

## The Phase Transformations and Thermal Expansion of the Solid Electrolyte $\text{Cu}_3\text{BiS}_3$ between 25 and 300°C

EMIL MAKOVICKY

*Institute of Mineralogy, University of Copenhagen, Østervoldgade 5-7, 1350 K, Denmark*

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Phase transformations and thermal expansion of  $\text{Cu}_3\text{BiS}_3$  were studied up to 300°C using heated Weissenberg and Guinier cameras. At 118.5°C a transformation takes place from the  $P2_12_12_1$  to a modulated  $Pn2_1a$  or  $Pnma$  polymorph. The modulation changes continuously, with decreasing intensities of X-ray satellites, from  $\sim 3.14c$  at 118.5°C toward  $\sim 2c$  at 190°C. At 191°C an unmodulated, high  $Pnma$  polymorph is formed. The lattice parameters are  $a = 7.705$ ,  $b = 10.400$ , and  $c = 6.720$  Å at room temperature. They expand only slightly in the low form;  $a$  and  $c$  contract in the intermediate form, and  $c$  contracts further in the high form. The unit cell volume remains nearly constant between 25 and 300°C. The observed phenomena result from redistributions of copper atoms over available structural sites and, at above  $\sim 135^\circ\text{C}$ , from the conversion of these atoms from a stationary to a mobile state.

### Introduction

$\text{Cu}_3\text{BiS}_3$  has been known since 1805 as the mineral *wittichenite* (1). A modern X-ray study at room temperature was performed by Nuffield (2).

The crystal structure at ambient conditions was determined by Matzat (3) and Kocman and Nuffield (4). According to the latter authors,  $\text{Cu}_3\text{BiS}_3$  has lattice parameters  $a = 7.723$  Å,  $b = 10.395$  Å and  $c = 6.716$  Å, space group  $P2_12_12_1$ ,  $Z = 4$ .

The preliminary results of our studies of the phase transformations in  $\text{Cu}_3\text{BiS}_3$  between 25 and 170°C were reported in Karup-Møller and Makovicky (5) and Makovicky and Skinner (6). From these X-ray data, the *solid electrolyte* character of  $\text{Cu}_3\text{BiS}_3$  was established, analogous to  $\text{Cu}_3\text{SbS}_3$  (loc. cit.). Our conclusions were

confirmed by the conductivity and tracer diffusion measurements of Lugakov *et al.* (7).

### Experimental

Most of the investigations were done with a Weissenberg camera equipped with a heating device and a high-precision cassette, described in detail in (8). Temperatures were calibrated by observing the melting points of several organic compounds mounted in a capillary in the same manner as for the observed crystal fragment of natural  $\text{Cu}_3\text{BiS}_3$ . Temperature differences between the sample and the thermocouple were found to be less than 2°C and the temperature stability during the majority of runs was better than 3°C. The errors in lattice parameters due to temperature instabil-

TABLE I  
LATTICE PARAMETERS  $a$  AND  $c$  OF  $\text{Cu}_3\text{BiS}_3$   
BETWEEN 25 AND 300°C FROM CALIBRATED  
WEISSENBERG PHOTOGRAPHS

$T$ (°C)	Hist. <sup>a</sup>	$a$ (Å)	$c$ (Å)
Low polymorph			
25.0	n	7.696	6.729
50.6	d	7.698	6.730
78.9	d	7.701	6.731
97.7	d	7.701	6.731
107.4	u	7.700	6.732
117.0	n	7.700	6.730
Intermediate polymorph			
117.0	n	7.658	6.733
121.6	d	7.663	6.729
133.6	<u>u</u>	7.659	6.728
134.0	<u>n</u>	7.661	6.722
134.2	d	7.660	6.723
134.9	n	7.661	6.721
135.5	d	7.659	6.728
136.2	<u>u</u>	7.660	6.722
137.9	<u>d</u>	7.659	6.725
139.0	<u>d</u>	7.657	6.728
142.0	<u>u</u>	7.660	6.722
145.2	<u>d</u>	7.656	6.727
147.5	<u>u</u>	7.649	6.728
148.9	u	7.655	6.726
155.6	u	7.652	6.722
157.1	n	7.653	6.728
157.6	u	7.652	6.724
177.1	n	7.642	6.722
186.0	u	7.643	6.723
High polymorph			
223.3	d	7.643	6.725
235.6	u	7.642	6.727
240.5	<u>u</u>	7.638	6.725
244.5	u	7.641	6.723
259.8	<u>u</u>	7.644	6.723
290.5	u	7.644	6.723

<sup>a</sup> Annealing history: n, u, d = temperature unchanged, raised, or lowered, respectively, before the run. Underlined indices indicate a substantial temperature change. Estimated standard deviation of lattice parameters is  $\leq 0.004$  Å.

ity remain far below the error limits of measurements of the X-ray films (Tables I and II).

The crystal fragment and X-ray powder are part of the wittichenite sample 1923.218

deposited at the Geological Museum, Copenhagen, with the locality given as the Daniel Mine, Wittichen, Germany. Natural material was used because it was proved to be stoichiometric (Gasparrini in (4)). For the synthetic material an increasing copper deficiency with increasing temperature of formation was reported by Buhlman (9) and Sugaki and Shima (10).

On each sheet of Weissenberg film, three to four exposures of the  $h0l$  section of the reciprocal lattice were taken at different temperatures, shifting the cassette by 3 mm after each exposure. The last exposure of each run was made at room temperature and served as an internal standard. The effective film radius was calculated separately for each  $h0l$  reflection and each wavelength, using the same reflection recorded at room temperature. About nine high-theta reflections split into the  $\alpha_1$  and  $\alpha_2$  components were used for the least-squares refinement of the  $a$  and  $c$  parameters at each temperature. The following  $a$ ,  $b$ , and  $c$  values for the room-temperature polymorph, used as the reference values for the above calculations, were obtained by least-squares refinement of the data from a quartz-calibrated room-temperature Guinier powder photograph:  $a = 7.696(5)$  Å,  $b = 10.364(12)$  Å, and  $c = 6.729(8)$  Å. The high accuracy and precision of the procedures used is reflected in Fig. 1 and Table I.

Since the  $h0l$  section of the reciprocal lattice is devoid of satellites, their positions had to be studied in the  $h1l$  section. A series of first level Weissenberg photographs was obtained at different temperatures and four distinct satellites together with adjacent main reflections were measured in detail for each exposure. For both the  $h0l$  and the  $h1l$  sections the exposures containing the closely overlapping reflections of two distinct polymorphs were not used in the ensuing linear regression calculations.

The third lattice parameter  $b$  and the

TABLE II  
SATELLITE POSITION IN THE INTERMEDIATE POLYMORPH OF  $\text{Cu}_3\text{BiS}_3$

Temperature (°C)	Previous annealing history <sup>a</sup>	Satellite position		Note
		$\Delta l$	$\sigma(\Delta l)$	
Temperature vs position studies				
120.6	d	0.323	0.002	2 polymorphs
120.5	n	0.323	0.004	2 polymorphs
123.8	u	0.320	0.002	
125.8	n	0.323	0.004	
127.4	n	0.323	0.001	
135.4	u	0.324	0.006	
136.3	n	0.326	0.002	
143.5	u	0.353	0.005	
153.8	u	0.382	0.003	
163.0	n	0.405	0.006	Satellites diffuse
Hysteresis studies				
140.8	d (2 days)	0.357	0.005	From 143.5°C
140.5	n (4 days)	0.355	0.003	
135.3	d (3 days)	0.357	0.004	
135.3	n (3 days)	0.353	0.001	
128.9	d (1 day)	0.356	0.007	Satellites smeared
124.1	d (1 day)	0.350	0.010	Satellites smeared
123.5	n (1 day)	0.346	0.004	
119.5	d (4 days)	0.337	0.002	2 polymorphs
124.5	$\overline{d}$	0.332	0.001	} Fast cooling from 220°C
137.9	$\overline{d}$	0.379	0.002	
137.8	n (3 days)	0.366	0.006	

<sup>a</sup> Annealing history: n = temperature unchanged, u = temperature raised, and d = temperature lowered before the run or before the equilibration time indicated.

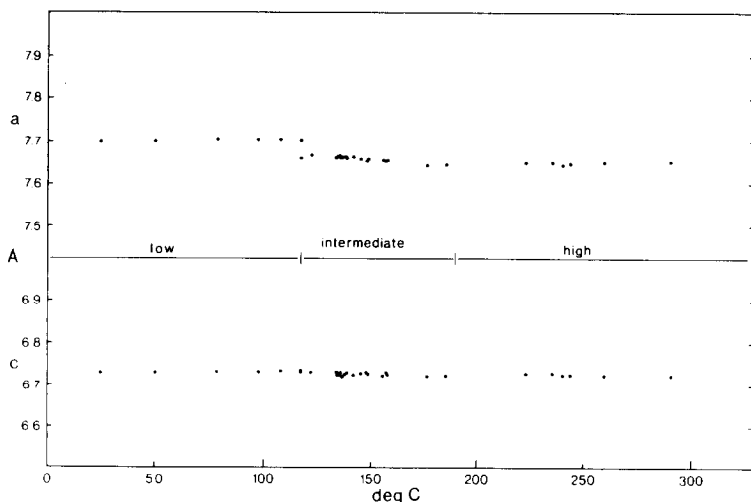


FIG. 1. The lattice parameters  $a$  and  $c$  of natural  $\text{Cu}_3\text{BiS}_3$  between 25 and 300°C from calibrated Weissenberg photographs.

unit-cell volumes of  $\text{Cu}_3\text{BiS}_3$  at temperatures from 18 to 350°C were obtained from powder diffraction photographs of synthetic  $\text{Cu}_3\text{BiS}_3$  synthesized from elements in an evacuated silica glass tube at 360°C. A high-temperature Nonius Guinier camera at the Institute for Mineral Industry of the Danish Technical University, Lyngby, was used. Temperatures and lattice parameters obtained in this way were recalibrated to obtain the best fit with the values obtained from the calibrated high-temperature Weissenberg photographs. The least-squares programs used in this work were written by lektor E. Leonardsen, University of Copenhagen.

### Polymorphism, Thermal Expansion, and Satellite Positions

Our data confirm the space group  $P2_12_12_1$  for  $\text{Cu}_3\text{BiS}_3$  between room temperature and the phase transformation at  $118.5 \pm 2^\circ\text{C}$ . No apparent changes in the X-ray intensities of the  $h0l$  and  $h1l$  reflections with temperature were observed in this range. Conspicuous is the small rate of thermal expansion of this *low polymorph*: the linear regression results for the Weissenberg recordings between 25 and 80°C are (in Å and °C).

$$a = 7.6935 + (9.300 \times 10^{-5})T$$

$$c = 6.7281 + (3.708 \times 10^{-5})T.$$

In the last 30°C below the phase transformation both lattice parameters remain virtually unchanged (Fig. 1), possibly as a precursor effect of the transformation, after which the lattice contracts.

The phase transformation is fast and, within our measurement uncertainty, occurs without hysteresis. The overall (i.e., subcell) space group of the *intermediate polymorph* is  $Pnma$  or  $Pn2_1a$ , but *satellites* appear on the reciprocal lattice rows parallel to  $c^*$ , indicating a modulation of the basic structure. The satellites are absent in

the  $h0l$  section of the reciprocal lattice but appear in both the  $h1l$  and  $h2l$  sections, positioned at  $+\Delta l$  and  $-\Delta l$  around the main (i.e., subcell) reflections in the regions of low and intermediate theta values. Although symmetrically positioned in the basic intervals of the reciprocal lattice, the members of any satellite pair exhibit generally widely different intensities. Satellite intensities preserve the symmetry of the basic weighted reciprocal lattice. Although the satellites are often associated with strong main reflections, they also occur at the systematically absent reflections  $0kl$  and  $hk0$  ( $k = 1, 2$ ). The satellites are generally sharply defined, with only faint traces of continuous streaks parallel to  $c^*$ .

In addition to the changes in systematic absences, the transformation from the low to the intermediate polymorph is marked by intensity changes in many of the main reflections. The interplay of the intensities of the main reflections and its surrounding satellites is exemplified by the 311 reflection; its intensity decreases and becomes commensurate with those of the adjacent satellites when they are strongest. This corresponds to the situation where  $\Delta l = \pm \frac{1}{3}$ .

As stated above, satellite positions and intensities in the reciprocal lattice are not fixed, but are *temperature-dependent*. For most of the temperatures the satellites are noncommensurate with the basic (sub)lattice. Careful measurements have revealed that they rearrange quickly with an increase in temperature and, within the accuracy of measurement, their position in the primitive orthorhombic reciprocal lattice (expressed as fractional  $\pm \Delta l$ ) is a linear function of temperature. Two linear  $\Delta l$  vs temperature relationships were observed. The first occurs between the phase transition at 118.5°C and the intersection with the higher-temperature linear trend at 135°C and  $\Delta l = \pm 0.326$ ; it reads as

$$\Delta l = 0.2680 + (4.270 \times 10^{-4})T \text{ (in } ^\circ\text{C)}.$$

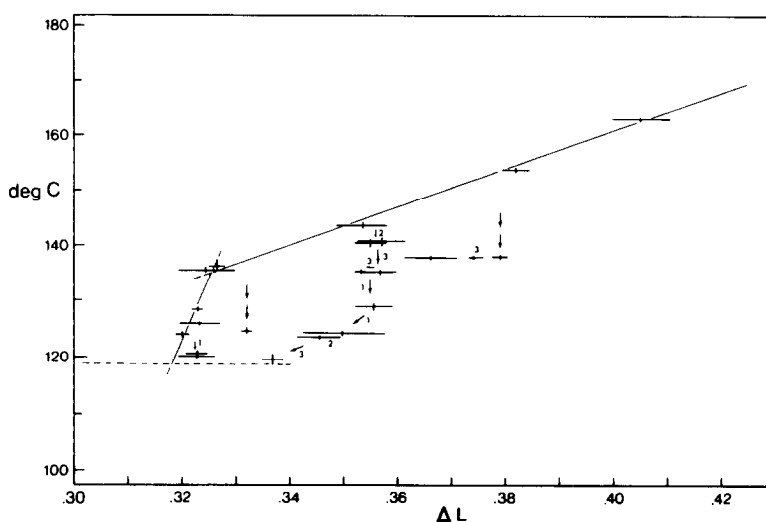


FIG. 2. Satellite position in the reciprocal lattice of the intermediate polymorph(s) of Cu<sub>3</sub>BiS<sub>3</sub>, expressed as fraction  $\Delta l$  of the integral  $c^*$  parameter. Linear dependence of  $\Delta l$  on rising temperature is indicated. Cooling cycles are indicated by arrows; time (in days) allowed for partial equilibration is indicated at the arrows.

The estimated value of  $\Delta l$  for the lower phase transformation temperature, i.e., the minimal  $\Delta l$  value, is then calculated as  $\pm 0.3185$ .

The upper  $\Delta l$  vs  $T$  relationship differs substantially from the lower one, intersecting it sharply and without a detectable transition interval. The regression equation

$$\Delta l = -0.0653 + (28.961 \times 10^{-4})T$$

suggests that  $\Delta l = \pm \frac{1}{3}$  ought to occur at 137.6°C, i.e., at the temperature (nearly) identical with the abrupt change in the  $\Delta l$  vs  $T$  function.  $\Delta l$  should become equal to  $\pm \frac{1}{2}$  at 195.2°C. However, the intensity of satellites decreases steadily with rising temperature in this interval, and the satellites, being somewhat diffuse, gradually fade out toward  $\sim 170^\circ\text{C}$ . Thus, the coalescence of satellites at  $\Delta l = \pm \frac{1}{2}$  could not be observed. The behavior of the satellites suggests that *two intermediate polymorphs* are present.

No systematic absences in addition to those occurring in the (sub)lattice were observed for the satellites. The few visible

satellites present in the lattice rows  $0kl$  ( $k = 1, 2$ ) can conform with (but do not prove) an  $n$ -glide plane parallel to (100) for a unit cell with  $c = 3c$  of low wittichenite, i.e., when  $\Delta l = \pm \frac{1}{3}$ . The same satellites displaced to  $\Delta l = \pm \frac{1}{2}$  will be entirely absent in the  $h0l$  section, thus defining a  $c$ -glide plane parallel to (010) of a unit cell with the  $c$  parameter equal to  $2c$  of low wittichenite. The observed symmetry of intensities is orthorhombic and the corresponding orthorhombic diffraction groups are  $Pn^*a$  and  $P2_1ca$ , respectively.

On cooling from equilibrium temperatures, or from the nonequilibrium situations below them, the satellites rearrange very sluggishly, requiring a number of days for the completion of the process. Variable  $\Delta l$  values obtained on abrupt cooling from 220°C confirm the observed hysteresis. The gradual, stepwise cooling evident in Fig. 2 shows that the rearrangement rate is primarily a function of supercooling below the equilibrium temperature for a given  $\Delta l$  value. The rate of change becomes more

appreciable with supercooling of about 15°C.

Above 170–190°C, with the gradual disappearance of satellites, the *intermediate polymorph(s)* change(s) into the *high polymorph* of Cu<sub>3</sub>BiS<sub>3</sub>. The space group is again *Pnma* (or *Pn2<sub>1</sub>a*) and the changes in intensities relative to those of the low polymorph persist in this modification. The high polymorph has been followed up to 290°C.

There is a clear difference in the thermal expansion behavior of the two polymorphs. In the modulated, *intermediate polymorph(s)* both the *a* and *c* parameters display a distinct *contraction* with rising temperature (Fig. 1). The contraction is a linear function of temperature (in Å and °C):

$$a = 7.7076 - (35.683 \times 10^{-5})T$$

$$c = 6.7320 - (4.909 \times 10^{-5})T.$$

Numerous measurements from slowly or quickly cooled/heated runs showed that the lattice parameters depend only on temperature and not on the previous thermal history of the sample which determined the position ( $\Delta l$ ) of the satellites. The marked contraction of the *a* parameter begins with its sizeable decrease by 0.042 Å during the low-to-intermediate phase transition (Fig. 1). The high, unmodulated phase preserves (up to 300°C) the slow contraction of the *c* axis with rising temperature:

$$c = 6.7353 - (4.412 \times 10^{-5})T$$

but it displays a reversed trend for the *a* axis, i.e., a small thermal expansion:

$$a = 7.6315 + (4.236 \times 10^{-5})T.$$

The intersection of the two trends for the *a* axis occurs at 190.8°C, yielding the lowest calculated *a* value of 7.640 Å. This temperature marks the upper stability limit for the intermediate phase.

The high-temperature Guinier data (Table III, Fig. 3) show that the constancy of the *c* parameter and the contraction of the *a*

TABLE III

LATTICE PARAMETERS OF Cu<sub>3</sub>BiS<sub>3</sub> BETWEEN 18 AND 350°C BY GUINIER METHOD<sup>a</sup>

<i>T</i> (°C)	<i>a</i> (Å)	<i>b</i> (Å)	<i>c</i> (Å)	<i>V</i> (Å <sup>3</sup> )
18	7.705	10.400	6.720	538.5
51.5	7.698	10.398	6.730	537.4
86	7.710	10.408	6.723	539.5
141.5	7.664	10.446	6.719	537.9
189	7.656	10.458	6.712	537.4
249.5	7.653	10.466	6.715	537.8
350	7.658	10.486	6.710	538.8

<sup>a</sup> Estimated standard deviation of lattice parameters is ±0.005 Å.

parameter for the phase transformation at 118.5°C are accompanied by an increase in the *b* parameter of approximately 0.04 Å. The *b* parameter, which averages 10.402 Å below the phase transformation, shows an appreciable thermal expansion above this transformation:

$$b = 10.4207 + (1.186 \times 10^{-4})T.$$

The calculated value of *b* is 10.443 Å for the intermediate phase at 118.5°C.

As a result of the interplay of the three lattice parameters the unit-cell volume displays no significant increase between 18 and 350°C (Fig. 3). It was noted that the satellites in the reciprocal lattice of the intermediate phase are too weak to show up in the complicated Guinier powder pattern of Cu<sub>3</sub>BiS<sub>3</sub>.

## Discussion

The crystal structure of the low polymorph of Cu<sub>3</sub>BiS<sub>3</sub>, as determined in Refs. (3) and (4), may be interpreted in terms of empty and Cu-occupied coordination triangles in the sulfur framework. Small shifts of sulfur atoms restore the ideal (i.e., high-temperature) symmetry of this framework, *Pnma*. A detailed study reveals that in such a framework there are six triangular coordi-

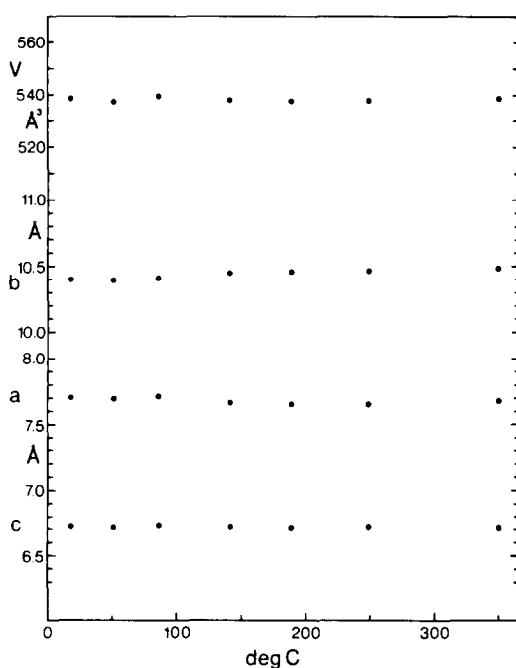


FIG. 3. Lattice parameters and unit cell volume of synthetic Cu<sub>3</sub>BiS<sub>3</sub> between 18 and 350°C from calibrated Guinier data.

nation sites available for the three copper atoms per formula unit, i.e., that there exists a potential for solid electrolyte behavior.

The space group *Pnma* (or *Pn2<sub>1</sub>a*) observed for the high polymorph implies the statistical occupation of all the available copper sites. A structure determination of the closely related high polymorph of Cu<sub>3</sub>SbS<sub>3</sub> ((6), not published in detail) confirms such a copper distribution for this phase. Furthermore, only a fraction of the Cu atoms was found to be localized in the triangular sites, the bulk of copper being mobile at this temperature. The conductivity measurements (7) confirm the solid electrolyte behavior of the high polymorph of Cu<sub>3</sub>BiS<sub>3</sub>.

The existence of the modulated intermediate phase(s) shows that the transition from the nonconducting low polymorph

with stationary copper atoms to the ion-conducting, high state is gradual and complicated. As the diffraction phenomena show, the intermediate states show a distribution of copper over the available sites (nearly) periodically modulated along the *d*(001) direction of the Cu<sub>3</sub>BiS<sub>3</sub> lattice. The *average periodicity* decreases continuously from  $\sim 3.14c$  to  $\sim 2.45c$  (and further towards  $2c$ ) with increasing temperature. The variation of satellite intensities suggests that the modulated structure is best organized for  $\Delta l = \pm \frac{1}{3}$ , i.e., when the large-scale periodicity is equal to  $3c_{\text{witt}}$ . Above this temperature, the satellites gradually fade out, indicating an increasing disorder in the Cu distribution throughout the structure. Simultaneously, the changes in the modulation pattern with temperature become much faster, as if the creation of short-periodical modulation arrangements were much alleviated above  $\sim 135^\circ\text{C}$ .

It is in this range, at  $\sim 150^\circ\text{C}$ , and not at the first-order transformation at  $118.5^\circ\text{C}$ , that the authors of Ref. (7) place the onset of ionic conductivity in Cu<sub>3</sub>BiS<sub>3</sub>. The spread of their data shows that our temperature value of  $135^\circ\text{C}$  and their value of  $150^\circ\text{C}$  may not be incompatible, and the changes in the satellite regime might reflect the suddenly increased mobility of a part of the copper atoms in Cu<sub>3</sub>BiS<sub>3</sub>.

The hysteresis observed in the rearrangements of the satellite, i.e., the modulation pattern with temperature suggests that the patterns of copper atoms can only rearrange by cooperative motion and not by individual independent jumps into free positions. This again is in agreement with the diffusion studies by (7).

Thus, from 25 to  $300^\circ\text{C}$  Cu<sub>3</sub>BiS<sub>3</sub> displays a series of phase transitions that involve both the reorganization of the distribution patterns of copper atoms and their conversion from a stationary to a mobile state. At  $118.5^\circ\text{C}$ , a first-order transition from the low, *P2<sub>1</sub>2<sub>1</sub>2<sub>1</sub>* polymorph to an intermediate,

modulated  $Pnma$  or  $Pn2_1a$  polymorph takes place. At 135°C, within the range of modulated structures, the onset of appreciable ionic conduction ought to occur, imparting somewhat different properties to the modulated structure above this temperature. Below or at 190°C the last traces of the continuously changing modulation pattern fade out and the high-temperature  $Pnma$  polymorph with good ionic conductivity persists up to the highest examined temperature of 290°C.

From morphological measurements on natural material, Borchert and Schroeder (11) defined the point group of wittichenite as  $2/m2/m2/m$  (although  $m2m$  is also compatible with their data). Their results seemed to contradict the X-ray data of Ref. (2) and of later investigators who found the space group of wittichenite to be  $P2_12_12_1$ , corresponding to the point group 222. The present study clarifies this apparent contradiction. The natural wittichenite undoubtedly crystallized above 120°C, and at room temperature the crystals represent pseudomorphs of low wittichenite ( $P2_12_12_1$ ) after the  $Pnma$  (or  $Pn2_1a$ ) modification.

The first-order transformation at 118.5°C is an interesting example of a nearly pressure-independent phase transformation which must be strongly stress-dependent in certain lattice directions. A silica glass tube filled with a massive coarse-grained wittichenite aggregate explodes on cooling and the aggregate shatters as a result of this transformation.

From the known structures of the low  $Cu_3BiS_3$  and high  $Cu_3SbS_3$  polymorphs it is possible to derive all the theoretical distribution patterns for Cu in the structures of  $Cu_3BiS_3$  and  $Cu_3SbS_3$ . Comparisons of the theoretical and observed data are in pro-

gress, together with electron microscope and further high-temperature structural studies of  $Cu_3BiS_3$ .  $Cu_3BiS_3$  is a member of a small but very interesting group of ternary solid electrolytes in the Cu-Sb-S and Cu-Bi-S systems which also includes  $Cu_3SbS_3$  and  $Cu_{12+x}Sb_{4+y}S_{13}$  ( $x = 0.3-2.0$ ,  $y = 0.0-0.3$ ) (5-8, 12, 13).

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