

A Triclinic Superlattice Structure for the Bended Sphalerite Unit Cell of the Compound Cu_2GeSe_3

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ABSTRACT. X-ray diffraction method has been used to determine the crystal structure of the ternary compound Cu_2GeSe_3 . A complete powder data is presented; and their analysis by Ito's method gives a Triclinic superlattice for the bended sphalerite unit cell of Cu_2GeSe_3 compound, with the lattice constants of $a = 3.9381 \text{ \AA}$, $b = 22.3796 \text{ \AA}$ and $c = 11.5626 \text{ \AA}$ and the angles are $\alpha = 90.039^\circ$, $\beta = 89.592^\circ$ and $\gamma = 89.945^\circ$.

The ternary compounds belonging to the $\text{I}_2\text{-IV-VI}_3$ type of the two cation diamond-like systems are crystallochemical analogues of group IV elements having tetrahedral binding (Averkieva *et al.* 1965) (Hahn 1959) and (Goryunova and Sokolova 1960) reported that the compound Cu_2GeSe_3 , which is a semiconductor chalcongenide, has a ZnS type structure with a tetragonal cell. Then the same structure was reported by (Palatnik *et al.* 1961), whereas, (Parthe and Garin 1971), reported that Cu_2GeSe_3 crystallizes in a slightly distorted sphalerite-type of structure with Se atoms occupying S sites, and Cu and Ge atoms sharing Zn sites in ordered fashion. It was found that this compound can dissolve Ge up to 14% and changes its lattice to cubic when excess Ge distributes between cation and anion sites equally. (Sharma and Singh 1974) who have investigated the system Cu-Ge-Se in the vicinity

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in the vicinity of the compound Cu_2GeSe_3 reported a disordered tetragonal unit cell with $a = 5.591 \text{ \AA}$ and $c = 5.485 \text{ \AA}$. They found that the unit cell symmetry is very sensitive to Ge concentration. Thus, a slight deficiency of Ge lowers the cell symmetry to monoclinic, while an excess of Ge raises it to cubic. The composition $\text{Cu}_2\text{Ge} 0.85 \text{ Se}_3$ has a monoclinic unit cell with $a = 5.512 \text{ \AA}$, $b = 5.598 \text{ \AA}$, $c = 5.486 \text{ \AA}$ and $\beta = 89.7^\circ$, but the composition $\text{Cu}_2\text{Ge} 1.55 \text{ Se}_3$ was cubic with $a = 5.569 \text{ \AA}$, however, (Suri *et al.* 1982) reported for the latter composition an orthorhombic superlattice of the face centered cubic cell with lattice constants $a = 3.932 \text{ \AA}$, $b = 22.242 \text{ \AA}$ and $c = 11.769 \text{ \AA}$.

A cubic structure was reported for solid solution based on this composition with binary and ternary compounds (Goryunova *et al.* 1965). She reported a sphalerite structure for 20% Cu_2GeSe_3 + 80% GaAs. Cubic structure was also reported when Ge is substituted by Sn for a $\text{Cu}_2\text{Ge}(x)\text{Sn}(1-x)\text{Se}_3$ when $x < 0.5$, which becomes tetragonal for $x > 0.5$ (Goryunova *et al.* 1965). However, a cubic phase was the result of the whole solid solution which exists between this compound Cu_2GeSe_3 and the ternary CuGe_2P_3 from the group I-IV2-V3 in the range $0.1 < x < 0.25$ when X is the fraction of CuGe_2P_3 (Omar 1990).

Sample Preparation

10 gm mostly single crystal ingots of the compound Cu_2GeSe_3 were prepared from 99.999% pure elements with selenium is a 5% excess to allow for the vapour phase. Two main problems had to be overcome, preventing an excess pressure of selenium building up during the reaction of the elements, and achieving a high temperature gradient at the melt-crystal interface during growth. To do this, a two zone furnace with an airgap was used. However, details can be found elsewhere (Omar 1988). Good quality ingots were obtained for all specimens and they were mostly 50-90% single crystals.

X-ray Powder Photography

X-ray powder patterns were taken in a 114.6 mm diameter Debye S'cherie camera using CuK_α radiation. Powder patterns taken from samples of polycrystalline and single crystal ingots were found to be identical in all respects.

The powder patterns were characterized by a set of sharp strong reflections along with a set of weak lines up to the highest angle. By using Ito's method (Ito 1950), the strong lines were indexed in sphalerites slightly distorted in their dimensions and a small deviation in their angles α , β and γ , while the weak lines

were indexed in superlattice for sphalerite unit cell mentioned above with lattice constant $a = 3.9381 \text{ \AA}$, $b = 22.3795 \text{ \AA}$, $c = 11.5626 \text{ \AA}$, $\alpha = 90.039^\circ$, $\beta = 89.592^\circ$ and $\gamma = 89.945^\circ$. The reflections used to calculate these constants were from (200, 220, 331, 422, 444 and 551) planes. However, the same method has been used successfully for analysis of Cu_2GeS_3 data as well (Omar *et al.* 1989).

The group of lines (311, 331, 620 and 622) were found to split into two components, whereas lines (220 and 531) split into three components. These new forms of lines indicate that the sphalerite shape of the cell should be deformed to a new shape of triclinic-like form as indexed in Table 1. However, the two new lines 022 and 202 as well as 620 and 602 gave the same reflections while the lines 620 and 622 were indexed only by α_2 reflections. If the lattice constants of the distorted sphalerite structure are a_0 , b_0 and c_0 , then its superlattice cell constants are related to a_0 , b_0 and c_0 by the relation $a = a_0\sqrt{2}$, $b = 4b_0$ and $c = 3c_0/\sqrt{2}$ (Omar *et al.* 1989).

Table (1) contains the powder data obtained from the Debye S'cherie camera and a part from visual intensity estimates.

Analysis

The relationship between the line intensities in Debye powder patterns and the number of atoms per cell unit with dimensions given in Table (1) indicates clearly that the atomic distribution in this unit cell is completely analogous to that in Zinc blende structure with the Copper and Germanium atoms in ordered positions.

The 'super structure' lines are found to be in low intensity as shown in Table (1), which is due to the small difference between the atomic factors for Copper and Germanium atoms, since their electron numbers are close. The same intensities were found for the superlattice lines of the compound Cu_2GeS_3 , however, the lines (200, 222, 420....) which belong to ZnS structure, became of very low or zero intensity for Cu_2GeSe_3 compared to that of Cu_2GeS_3 lines (Omar *et al.* 1989). This is probably due to the size similarity of the Se atoms to that of Ge and Cu in the crystal lattice, while S atoms in Cu_2GeS_3 are of a different size.

It has been reported that the concentration of group IV atom in the ternary Cu_2GeSe_3 greatly effects the symmetry of the lattice, (Parthe and Garin 1971). However, it is also found that the structure form of Cu_2GeSe_3 is very sensitive to Ge percentage in the compound.

This work indicates that the replacement of S by Se will create a distortion in

two dimensions rather than one which reported earlier (Averkiewa *et al.* 1965) and (Parthe and Garin 1971); and makes the angles α , β and γ slightly bended. These two new effects changes the shape of the unit cell of the compound Cu_2GeSe_3 to triclinic-like symmetry.

It is interesting to explain the new deformation of the sphalerite lattice of Cu_2GeSe_3 employing the relative ionicity of the cation-anion bonds in Cu-Se and Ge-Se binary systems. But, since the electro-negativities of Cu and Ge are not far apart, the difference in the relative ionicity between the two binary Cu-Se and Ge-Se bonds is very small. Generally this should make the structure remain in its isotropic shape. This was observed in Cu_2GeS_3 , which was in the form of the orthorhombic super-lattice of F.C.C. unit cell (Omar *et al.* 1989), whereas this was not the case for the compound Cu_2GeSe_3 .

It has been reported that the interaction between Ge-Se is stronger than that of Cu-Se (Sharma and Singh 1974). The latter makes the bonds more distorted in the directions having Ge atoms than those having Cu atoms. The difference therefore, in the lattice spacing of a , b and c as well as the angles α , β and γ indicates uneven distribution of the concentration of these bonds corresponding to the indicated lattices and angles.

However, work is in progress to explore the atomic distribution in the compounds Cu_2GeS_3 and Cu_2GeSe_3 which may help in the explanation of the structure deformation of the compound Cu_2GeSe_3 .

Conclusion

The results of the present investigation of the structure determination of the ternary compound Cu_2GeSe_3 confirms that:

1. The existance of a Triclinic like shape for the face-centered diamond like structure.
2. The existance of a superlattice structure for the structure type mentioned above in this ternary compound.

Table 1. Powder Data for Cu_2GeSe_3

d (A°) obs.	I \ I ₀	hkl ^x	hkl [*]	d (A°) calc.
	00		040, 012 (S)	5.5965
4.4682	01		050 (S)	4.4759
3.9377	01		100 (S)	3.9381
3.2018	100	111	070	3.1971
2.8915	01		004 (S)	2.8906
2.7841	04	200	080, 024	2.7975
2.5140	01		082 (S)	2.5175
2.2116	02		035 (S)	2.2083
1.9689	60	220	200, 125	1.9691
1.9489	85	022, 202	110 ₀	1.9465
1.6780	50	311	0123, 234	1.6783
1.6563	35	113	007	1.6563
1.6016	02	222	0140	1.6025
1.3921	12	400	265	1.3921
1.3682	08		226 (S)	1.3682
1.2758	09	331	302	1.2805
1.2665	16	133	039	1.1365
1.1357	23	422	325	1.1365
1.0723	11	511	229, 312 ₀	1.0717
1.0659	07		346, 239, 0210 (S)	1.0659
1.0549	07		356, 312 ₂ (S)	1.0552
0.9844	04		400, 0811 (S)	0.9845
0.9765	09	404	421	0.9774
0.9426	05	531	0512	0.9418
0.9387	09	513	471, 462	0.9382
0.9304	10	315	378	0.9304
0.8824	05		0313, 379 (S)	0.8831
0.8805	07	620, 602	2811, 465	0.8805
0.8678	08		3110, 1013 (S)	0.8677
0.8483	07	533	0813	0.8474
0.8422	06	262	3202, 1260	0.8429
0.8401	011	622	0263	0.8400
0.8012	09	444	458	0.8011
0.7821	11	551	323 ₀	0.7821
0.7786	02		522, 541 (S)	0.7787
0.7753	06		3212 (S)	0.7754

+ The superlattice lines are denoted by the letter(S).

x $a_0 = 5.5693 \text{ \AA}$, $b_0 = 5.5949 \text{ \AA}$, $c_0 = 5.4507 \text{ \AA}$.

$\alpha = 90.039^\circ$, $\beta = 89.592^\circ$, $\gamma = 89.945^\circ$

* The superlattice for the deformed sphalerite unit cell of a triclinic-like shape.

$a = 3.9381 \text{ \AA}$, $b = 22.3796 \text{ \AA}$ and $c = 11.5626 \text{ \AA}$

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التركيب البلوري الثلاثي الميل المثالية لوحدية بلورة السفيلرايت المتتوي للمركب Cu_2GeSe_3

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استخدمت طريقة حيود أشعة إكس لإيجاد التركيب البلوري للمركب الثلاثي Cu_2GeSe_3 . كما وقدمت بيانات كاملة لتنتائج أشعة إكس للمسحوق وأعطت تحليلات هذه البيانات باستخدام طريقة ايتو تركيب بلوري مثالي لثلاثي الميل لوحدية خلية للسفيلرايت المتتوي للمركب Cu_2GeSe_3 ، مع ثوابت البعد البؤري $a=3.9381\text{Å}$ و $b=22.3796\text{Å}$ ، $c=11.5626\text{Å}$ ، والزوايا هما $\alpha=90.039^\circ$ ، $\beta=89.592^\circ$ وكذلك $\gamma=89.945^\circ$.

العنوان الحالي :

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