

X-ray and Neutron Diffraction Studies of the High-Temperature β -Phase of the $\text{AgBiSe}_2/\text{AgBiS}_2$ System

A. C. GLATZ, A. PINELLA

National Aeronautics and Space Administration, Electronics Research Center, Cambridge, Mass, USA

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An X-ray and neutron diffraction study of the high-temperature, NaCl-type β -phases of the $\text{AgBiSe}_2/\text{AgBiS}_2$ system was performed to determine if the crystal structures are ordered or random arrangements. X-ray diffraction studies established that the Ag and Bi species are present at random on the cation sites, and neutron diffraction studies established that the S and Se species are present at random on the anion sites.

1. Introduction

A phase diagram of the $\text{AgBiSe}_2/\text{AgBiS}_2$ system was reported by Wernick [1], which indicated a complete series of α (low temperature, hexagonal) and β (high temperature, cubic) solid solutions having transformation temperatures varying from 200 to 300° C. Geller and Wernick [2] showed that upon heating, hexagonal AgBiSe_2 transforms at 120° C to a rhombohedral form (R3m) and on further heating transforms to the NaCl structure at 287° C. However, no attempt was made to establish the existence of this rhombohedral structure in AgBiS_2 , although it was assumed to exist. It was also shown [2] that for these ternary compounds the high-temperature, cubic form can be stabilised at room temperature by quenching from above the transition temperature.

This present study of the $\text{AgBiSe}_2/\text{AgBiS}_2$ system was initiated to determine the structures of the high-temperature β -phases of intermediate compositions in this system in relation to the terminal compounds, AgBiSe_2 and AgBiS_2 . Geller and Wernick have shown [2] that the high-temperature forms of AgBiSe_2 and AgBiS_2 have a disordered NaCl structure in which the Ag and Bi atoms are present at random on the sodium sites, and the Se and S atoms, respectively, are present on the chloride sites. Since AgBiSe_2 and AgBiS_2 form a complete series of solid

solutions, the positions of the Group VI species at intermediate compositions could be either ordered or at random on the chloride sites. Therefore, it is the purpose of this study to determine the positions of the Ag and Bi as well as the Group VI species for the high-temperature cubic phases of the $\text{AgBiSe}_2/\text{AgBiS}_2$ system.

2. Experimental Procedures

2.1. Materials and Alloy Preparations

Silver metal shot (99.999 + %), bismuth metal shot (99.999 + %), elemental sulphur (99.999 + %) and selenium pellets (99.999 + %) were obtained from American Smelting and Refining Company* and used in the preparation of the samples. These were prepared by melting stoichiometric amounts of the component elements in evacuated, sealed quartz ampoules. Five, 15 g samples were prepared having compositions of 0, 25, 50, 75, and 100 mole per cent AgBiSe_2 . The samples were placed in a high thermal capacity furnace and the temperature was raised above the liquidus temperature of the alloys (approximately 850° C) for about 30 min. The furnace temperature was then lowered to about 400° C and the samples air-quenched to room temperature. DTA and X-ray diffraction studies verified that the high-temperature β -phase was obtained by this procedure. The samples

*Address: South Plainfield, New Jersey, USA

were then ground in a mortar, and aliquot portions taken for diffraction and thermal analysis studies.

2.2. DTA Studies

The DTA thermograms were obtained using a DTA apparatus similar to that described previously [3]. For the DTA studies, the samples were annealed at 175°C for two weeks to stabilise the low-temperature α -phase. The heating curves of the DTA thermograms verified the phase study reported previously by Wernick [1]. The cooling curves of the DTA thermograms verified that the high-temperature phase is preserved at room temperature, as no enthalpic effect is observed at temperatures corresponding to the α - β phase transformation temperature.

2.3. X-ray and Neutron Diffraction Studies

Powder X-ray diffraction studies of the samples were performed at room temperature using $\text{CuK}\alpha$ radiation with a Norelco Diffractometer System, a Jarrell-Ash Microfocus Diffractometer System, and a 14.3 cm Debye-Scherrer Camera. Lattice parameters of the high-temperature cubic forms, which were quenched to room temperature, were determined by a least squares computer program [4]. These results, which are in agreement within experimental error to those reported by Wernick [1], are shown in fig. 1.

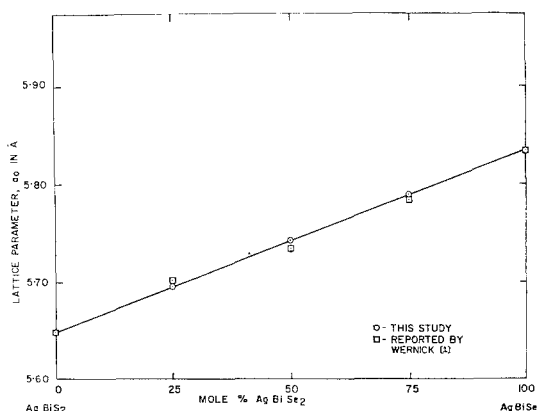


Figure 1 Lattice constants at room temperature for the cubic β -phase in the $\text{AgBiSe}_2/\text{AgBiS}_2$ system.

Powder neutron diffraction studies were performed at the MIT Research Reactor under the direction of Professor C. G. Shull. For the studies reported in this paper, primary beam

neutron fluxes of 50 to 400 kiloneutrons with a wavelength of 1.044 \AA were used.

The intensities of the X-ray and neutron diffractometer profiles were measured with an Ott Planimeter.

3. Structure Determination and Discussion

3.1. X-Ray Diffraction Studies

Previous studies by Geller and Wernick [2] have demonstrated that the high-temperature β -phases of the terminal compounds, AgBiSe_2 and AgBiS_2 , have disordered, cubic NaCl-type, structures with the Ag and Bi atoms indistinguishable on the positions: $(0, 0, 0; \frac{1}{2}, \frac{1}{2}, 0; \frac{1}{2}, 0, \frac{1}{2}; 0, \frac{1}{2}, \frac{1}{2})$ and the Se and S atoms, respectively, on the $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2}; 0, 0, \frac{1}{2}; 0, \frac{1}{2}, 0; \frac{1}{2}, 0, 0)$ positions.

X-ray diffraction studies were performed for the high-temperature, cubic phases of intermediate compositions in the $\text{AgBiSe}_2/\text{AgBiS}_2$ system. These studies established that: (i) the Ag and Bi species were present at random on the cation sites, and (ii) the positions of the Group VI species could not be definitely established by X-ray diffraction.

The positions of the atomic components were determined by comparison of observed and calculated X-ray diffraction intensities, the latter being calculated from the structure factor equation [5]. Calculations were performed for the Ag and Bi species present at random and on ordered cation sites $(0, 0, 0; \frac{1}{2}, \frac{1}{2}, 0; \odot)$ with the Group VI species having similar distributions on the anion sites $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2}; 0, 0, \frac{1}{2}; \odot)$. These intensity calculations showed that (i) if the Ag and Bi, or Group VI, species are present on ordered cation sites, or anion sites, planes having even and odd values for hkl (called "mixed" indices) will satisfy the diffraction conditions. These are called superlattice lines. (ii) If the Ag and Bi, and Group VI, species are present at random on the cation sites, and anion sites, only planes having even or odd values for hkl (called "unmixed" indices) will satisfy the diffraction conditions. In this case no superlattice lines will be observed.

It may be observed from table I for $\text{AgBiSe}_{0.5}\text{S}_{1.5}$ that only planes having unmixed indices are present with a measurable intensity, i.e. no superlattice lines are observed. This would imply that both the Ag and Bi as well as the Group VI species are present at random on the cation and anion sites, respectively. The calculated intensities show by comparison to the

TABLE I Calculated and observed d -values and relative intensities for $\text{AgBiSe}_{0.5}\text{S}_{1.5}$ using X-ray diffraction (CuK_α radiation).

hkl	d (Å)		I/I_0	
	Calculated	Observed	Calculated	Observed
111	3.2851	3.2568	0.606	0.524
200	2.8450	2.8257	1.000	1.000
220	2.0117	2.0040	0.720	0.764
311	1.7156	1.7105	0.294	0.226
222	1.6425	1.6382	0.249	0.265
400	1.4225	1.4207	0.115	0.070
331	1.3054	1.3040	0.117	0.101
420	1.2723	1.2708	0.315	0.198
422	1.1615	1.1603	0.224	0.130
511	1.0950	1.0946	0.0703	0.0553
440	1.0058	1.0057	0.0896	0.0263
531	0.96178	0.96186	0.121	0.0526
600	0.94832	0.94816	0.0436	0.0703
620	0.89966	0.89992	0.185	0.119
533	0.86771	0.86815		
622	0.85779	0.85807	0.211	0.0523
444	0.82127	0.82155		
551	0.79675	0.79728		
640	0.78905	0.78955		

measured values that the Ag and Bi species are present at random on the cation sites. For example, for $\text{AgBiSe}_{0.5}\text{S}_{1.5}$ having the ordered cation structure with Ag at $(0, 0, 0; \frac{1}{2}, \frac{1}{2}, 0)$ and Bi at $(\frac{1}{2}, 0, \frac{1}{2}; 0, \frac{1}{2}, \frac{1}{2})$ and a random anion structure, the (110) superlattice line should be observed having a relative intensity of approximately 25%. It may be observed in fig. 2 that no measurable diffraction is observed at the (110) position. Similar calculations of other compositions and structures with Ag and Bi species on ordered cation sites yields superlattice lines of measurable intensity that are not observed experimentally. Only the random distribution of the Ag and Bi species on the cation sites yields calculated intensities in agreement with observed intensities, as may be observed for $\text{AgBiSe}_{0.5}\text{S}_{1.5}$ in table I. It is, therefore, concluded that the Ag and Bi species are present on the cation sites in a random distribution.

The calculated intensities for the random cation structure with the Group VI species (S and Se) present at random and on ordered anion sites clearly demonstrates that the intensities of the superlattice lines are too small to be observed experimentally. For example, for $\text{AgBiSe}_{0.5}\text{S}_{1.5}$ the superlattice lines having the largest intensity for the ordered structure are the (100) and (110) planes, which have calculated relative intensities of 1.6 and 1.5%,

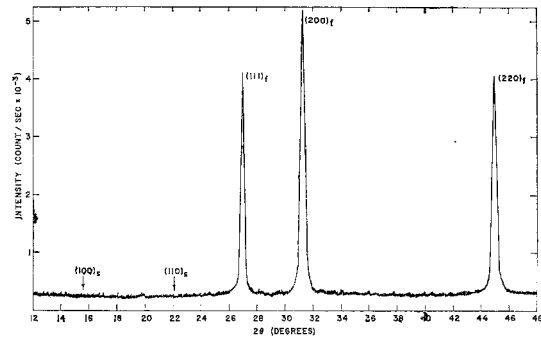


Figure 2 X-ray diffraction pattern for $\text{AgBiSe}_{0.5}\text{S}_{1.5}$.

respectively. These intensities are below the background level for the X-ray diffraction studies as shown in fig. 2. Also, shown in fig. 2 are the expected positions for the (100) and (110) superlattice lines. Therefore, it may be concluded, that for the $\text{AgBiSe}_2/\text{AgBiS}_2$ system, it is impossible to determine by X-ray diffraction whether or not the Group VI species are on ordered or random anion sites.

3.2. Neutron Diffraction Studies

It is well known that a structure analysis that is extremely difficult, or impossible, with X-ray diffraction, can often be carried out with neutron diffraction. This is because the scattering power for neutrons shows no regular variation with atomic number, and is independent of the diffraction angle.

Neutron diffraction studies were performed on powdered samples for $\text{AgBiSe}_{0.5}\text{S}_{1.5}$ from $2\theta = 9$ to 22° and for $\text{AgBiSe}_{1.5}\text{S}_{0.5}$ from $2\theta = 9$ to 40° . The relative intensities were calculated for the same conditions as for X-ray diffraction, i.e. the Ag and Bi species indistinguishable on the cation sites and the Group VI species, S and Se, present at random and on ordered anion sites. With these conditions relative intensities were calculated using the relationship [6] given in equation 1.

$$I_r = \frac{j |F_{hkl}|^2}{\sin \theta \sin 2\theta} \quad (1)$$

where, j = multiplicity; F_{hkl} = structure factor; θ = diffraction angle; I = integrated intensity. For these calculations, scattering amplitudes of 0.61 for silver, 0.864 for bismuth, 0.78 for selenium, and 0.27 for sulphur (all $\times 10^{-12}$ cm) were used [7]. The observed and calculated relative intensities for $\text{AgBiSe}_{0.5}\text{S}_{1.5}$ are given in table II, a comparison of the

calculated and observed relative intensities for X-ray diffraction and neutron diffraction for certain fundamental and superlattice lines is given in table III. It may be observed that for the ordered anion structure, the superlattice lines should have significantly greater relative intensities for neutron diffraction than for X-ray diffraction. This calculation shows that for neutron diffraction the (100) and (110) superlattice lines should have relative intensities of approximately 5% for the ordered anion structure.

TABLE II Calculated and observed d -values and relative intensities for $\text{AgBiSe}_{0.5}\text{S}_{1.5}$ using neutron diffraction ($\lambda = 1.044 \text{ \AA}$).

hkl	d (\AA)		I/I_0	
	Calculated	Observed	Calculated	Observed
111	3.2880	3.2915	0.156	0.140
200	2.8475	2.8465	0.983	1.000

TABLE III Calculated and observed relative intensities of superlattice and fundamental lines for X-ray and neutron diffraction of $\text{AgBiSe}_{0.5}\text{S}_{1.5}$

hkl	(I/I_0) (X-ray)		(I/I_0) (neut. diff.)	
	Calculated	Observed	Calculated	Observed
(100) _s	0.0162	NO	0.0489	NO
(110) _s	0.0148	NO	0.0492	NO
(111) _f	0.606	0.524	0.156	0.140
(200) _f	1.000	1.000	0.983	1.000

Subscripts s and f = superlattice line and fundamental line respectively; NO = not observed.

The observed neutron diffraction profile for $\text{AgBiSe}_{0.5}\text{S}_{1.5}$ is given in fig. 3. It may be seen that there are no diffraction peaks at $2\theta = 10.52$ and 14.90° , which are the expected positions for (100) and (110) planes of the ordered anion structure. It may also be observed that the (111) diffraction profile, which should have a relative intensity of about 16% can be seen clearly. Therefore, if the (100) and (110) planes were present, they should be very clearly observed above the background of this neutron diffraction trace. It is, therefore, concluded from these studies that the structure corresponds to both the Ag and Bi species and S and Se species being present at random on the cation and anion-sites, respectively. The neutron diffraction studies for the $\text{AgBiSe}_{1.5}\text{S}_{0.5}$ composition also verified these

results. It is, therefore, concluded that all the β -phase compositions in the $\text{AgBiSe}_2/\text{AgBiS}_2$ system have disordered anion and cation structures; and the fact that the high-temperature, cubic phases obey Vegard's Law, as shown in fig. 1, is consistent with this conclusion.

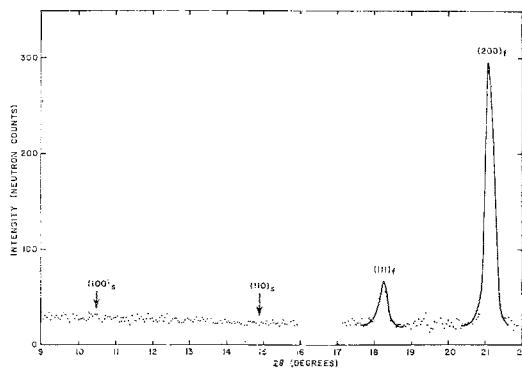


Figure 3 Neutron diffraction pattern for $\text{AgBiSe}_{0.5}\text{S}_{1.5}$.

4. Conclusions

This structural study of the high-temperature cubic, β -phases of the $\text{AgBiSe}_2/\text{AgBiS}_2$ system has shown that the Ag and Bi and S and Se species are present at random on the sodium and chloride positions, respectively, of the face-centred NaCl unit cell.

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