsu, T.; Yokota, R. J. Mater. Sci. 1984, 19, 291.
- [8] Lasocka, M. Mater. Sci. Eng. 1976, 1976, 173.
- [9] Kissinger, H. E. J. Res. Natl. Bur. Stand. 1956, 57, 217.
- [10] McMillan, P. F.; Wilding, M. C. J. Non-Cryst. Solids 2008, 354, 1015 1025.
- [11] Aasland, S.; McMillan, P. F. *Nature* **1994**, *369*, 633 636.
- [12] Angell, C. A. Science **1995**, 267, 1924 1935.

CHAPTER 5

Synthesis and phase-change behavior of $K_2Bi_8S_{13}$ thin films

5.1 Introduction

The previous chapters have reported on several new antimony chalcogenide-based phase change materials. Attempts to quench bismuth chalcogenides were unsuccessful in that the glassy phases could not be formed through standard quenching techniques such as water, air, and splat quenching (1). The more rigid frameworks in bismuth-based structures (2) require ultra-rapid quenching to afford the amorphous phase; however, this makes those phases particularly lucrative from a data storage material standpoint, as the resulting glasses should crystallize exceptionally fast (3).

Gutwirth et al. (4) have demonstrated the synthesis of Ag-Sb-S glasses, which are unable to be synthesized through rapid bulk quench methods, by pulsed-laser deposition. In this technique, a target of the bulk, crystalline sample is irradiated by a high energy, pulsed laser, releasing a plume of small particles that settle onto a substrate placed in front of the target (5). The rapid cooling of the particles as they settle on the substrate results in the amorphous structure.

An additional advantage of producing films of the phase-change materials is to investigate their utility in data storage devices and media. All currently-used, phase-change materialbased solid state memory devices require thin layers of the material to be deposited onto the device, often layered with electrodes (6). Synthesizing films of A-Sb/Bi-S-type PCMs has been difficult using conventional techniques such as chemical vapor deposition (CVD) because of the great variation in vapor pressures among alkali metal ions, antimony, bismuth, and sulfur, though there has been some success with solution techniques (7).

Here we describe the first synthesis of glassy $K_2Bi_8S_{13}$ films, using the pulsed-laser deposition technique. The films, which have phase-change properties, were analyzed using conventional solid-state techniques and found to exhibit excellent potential for use in data storage devices.

5.2 Experimental section

5.2.1 Synthesis of crystalline $K_2Bi_8S_{13}$

Crystalline $K_2Bi_8S_{13}$ was synthesized by combining K_2S , and Bi_2S_3 powders in a 1:4 ratio under a nitrogen atmosphere in a 13 mm diameter, fused silica tube, which was then sealed under reduced pressure ($<10^{-4}$ torr) and heated at 850°C for 24 h, when heating was ceased and the tube was allowed to cool in the furnace. The resulting ingot was proven to have the $K_2Bi_8S_{13}$ stoichiometry by energy dispersive X-ray elemental analysis and its crystallinity and structure were confirmed by powder X-ray diffraction.

5.2.2 Synthesis of amorphous $K_2Bi_8S_{13}$ thin films

Thin films of $K_2Bi_8S_{13}$ were synthesized by irradiating the ingot with a 200 mJ/pulse KrF laser ($\lambda = 248$ nm) under reduced pressure ($\sim 10^{-2}$ torr) at 20 Hz for 10 min. A glass slide was placed in front of the ingot, onto which the film deposited. The amorphous nature of the thin film was confirmed by powder X-ray diffraction.

5.2.3 Differential Scanning Calorimetry (DSC)

The differential scanning calorimetric (DSC) measurements were carried out with a Shimadzu DSC-50 calorimeter. Temperature and energy calibrations of the instrument were performed, for different heating rates, using the well-known melting temperatures and melting enthalpies of high-purity zinc, indium and tin. Material from several film samples (~ 0.7 mg) was

scraped off the glass substrates and into an aluminum crucible; an empty aluminum crucible was used as reference. A constant flow of nitrogen was maintained to provide a constant thermal blanket within the DSC cell, thus eliminating thermal gradients and ensuring the validity of the applied calibration standard from sample to sample.

5.2.4 Transmission electron microscopy (TEM)

Transmission electron microscopy was performed on as-deposited and annealed $K_2Bi_8S_{13}$ films using a JEOL 2200FS field emission TEM running at 200kV. Samples were prepared by pulsed-laser deposition as described above, using a copper grid as the substrate.

5.2.5 Scanning electron microscopy (SEM)

Images and quantitative microprobe analyses of the compounds were performed with a JEOL JSM-35C scanning electron microscope (SEM) equipped with a Tracor Northern energydispersive spectroscopy (EDS) detector. Data were acquired using an accelerating voltage of 25 kV and a 1-min acquisition time. Samples were coated with carbon prior to analysis.

5.3 Results and discussion

5.3.1 Structural analysis

Crystalline K₂Bi₈S₁₃ was first reported by Kanatzidis et al (2). Like other members of the A-Bi-S system, it is made up of NaCl- or Bi₂Te₃-type and CdI₂-type rod-shaped fragments along the *b* axis that connect via highly coordinated Bi atoms to form tunnels. Unlike most other alkali bismuth (or antimony) chalcogenides, the K⁺ ions are not found in these tunnels but are disordered with one of the Bi³⁺ ions. It is postulated that the disorder, coupled with the rigidity of the cubic fragments, leads to the rich phase change chemistry recently observed in these systems (8-10). Amorphous K₂Bi₈S₁₃ could not be synthesized through quenching of the melt, either with traditional water-quench techniques or with the more rapid splat-quenching.

5.3.2 Analysis of films

The high energy involved in pulsed-laser deposition allowed the material to cool quickly enough to form an amorphous film, which was previously inaccessible by other techniques. Figure 5.1 shows XRPD patterns for the as-synthesized $K_2Bi_8S_{13}$ film and for annealed films at progressively higher temperatures, showing a clear transformation from amorphous to crystalline. Annealing at higher temperatures did not alter the structure, highlighting the robust nature of the crystalline phase. The small amount of material in the film led to a low signal-to-noise in the XRPD, so long scans (16 h) were required in order to determine the crystal structure of the crystalline phase.

Comparison with calculated XRPD patterns showed that the annealed film contained a Bi_2S_3 -type structure, with no other crystalline phase observed. This was unexpected, since similar systems have been shown to undergo stoichiometric phase transitions, and the structure of the crystalline film here was clearly not $K_2Bi_8S_{13}$. Therefore, the K must have either formed a $K_xBi_{2-x}S_3$ -type solid solution, a compound that has not been previously reported, or the phase change was nonstoichiometric, that is, upon crystallization the glass phase separates into pure Bi_2S_3 and an amorphous, K-containing phase. The local structure of the crystalline film was further examined using TEM.

5.3.3 Electron microscopy

TEM of the annealed films showed clearly visible crystalline domains throughout the sample (Figure 5.2), confirmed by electron diffraction. Energy-dispersive X-ray analysis (EDS) and scanning transmission electron microscopy (STEM) show an absence of K in crystalline domains, giving an average composition of $Bi_{1.88}S_3$, a good match for bismuth sulfide. This evidence shows the non-stoichiometric nature of the glass-to-crystal phase transition in $K_2Bi_8S_{13}$, indicating that the reversibility and long-term cycling ability of the phase transition may be compromised and therefore less suitable for use in electronic devices that require more robust phase-change behavior.



Figure 5.1. XRPD of $K_2Bi_8S_{13}$ film after annealing at temperatures (from top) of 350, 325, 275, 250, 150, and 100°C, showing the glass-to-crystal phase change and stability of the crystal up to $350^{\circ}C$.



Figure 5.2. TEM image of $\rm K_2Bi_8S_{13}$ film after annealing. Crystalline $\rm Bi_2S_3$ domains are visible.



Figure 5.3. SEM image of as-synthesized $\mathrm{K_2Bi_8S_{13}}$ glass film.

Material	$E_c \; (kJ/mol)$	T_{rg}
$\begin{array}{l} \mathrm{K_{2}Bi_{8}S_{13}}\\ \mathrm{K_{2}Sb_{8}Se_{13}}\\ \mathrm{KSb_{5}S_{8}}\\ \mathrm{Ge_{2}Sb_{2}Te_{5}} \end{array}$	$120 \\ 316 \\ 167 \\ 215$	$\begin{array}{c} 0.44 \\ 0.63 \\ 0.78 \\ 0.46 \end{array}$

Table 5.1. Comparison of crystallization energy, E_c , and reduced glass transition temperature, $T_{rg} = T_g/T_m$ (3), of K₂Bi₈S₁₃ with KSb₅S₈, K₂Sb₈Se₁₃ and Ge₂Sb₂Te₅.

Side-on SEM images of the as-synthesized film (Figure 5.3) showed a homogeneous glass 4.5 μ m thick. EDS analysis gave an average composition of K_{2.17}Bi_{7.97}S₁₃, indicating stoichiometric transfer of material during the laser deposition process.

5.3.4 Thermal analysis

Though the glass-to-crystal phase change of K₂Bi₈S₁₃ was found to be non-stoichiometric, it can still have utility as a phase-change material provided the crystallization process is rapid, as several currently-used PCMs display non-stoichiometric phase changes (11-13). A DSC measurement of the as-synthesized K₂Bi₈S₁₃ film is shown in Figure 5.4. There is clear evidence of crystallization at 181°C and glass transition ~100°C. Kissinger analysis (14) of the DSC data (15), shown in Figure 5.5 allows for the calculation of activation energy of crystallization, E_c , and rate constant k(T). These values are shown in Table 5.1 compared to other phase-change materials (8, 9, 16, 17). The low activation energy of crystallization and reduced glass transition temperature (3) demonstrate the unusually rapid nature of glass-to-crystal conversion in K₂Bi₈S₁₃; indeed, it is one of the lowest T_{rg} values reported in the literature for phase change materials. These values are encouraging for the potential performance of K₂Bi₈S₁₃ as a data storage material.

To investigate the mechanism of the phase change, Ozawa-Flynn-Wall (18) and Johnson-Mehl-Avrami (19, 20) analyses were performed on the DSC data. For detailed descriptions of these kinetic methods, see Chapter 4. The OFW plots (Figure 5.6) show minimal variation in the activation energy with extent of reaction α (Figure 5.7), demonstrating a possible one-



Figure 5.4. DSC trace of $K_2Bi_8S_{13}$ glass film at a heating rate of 15 K/min. The exotherm at $181^{\circ}C$ shows crystallization of the glass, confirmed by XRPD after the scan.



Figure 5.5. Kissinger plot of K₂Bi₈S₁₃ film for heating rates of 5, 10, and 15 K/min. Regression line has the equation $\ln(\beta/T_p^2) = 14.48/T_p - 12756.88$.

step mechanism. This allows for an accurate comparison to the current industry-standard phase-change material for data storage, $Ge_2Sb_2Te_5$, which has been shown to undergo a one-step phase change mechanism (21).

Since the mechanism appears to be one step, it is appropriate to use the JMA method to probe the nucleation and growth mechanism. The Matusita extention (22) of the JMA equation (Equation 4.6) was applied, where α is the fractional extent of reaction, β is heating rate, and n and m are numerical factors depending on the nucleation process and growth morphology. Here, n is equal to (m + 1) for a quenched glass containing no nuclei and n is



Figure 5.6. Ozawa-Flynn-Wall plots, $\ln\beta$ vs. 1/T for $\alpha{=}0.2{\text{-}}0.85,$ of $\mathrm{K_{2}Bi_{8}S_{13}}$ film.



Figure 5.7. Activation energy of crystallization E_c vs. extent of reaction α for K₂Bi₈S₁₃ film.



Figure 5.8. JMA-Matusita plot of $K_2Bi_8S_{13}$ films at heating rates of 5, 10, and 15 K/min.

equal to m (23) for a glass containing a sufficiently large number of nuclei. Also, m = 3 for three-dimensional growth of crystal particles, m = 2 for two-dimensional growth, and m = 1for one-dimensional growth. The Avrami plots are shown in Figure 5.8, showing substantial linearity; however, double logarithmic functions are known to be insensitive to small changes in their arguments, so linear JMA plots may not necessarily indicate adherence to the JMA model.

5.4 Conclusions

 $K_2Bi_8S_{13}$ was successfully quenched into an amorphous form through pulsed-laser deposition. Though the non-stoichiometric nature of the crystallization of $K_2Bi_8S_{13}$, as shown by TEM and XRPD, is a potential drawback to its use as a multi-use, cyclable phase-change material, its rapid kinetics of crystallization make it ideal for applications requiring ultrafast switching. **References and Notes**

References and Notes

- (a) Nagashio, K.; Kuribayashi, K.; Yamaguchi, O. J. Am. Ceram. Soc. 2007, 90, 238 243;
 (b) Amano, M.; Sasaki, Y.; Watanabe, R. J. Less-Common Met. 1983, 89, 513 518.
- [2] Kanatzidis, M. G.; McCarthy, T. J.; Tanzer, T. A.; Chen, L. H.; Iordanidis, L.; Hogan, T.; Kannewurf, C. R.; Uher, C.; Chen, B. X. Chem. Mater. 1996, 8, 1465 – 1474.
- [3] Turnbull, D. Contemporary Physics **1969**, 10, 473 and.
- [4] (a) Gutwirth, J.; Wagner, T.; Bezdicka, P.; Pokorny, J.; Vlcek, M.; Frumar, M. J. Non-Cryst. Solids 2005, 351, 3556 3561; (b) Gutwirth, J.; Wagner, T.; Frumar, M.; Bezdicka, P.; Vlcek, M. Phys. Chem. Glasses 2006, 47, 229 232; (c) Gutwirth, J.; Wagner, T.; Nemec, P.; Kasap, S. O.; Frumar, M. J. Non-Cryst. Solids 2008, 354, 497 502.
- [5] Nemec, P.; Frumar, M.; Jedelsky, J.; Jelinek, M.; Lancok, J.; Gregora, I. J. Non-Cryst. Solids 2002, 299, 1013 – 1017.
- Borg, H. J.; van woudenberg, R. Journal Of Magnetism And Magnetic Materials 1999, 193, 519 - 525.
- [7] Mitzi, D. B. Adv. Mater. **2009**, 21, 3141 3158.
- [8] Kyratsi, T.; Chrissafis, K.; Wachter, J.; Paraskevopoulos, K. M.; Kanatzidis, M. G. Advanced Materials 2003, 15, 1428 – 1431.
- [9] Wachter, J. B.; Chung, D.-Y.; Kyratsi, T.; Malliakas, C.; Chrissafis, K.; Sootsman, J. R.; Kanatzidis, M. G. Science 2010, submitted, .
- [10] Wachter, J. B.; Chrissafis, K.; Petkov, V.; Malliakas, C. D.; Bilc, D.; Kyratsi, T.; Paraskevopoulos, K. M.; Mahanti, S. D.; Torbrügge, T.; Eckert, H.; Kanatzidis, M. G. J. Solid State Chem. 2007, 180, 425 – 436.
- [11] Wang, Y.; Boolchand, P.; Micoulaut, M. Europhys. Lett. 2000, 52, 633.

- [12] Balan, V.; Vigreux, C.; Pradel, A.; Ribes, M. Adv. Mater. 2001, 3, 367.
- [13] Etienne, S.; Perez, J.; Peytavin, S.; Ribes, M. J. Solid State Chem. 1991, 92, 27.
- [14] Kissinger, H. E. J. Res. Natl. Bur. Stand. 1956, 57, 217.
- [15] Kissinger analysis allows for the calculation of activation energy and rate constant by plotting the dependence of crystallization temperature on heating rate under the equation $ln(\beta/T_p^2) = -E_c/RT_p + \ln(A \cdot R/E_c)$.
- [16] Chrissafis, K.; Kyratsi, T.; Paraskevopoulos, K. M.; Kanatzidis, M. G. Chemistry Of Materials 2004, 16, 1932 – 1937.
- [17] Kaidatzis, A.; Wachter, J. B.; Chrissafis, K.; Paraskevopoulos, K. M.; Kanatzidis, M. G. J. Non-Cryst. Solids 2008, 354, 3643 – 3648.
- [18] Ozawa, T. J. Therm. Anal. 1970, 2, 301.
- [19] Johnson, W. A.; Mehl, R. F. Trans. Am. Inst. Min. (Metall.) Eng 1939, 135, 416.
- [20] Avrami, M. J. Chem. Phys. **1941**, 9, 177.
- [21] Park, J.; Kim, M. R.; Choi, W. S.; Seo, H.; Yeon, C. Japanese Journal Of Applied Physics Part 1-Regular Papers Short Notes and Review Papers 1999, 38, 4775 – 4779.
- [22] Matusita, K.; Sakka, S. Phys. Chem. Glasses 1979, 20, 81.
- [23] Matusita, K.; Konatsu, T.; Yokota, R. J. Mater. Sci. 1984, 19, 291.

APPENDICES

A.1 Design of an analytical laser-switching device

In order to better compare the newly-synthesized films to the current industry standards, a laser testing device was constructed. The device was designed to expel a laser pulse of given intensity and time, which would crystallize or melt the material depending on the incident power. Existing table top lasers were not the best choices for this device for several reasons. From a practical standpoint, they are expensive and require large amounts of laser table space, optics, and power supplies. Also, the lasing threshold for many common large lasers makes power control difficult or impossible. The time variable is also difficult to control with large laser systems. For longer pulses, a mechanical shutter can be used, and much research has been done on very short pulses (on the order of 10^{-12} s or faster), but the range in which laser storage devices operate $(10^{-6} - 10^{-9} \text{ s})$ is best accessed by electronic control. To this end, a device was constructed based around the Atmel Atmega128 microcontroller, Maxim MAX9483 laser diode driver, and a 650 nm laser diode extracted from a DVD-RW drive.

In an optical data storage device, the binary data signal is fed at signal level (μ A) into the driver, which amplifies the current to writing level (mA) and drives the laser diode. The diode is switched on and off in sync with the spinning disc, depending on the binary state of the input waveform. A similar philosophy is used for this device, but the input waveform is a constant, pre-determined current and the laser diode driver output is switched on and off by the microcontroller, which is calibrated by a 16 MHz quartz crystal for precision. A general flowchart of the signal path is shown in Figure A.9.

The user sets the "Power" and "Pulse length" parameters via buttons on the control board, which in this case is an Olimex AVR-MT-128 development board but could be any board designed to support the Atmega128 microcontroller.

The "Power" value is used to set a variable resistor to control the current sent as input to the driver. The variable resistor used for this device is the Analog Devices AD5206 6channel digital potentiometer. The AD5206 contains six 256-position, digitally-controlled variable resistor devices with maximum resistances of 10 k Ω . They function in much the



Figure A.9. Schematic of data flow in the laser device.

same way as an analog resistor, with two end terminals and a wiper contact that can tap the resistance. The tap point is determined by a digital 8-bit word loaded into the serial-input register. Based on the user input, the Atmega128 microcontroller sends the data through the serial peripheral interface (SPI) into the serial-input register of the AD5206, thus setting the wiper. The input current for the laser driver passes through this resistor, attenuating it to the degree necessary based on the user's power selection.

The microcontroller is also utilized to send a perfectly timed on/off pulse to the laser driver. The Atmega128's Timer/Counter0, an 8-bit timer/counter, can be set to count based upon an input from an external crystal (oscillating at 32.7 kHz) or from the internal oscillator (running at 16 MHz). Each time the counter register overflows (at 256), an interrupt signal is actuated and the interrupt subroutine runs before returning to the now-reset count. By introducing a divider and compare-to-count (CTC) term, the timer can be manipulated to overflow in a specific amount of time. This timer cycle is then contained in a loop that is repeated depending upon the pulse width as determined by the user.

The laser diode is directly controlled by the Maxim MAX9483 laser diode driver, a commercial chip used in CD/DVD-RW drives, which accomplishes the dual tasks of providing the appropriate output current for the laser diode and acting as an ultra-fast gate, turning the laser on or off as directed by the microcontroller program. It contains a precision current amplifier with a peak total output current of 400mA and can respond to on/off instructions in 1.0ns (output-current pulse rise and fall time).



Figure A.10. The extracted laser diode module.



Figure A.11. The user input module (Olimex AVR-MT-128).

The devices were connected as shown in Tables A.2 and A.3, with an additional connection between the wiper of RDAC 3 on the variable resistor (W3, pin 14) and the input of the laser driver (IN1, pin 1).

Function	Connection to Atmega128	Connection on AD5206
Data transfer Chip select Serial clock	MOSI/PB2 Pin 12 SS/PB0 Pin 10 SCK/PB1 Pin 11	SDI (Serial Data Input) Pin 7 \overline{CS} (Chip Select) Pin 5 CLK Pin 8

Table A.2. Connections from Atmega128 to AD5206.

Function	Connection to Atmega128	Connection on MAX9483
Enable device	OC1B/PB6 Pin 16	ENABLE Pin 7
On/off	OC1A/PB5 Pin 15	ÑE2 Pin 5
Select output	OC0/PB4 Pin 14	OUTSEL Pin 10

Table A.3. Connections from Atmega128 to MAX9483.

The outputs from the Atmega128 microcontroller were connected from the appropriate output pins on the Olimex board. A standard breadboard was used to connect the AD5206 and MAX9483, and a benchtop power supply was used to supply the input current. The MAX9483 chip required some additional preparation as it is a QSOP packaged, surfacemount device and thus cannot be directly connected to the breadboard. A copper printed circuit board was constructed using the photoresist-etch process to extend the small contacts on the chip to standard pins, which were spaced appropriately to fit onto the breadboard (Fig. A.12). The output from the MAX9483 chip (OUT1, pin 15) was connected to the positive terminal of the laser diode. The laser head itself was extracted from a DVD+RW



Figure A.12. The MAX9483 laser driver mounted to a printed circuit board. Extension pins are spaced 0.001" apart.

drive. The outer metal casing was easily removed after unscrewing the screws at the corners of the case, and the laser diode module was removed from the inside of the drive. All optics were left intact so that the spot size remains the same (Fig. A.10). It should also be noted that there are two laser diodes in the module, an infrared diode for CD writing and a visible diode for DVD writing. This device utilizes the visible diode, but either could be used.

In order to function as a stand-alone device (i.e. no computer connection needed while measuring), the Atmega128 microcontroller was programmed. The C language was used to write the program, which was compiled into a hex file by AVR Studio and loaded onto the device though the ICSP (intra-circuit serial programmer) interface. The main program ("laser.c") is shown below:

```
#include <sharedCode.h>
#include "lcd.h"
#include <string.h>
#include "laser.h"
```

int seconds=100;

int amps=255;

char s[6];

char a[6];

```
void updateData(void)
{
    int i;
    for (i=0; i<25; i++)
    {
        msDelay(100);
    }
    sprintf(s,"%d",seconds);
    sprintf(a,"%d",amps);
    LCD_moveTo(0,11);
    LCD_string(" ");
    LCD_moveTo(1,11);</pre>
```

```
LCD_string(" ");
LCD_moveTo(0,11);
LCD_string(s);
LCD_moveTo(1,11);
LCD_string(a);
}
```

```
int main(void)
{
initializeLCD();
//LCD_clear();
LCD_string("Pulse(ms):\0");
LCD_moveTo(1,0);
LCD_string("Power(xx):\0");
spi_setup();
updateData();
while(1==1)
{
if (readButton()==1)
{
seconds += 10;
updateData();
}
if (readButton()==5)
{
seconds -= 10;
```

```
updateData();
}
if (readButton()==4)
{
amps++;
if (amps<256)
{
updateData();
}
else
{
amps--;
updateData();
}
}
if (readButton()==2)
{
amps--;
if (amps>99)
{
updateData();
}
else
{
amps++;
updateData();
```

```
}
}
if (readButton()==3)
{
write_pot(Ob100,amps);
updateData();
pulseExecute();
}
}
}
```

The functions and subroutines not defined in the above program are taken from spi.c and sharedcode.c, whose contents are shown below:

```
#include <sharedCode.h>
#include "lcd.h"
#include "laser.h"
int pot=0;
int resistance=0;
char spi_transfer(volatile char data)
{
   SPDR = data; // Start the transmission
   while (!(SPSR & (1<<SPIF))) // Wait the end of the transmission
   {
</pre>
```

```
};
  return SPDR;
                                   // return the received byte
}
void spi_setup(void)
{
  int i;
  int clr;
  DDRB = (1<<DDB2) | (1<<DDB1) | (1<<DDB0);
  PORTB = (1<<PB0); //set SS high</pre>
    // SPCR = 01010000
  //interrupt disabled, spi enabled, msb 1st, master, clk low when idle,
  //sample on leading edge of clk,system clock/4 (fastest)
  SPCR = (1 < < SPE) | (1 < < MSTR);
  clr=SPSR;
  clr=SPDR;
 msDelay(100);
// for (i=0;i<6;i++)</pre>
// {
// write_pot(i,255);
// }
}
void write_pot(int address, int value)
{
   PORTB = (0<<PB0); //set SS low
   spi_transfer(address);
```

```
spi_transfer(value);
PORTB = (1<<PB0); //set SS high
}</pre>
```

```
#include "sharedCode.h"
```

```
//memory routines
void EEPROM_write(unsigned int uiAddress, unsigned char ucData)
{
/* Wait for completion of previous write */
while(EECR & (1<<EEWE))</pre>
;
/* Set up address and data registers */
EEAR = uiAddress;
EEDR = ucData;
/* Write logical one to EEMWE */
EECR |= (1<<EEMWE);
/* Start eeprom write by setting EEWE */
EECR \mid = (1<<EEWE);
}
unsigned char EEPROM_read(unsigned int uiAddress)
{
/* Wait for completion of previous write */
```

while(EECR & (1<<EEWE))

;

/* Set up address register */

```
EEAR = uiAddress;
/* Start eeprom read by writing EERE */
EECR |= (1<<EERE);
/* Return data from data register */
return EEDR;
}</pre>
```

```
//IO Section
int readButton(void)
{
  int returnValue=0;
  int buttonValue;
  while(returnValue=0)
  {
  returnValue=DepressedButton();
  //if(buttonValue!=0)
  //{
  //{
  // returnValue=buttonValue;
  // while(DepressedButton!=0){}
  //}
  //msDelay(200);
  }
```

//delay for debounce

```
// int j;
//for(j=0;j<50;j++)</pre>
```

```
// _delay_ms(1);
return returnValue;
}
int GetBit(int Address, int Bit)
{
return bit_is_set(Address,Bit);
}
void msDelay(int cycles)
{
int j;
for(j=0;j<cycles;j++)</pre>
_delay_ms(1);
}
```

```
void SetBit(int Address,int Bit)
{
    bit_set(Address,Bit);
}
int DepressedButton(void)
```

```
{
int result=0;
```

```
if(GetBit(BUTTON1)==0)
{
    _delay_ms(25);
    if(GetBit(BUTTON1)==0)
    result=1;
}
```

```
if(GetBit(BUTTON2)==0)
{
    _delay_ms(25);
    if(GetBit(BUTTON2)==0)
    result=2;
}
```

```
if(GetBit(BUTTON3)==0)
{ _delay_ms(25);
if(GetBit(BUTTON3)==0)
result=3;
}
```

if(GetBit(BUTTON4)==0)

{ _delay_ms(25);

if(GetBit(BUTTON4)==0)

```
result=4;
}
if(GetBit(BUTTON5)==0)
```

```
{ _delay_ms(25);
if(GetBit(BUTTON5)==0)
result=5;
}
```

return result;
}}

The front end of the program, that with which the user interacts, is comprised of a set of functions meant to read the button inputs and then update the variables seconds and amps, which control the pulse length and laser power, respectively. As described above, the amps variable relates to the resulting laser power by controlling the wiper on the digital potentiometer, attenuating the input current to the laser driver, while seconds tells the Timer/Counter0 how long to wait before turning the laser off.

Once the appropriate connections are made, the device is powered up by bringing power to the user input module. In this case, the development board is powered by 12 VDC. The laser should be positioned above the film to be tested at the desired height. The user then increases or decreases the pulse length and power by pressing the buttons on the horizontal and vertical corners, respectively. When the appropriate parameters are set, pressing the middle button activates the pulseExecute() subroutine, which cycles the laser on and off in the given time with the appropriate power.