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Stability of the Tetrahedral Phase in Cu–Ge–Se System

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The Cu–Ge–Se system has been investigated in the vicinity of the compound $Cu_2Ge Se_3$, which is known to have a disordered tetragonal unit cell with $a = 5.591$ Å and $c = 5.485$ Å. The unit cell symmetry has been found to be very sensitive to Ge concentration. A slight deficiency of Ge lowers the cell symmetry to monoclinic, while an excess of Ge raises it to cubic. The composition $Cu_2Ge_{0.85}Se_3$ has a monoclinic unit cell with $a = 5.512$ Å, $b = 5.598$ Å, $c = 5.486$ Å, and $\beta = 89.7°$, while the composition $Cu_2Ge_{1.55}Se_3$ is cubic with $a = 5.569$ Å.

The results of this investigation indicate that the structure and stability of the $A_2{}^{I}B^{IV}C_3^{VI}$ group of compounds (subscripts denote number of atoms while superscripts denote the group in the periodic table) depend on the valence state of the participating group IV elements, which are known to exhibit variable valency (tetravalency and divalency). The tetravalent state favors more distorted but more stable phase while divalent state favors less distorted and less stable phase.

Introduction

The compounds represented by the general formula $A_2{}^{I}B^{IV}C_3^{VI}$ (subscripts denote the number of atoms and superscripts the group number in the periodic table) are ternary crystallochemical analogs of group IV elements having tetrahedral binding (*1*). The compounds with A = Cu, Ag, B = Si, Ge, Sn, and C = S, Se, Te, are known to crystallize in ZnS-type structures (wurtzite or sphalerite) with group VI atoms occupying S sites and group I and IV atoms sharing Zn sites (*2*). There is a possibility of ordering among the group I and IV atoms occupying Zn sites, and it has actually been confirmed in some cases (*2, 3*).

The disordered unit cell (group I and IV atoms not distinguished) for the compounds containing Si as the group IV elements is hexagonal (wurtzite type), for Sn compounds it is cubic (sphalerite type), and for Ge compounds the unit cell is tetragonal with *c*/*a* ratio slightly less than unity. It has been reported that Ge compounds, particularly Cu_2GeS_3 and Cu_2GeSe_3, dissolve substantial amount of Ge (up to 14%) and the unit cell becomes cubic in the process (*2*). A compound $Cu_2Ge_2Se_3$ with a cubic cell has also been reported (*4*). In the present work on Cu_2GeSe_3 we found that some deficiency of Ge is also tolerated in the overall tetrahedral arrangement of atoms, only the unit cell gets distorted and adopts monoclinic symmetry. In the composition containing excess of Ge it is shown that the excess Ge atoms go substitutionally into the Cu_2GeSe_3 lattice.

We came across the Ge-deficient monoclinic phase while attempting to grow single crystals of Cu_2GeSe_3 by the solution growth technique using molten Se as solvent. The technique did not yield single crystals; instead, a two-phase material was precipitated out. The two phases were found to have vastly different microhardness numbers, one nearer to that of Cu_2GeSe_3, the other nearer to Se. The X-ray powder pattern of this double-phase material resembled that of Cu_2GeSe_3 but showed slight line splitting, indicating lowering of unit cell symmetry which was subsequently found to be monoclinic. The other phase did not give any diffraction pattern.

Since the starting composition contained a large excess of Se, it was thought in the begin-

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ning that some Se excess is responsible for lowering the cell symmetry. We therefore investigated several compositions with the formula $Cu_2GeSe_{(3+x)}$, x varying from 0 to 3. At $x = 2$, the material gave the X-ray pattern belonging to the monoclinic unit cell, though microstructure showed two phases. At this stage it was decided to carry out electron microprobe analysis to determine the composition of this monoclinic phase. It revealed some deficiency of Ge as compared to normal Cu_2GeSe_3. We then investigated few compositions with the formula $Cu_2Ge_{1-x}Se_3$, x varying from 0 to 0.5. At $x = 0.15$ we could get a single-phase material which produced the same monoclinic X-ray powder pattern.

The results of the present investigation answer some of the important questions regarding the stability and lattice distortion of this group of compounds.

The experimental techniques employed were thermal analysis, microhardness testing, and X-ray powder diffraction. The details of techniques and results obtained are discussed below.

Experimental

All the materials were synthesized by melting the stoichiometric amounts of constituent elements (5 *N* grade) in sealed silica tubes evacuated to 10^{-4} Torr. A continuous vibration mixing arrangement was used to homogenize the melt. The furnace was then switched off and the melt allowed to cool. A Pt–Pt 13% Rh thermocouple was used to record the temperature of the melt while cooling. This thermocouple was kept in a narrow-bore thin-walled quartz tube with one end (carrying thermocouple tip) closed and surrounded by the melt. The thermocouple output was fed to a Honeywell recorder for obtaining cooling curves. The arrangement proved to be sensitive for recording thermal arrests up to 400°C only. Below this the rate of temperature fall became very slow, and thermal arrests could not be resolved.

The cooled ingots were cut and polished for microscopic examination. Microhardness tests were carried out on a PMT-3 Soviet-made instrument. The indentations were made with a knoop diamond pyramid with an apex angle of 136° under a weight of 50 g.

All X-ray powder patterns were taken in a 114.6-mm-diam Debye–Scherrer camera using CuK_α radiation.

Results

1. $Cu_2GeSe_{(3+x)}$ *System*

Although the investigation of the ternary phase diagram as such was not intended in the present work, some data on thermal analysis obtained in the course of investigation are also presented.

The cooling curves obtained for the compositions $Cu_2GeSe_{(3+x)}$ (x varying from 0 to 3) contained a sharp arrest followed by another arrest extending over a temperature range of ~15°C. The upper smooth curve in Fig. 1 gives the temperatures for sharp arrests while the shaded area shows the second arrest.

A microscopic examination of the cooled ingot revealed the presence of two phases for $x > 0.5$. The amount of the second phase increased with increasing x. The microhardness number of the main phase was always 340 ± 20 kg/mm². For the other phase it varied between 28 and 100 kg/mm². For comparison's sake it may be mentioned that the microhardness numbers for pure Se and Cu_2GeSe_3 are 28 and 327 kg/mm², respectively.

Figure 1 indicates a eutectic type of reaction in this system with Cu_2GeSe_6 as the eutectic composition and 650°C as the eutectic temperature. A micrograph for the composition Cu_2GeSe_6, shown in Fig. 2, is also typical for a eutectic system. Since the melting point for pure Se is 220°C, which is lower than the apparent eutectic temperature 650°C, another intermediate phase should be forming.

The X-ray powder pattern for $x \leqslant 0.5$ did not show any change and gave the same lattice constants as for Cu_2GeSe_3, that is, $a = 5.591$ Å and $c = 5.485$ Å.[1] For values of x between

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[1] This cell comes out to be a face-centered one. Although no face-centered cell is recognized in tetragonal system, because a smaller body-centered cell is available, we have used the face-centered cell in our further discussion because of its resemblance to a cubic cell.

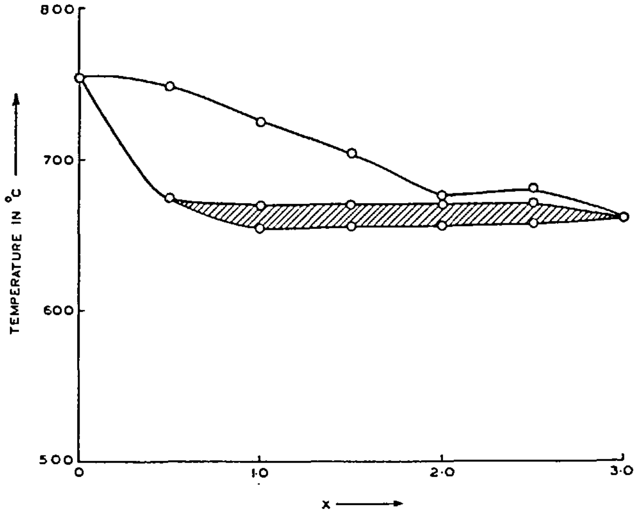

FIG. 1. Thermal arrests in $Cu_2GeSe_{(3+x)}$ system.

0.5 and 1.5, a slight variation in the relative line intensities could be observed, but the cell remained tetragonal with the same lattice constants. For x between 2 and 3 the pattern showed considerable line splitting as compared to the pattern of Cu_2GeSe_3, though there was close resemblance between the two patterns. This shows that the unit cell has been slightly distorted with slight change in the lattice parameters.

The (400) group of lines which split into two components (400 or 040 and 004) in the tetragonal Cu_2GeSe_3, now split into three components (400, 040, and 004). This indicated that the cell has become either orthorhombic or monoclinic. Another reflection (444) which was a single line in tetragonal system, and should have remained single in an orthorhombic system also, was found to be split into two components (444 and $44\bar{4}$). This fixed the cell symmetry as monoclinic. The interaxial angle was also calculated using these (444) and ($44\bar{4}$) reflections and found to be 89.7°. A systematic indexing could then be done for all lines on the basis of the following parameters: $a = 5.512$ Å, $b = 5.598$ Å, $c = 5.486$ Å, $\beta = 89.7$°C. Table I gives the observed and calculated values of interplaner spacings for the monoclinic phase.

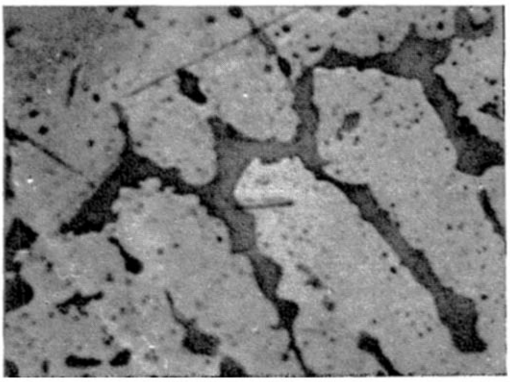

FIG. 2. A micrograph for the composition Cu_2GeSe_6 (×175).

The second phase present did not give rise to any X-ray pattern as all the lines present could be indexed on the above-mentioned monoclinic cell.

An electron microprobe analysis was carried out to determine the composition of the two phases. The main phase was found to be slightly deficient in Ge as compared to the normal Cu_2GeSe_3 compound. The other phase with lower hardness number burnt under the electron beam of the microprobe analyzer. The beam could not be very well focused on this phase because of the space charge effect. It was therefore concluded that this phase has a very high resistivity and,

TABLE I

THE INTERPLANAR SPACINGS (OBSERVED AND CALCULATED FOR THE MONOCLINIC PHASE

S N°	*h k l*	d_{calc}	d_{obs}	Intensity
1	1 1 1	3.210	3.194	vs
2	1 1 $\bar{1}$	3.187		
3	2 2 0	1.9639	1.964	s
4	0 2 2	1.9591	1.963	m
5	2 0 2	1.9499		
6	2 0 $\bar{2}$	1.9386	1.939	m
7	1 3 1	1.6832	1.6836	m
8	1 3 $\bar{1}$	1.6814		
9	3 1 1	1.6663		
10	3 1 $\bar{1}$	1.6610	1.6626	m$^+$
11	1 1 3	1.6604		
12	1 1 $\bar{3}$	1.6551		
13	0 4 0	1.3995	1.3982	m$^-$
14	4 0 0	1.3781	1.3786	m$^-$
15	0 0 4	1.3715	1.3722	w
16	3 3 1	1.2747	1.2737	m$^+$
17	3 3 $\bar{1}$	1.2723		
18	1 3 3	1.2720		
19	1 3 $\bar{3}$	1.2697	1.2693	m$^+$
20	3 1 3	1.2662		
21	3 1 $\bar{3}$	1.2593	1.2599	w
22	2 4 2	1.1370	1.1361	m
23	2 4 $\bar{2}$	1.1347		
24	4 2 2	1.1293	1.1286	m
25	2 2 4	1.1266		
26	4 2 $\bar{2}$	1.1250	1.1250	m
27	2 2 $\bar{4}$	1.1222		
28	1 5 1	1.07612	1.0763	m$^-$
29	1 5 $\bar{1}$	1.07564		
30	5 1 1	1.06240	1.0627	m$^-$
31	5 1 $\bar{1}$	1.06010		
32	1 1 5	1.05784	1.0584	m$^-$
33	1 1 $\bar{5}$	1.05558		
34	4 4 0	0.98193	0.98210	m$^-$
35	0 4 4	0.97952	0.98015	m$^-$
36	4 0 4	0.97493		
37	4 0 $\bar{4}$	0.96929		

TABLE I (CONT.)

S N°	*h k l*	d_{calc}	d_{obs}	Intensity
38	3 5 1	0.94237		
39	3 5 $\bar{1}$	0.94140	0.94165	m
40	1 5 3	0.94130		
41	1 5 $\bar{3}$	0.94034		
42	5 3 1	0.93606		
43	5 3 $\bar{1}$	0.93449		
44	5 1 3	0.93332	0.93385	m
45	1 3 5	0.93294		
46	1 3 $\bar{5}$	0.93139	0.93200	m
47	3 1 5	0.93126		
48	5 1 3	0.92868	0.92935	w
49	3 1 $\bar{5}$	0.92664	0.92705	w
50	2 6 0	0.88373	0.88365	m$^+$
51	0 6 2	0.88329		
52	6 2 0	0.87290	0.87290	m
53	6 0 2	0.87268		
54	6 0 $\bar{2}$	0.86963	0.86980	w
55	2 0 6	0.86930		
56	0 2 6	0.86910		
57	2 0 $\bar{6}$	0.86630		
58	3 5 3	0.84831	0.84854	w
59	3 5 $\bar{3}$	0.84621	0.84654	vw
60	5 3 3	0.84417	0.84434	vw
61	3 3 5	0.84264		
62	5 3 $\bar{3}$	0.84073	0.84026	vw
63	3 3 $\bar{5}$	0.83922	0.8396	vw
64	4 4 4	0.79995	0.80016	m
65	4 4 $\bar{4}$	0.79683	0.79695	m
66	1 7 1	0.78340	0.78341	m$^-$
67	1 7 $\bar{1}$	0.78322		
68	5 5 1	0.77806	0.77803	m$^-$
69	5 5 $\bar{1}$	0.77716	0.77720	w
70	1 5 5	0.77626	0.77643	m$^-$
71	1 5 $\bar{5}$	0.77537	0.77536	w
72	7 1 1	0.77265	0.77265	m
73	5 1 5	0.77248		
74	7 1 $\bar{1}$	0.77142		
75	5 1 $\bar{5}$	0.76810		

since it did not give any X-ray pattern, should be amorphous also.

The main phase, as mentioned above, was deficient in Ge and, since the initial composition had a large excess of Se, this amorphous and high-resistivity phase could be a Ge–Se glass. Its hardness was more than that of pure Se. Some glasses have been reported in Ge–Se system with a large percentage of Se (5). Just to check whether slight addition of Ge increases the hardness of Se, we prepared a composition $GeSe_{10}$. The melt was quenched from 700°C after continuous heating and shaking for 6 hr. We got a single-phase amorphous material with a hardness number 46 kg/mm^2. It may be mentioned that slow cooling of the melt did not give a single phase; instead, $GeSe_2$ compound was precipitated out. Thus the second phase in the $Cu_2GeSe_{(3+x)}$ system, although it could not be analyzed by the electron microprobe analyzer, appears to be a Ge–Se glass.

2. $Cu_2Ge_{(1-x)}Se_3$ *System*

Taking the clue from the microprobe analysis that the monoclinic phase is deficient in Ge, we synthesized several compositions with formula $Cu_2Ge_{(1-x)}Se_3$, with x varying from 0 to 0.5. Figure 3 shows the first sharp thermal arrests for various values of x. The corresponding microhardness numbers are shown in Fig. 4. A microscopic examination revealed the presence of two phases for $x \geqslant 0.2$. For $x < 0.2$, a single phase was obtained. At $x = 0.15$, microhardness shows a maximum (Fig. 4), while the melting point-vs-x curve (Fig. 3) changes slope. We then synthesized a composition with $x = 0.15$, that is, with the formula $Cu_2Ge_{0.85}Se_3$. It was a single phase material and gave the same monoclinic X-ray pattern as mentioned earlier.

It is thus seen that addition of excess Se extracts some Ge out of the normal compound Cu_2GeSe_3, indicating a strong interaction in the Ge–Se system as compared to the Cu–Se system. Another observation in this connection may also be mentioned. Several times, while synthesizing Cu_2GeSe_3 we found a small amount of a yellow deposit near the tip of the ampoule which was probably left in a colder zone. If the ampoule was carefully kept in a constant temperature zone no such deposit formed. X-ray diffraction and spectroscopic analysis revealed the composition of this deposit to be $GeSe_2$. To check whether this is one of the normal dissociation products of Cu_2GeSe_3, we sealed a small amount of the compound in an evacuated quartz capsule whose one end carrying the material was kept at 800°C and the other at room temperature. After 6 hr, almost half of the material was transported to the colder zone and deposited there as $GeSe_2$. In an attempt to grow single crystals of Cu_2GeSe_3 by vapor transport technique using Cl as transporting agent, we got crystals of $GeSe_2$ only. Further consequences of this observation will be examined in subsequent discussion.

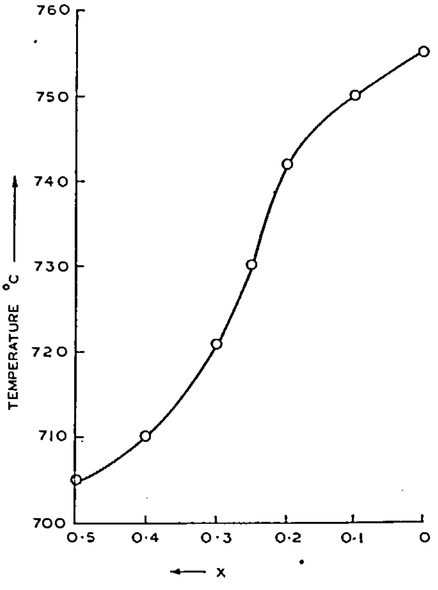

FIG. 3. Melting point vs composition for $Cu_2Ge_{(1-x)}Se_3$ system.

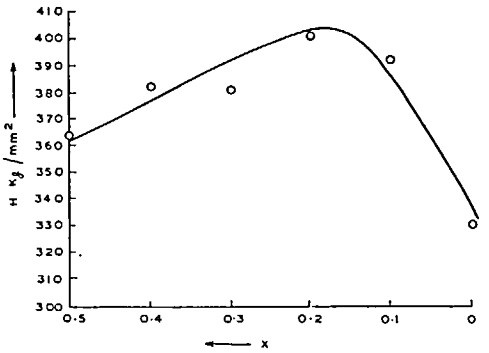

FIG. 4. Microhardness vs composition for $Cu_2Ge_{(1-x)}Se_3$ system.

3. $Cu_2Ge_{(1+x)}Se_3$ *System*

Several compositions with x varying from from 0 to 2 were synthesized. The melting point fell sharply with increasing x up to $x = 0.6$ where it was 545°C. Thereafter, it increased with increasing x, and at $x = 2$ it was 773°C. For $x \geqslant 0.6$ the material showed two phases indicating a eutectic type of reaction in Cu_2GeSe_3–Ge system. At $x = 0.55$ a single-phase material with cubic cell, $a = 5.568$ Å, was obtained. For $x < 0.5$, though the material is single phase, the unit cell seems to be less symmetric (probably orthorhombic) than that of Cu_2GeSe_3. Detailed results of unit cell dimensions and symmetry are being finalized and will be reported shortly.

To understand how excess Ge removes tetragonal distortion, it seemed useful to have an idea about the sites it occupies in the lattice. The unit cell volumes for $Cu_2Ge_{1.55}Se_3$ and Cu_2GeSe_3 are 172 Å and 171 $Å^3$, respectively, and bulk densities 5.46 and 5.48 g/cc, respectively. It can easily be seen that the unit cell mass has not changed. If it is remembered that the mass of Ge atom and the average mass per atom for Cu_2GeSe_3 compound are almost the same, it is apparent that $Cu_2Ge_{1.55}$ Se_3 is only a substitutional solid solution. As mentioned in the beginning, there are two lattice sites in Cu_2GeSe_3, one occupied by Se atoms (anions) the other shared by Cu and Ge atoms (cations). The structure of pure Ge is also similar, with the difference that both the sites are now occupied by identical atoms. The cell constants are also not much different (for Ge, $a = 5.6576$ Å). Therefore, if excess Ge goes substitutionally into the Cu_2GeSe_3 lattice, it must be replacing atoms on both sites with equal probability. Final confirmation of this conclusion can be obtained by examining the relative line intensities of the X-ray powder pattern of $Cu_2Ge_{1.55}Se_3$. This intensity distribution is typical for a diamond lattice. The atomic scattering factors for Cu, Ge, and Se atoms are very close, and hence the intensity pattern in $Cu_2Ge_{1.55}Se_3$ should be identical to the one found in Ge. This is exactly so. Thus in $Cu_2Ge_{1.55}Se_3$ also the atomic arrangement remains tetrahedral.

An observation made while synthesizing excess Ge compounds may also be mentioned. In the colder part of the ampoule we sometimes got few small shinning crystals greyish white in color. On spectroscopic and X-ray diffraction analysis they were identified as GeSe crystals. On decomposition in an evacuated and sealed silica tube $Cu_2Ge_{1.55}Se_3$ gave GeSe at the colder end of the capsule. As mentioned earlier, Cu_2GeSe_3 gave $GeSe_2$ under similar circumstances.

In case of the compound $Cu_2Ge_{0.85}Se_3$ (Ge deficit monoclinic phase), the cooled ingot contained large number of holes and cracks. Its density and, therefore, the unit cell mass could not be determined with sufficient accuracy. However, from the similarity in the three powder patterns it is clear that the atomic coordination is similar, that is, tetrahedral, only the cell symmetry is changing.

Discussion

Gibbs composition triangle (Fig. 5) is helpful in discussing the results of the present investigation. The two straight lines represent the following two conditions for the formation of tetrahedral diamondlike phases (*6*).

(i) The average number of valence electrons should be four.

(ii) All the participating elements should exhibit their normal valency, that is, equal to their group number in the periodic table.

The first condition ensures correct number of electrons for sp^3 hybridization necessary for tetrahedral coordination. It is satisfied along the tie-line Ge–Cu_2Se_3. The Ge excess and deficit phases lie on this line. The stability of tetrahedral coordination in these phases is possible because the average number of electrons remains four.

The second condition ensures bond saturation, a necessary condition for semiconduct-

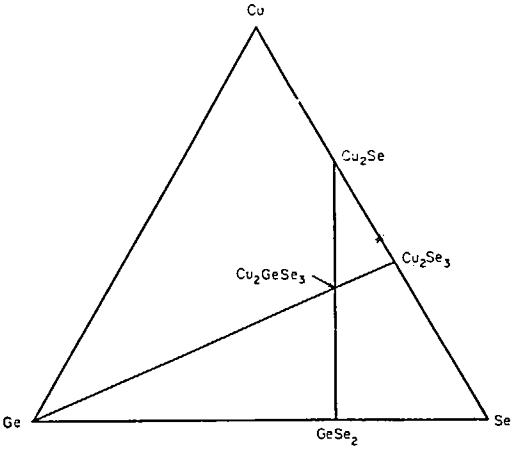

FIG. 5. Composition triangle depicting the two conditions for the formation of ternary tetrahedral compound in Cu–Ge–Se system.

ivity (*7*). It is satisfied along the tie line Cu_2Se–$GeSe_2$. The point of intersection of these two lines corresponds to the composition Cu_2GeSe_3, which is known to be a tetrahedral semiconductor.

It was pointed out by Goryunova (*8*) that the ternary compounds are stable only when there is chemical interaction in the two basic binary systems (cation–anion systems). According to her, the formation of a chemical compound in the basic system indicates the existence of chemical interaction while formation of a solid solution or a eutectic indicates its absence. She also pointed out that this is a necessary but not sufficient condition for the actual existence of the ternary compound. However, the way this interaction influences the stability and structure of the ternary compound is not clear. The results of the present investigation on Cu–Ge–Se systems throw some light on this aspect of the question.

Two basic binary systems, viz., Cu–Se and Ge–Se, can be identified for discussion. It was mentioned in the beginning that the ternary compounds containing Si are hexagonal while those containing Ge and Sn are tetragonal and cubic, respectively. We have seen that Ge deficiency in Cu_2GeSe_3 lowers the symmetry from tetragonal to monoclinic while excess of Ge raises it to cubic. It appears, therefore, that it is the group IV atom that decides the symmetry which the lattice is going to have. We have also seen that excess Se extracts some Ge out of Cu_2GeSe_3, leaving it a Ge-deficient monoclinic phase. This indicates a very strong interaction in Ge–Se system. We mentioned that the compounds Cu_2GeSe_3 and $Cu_2Ge_2Se_3$ give out $GeSe_2$ and GeSe, respectively, as dissociation products. In $GeSe_2$, Ge behaves as a tetravalent atom, while in GeSe it is diavalent. It is known that group IV atoms show variable valency, tetravalency and divalency. It seems possible and reasonable to relate the valence state of the participating group IV atom, as indicated by the interaction in the concerned IV–VI basic system, to the stability and lattice symmetry of the ternary compound.

To understand the nature of this interaction, we examine the A^{IV}–B^{VI} system in general (where A = Si, Ge, Sn, Pb and B = S, Se, Te). Two compounds are known to exist in this system. These are monochalcogenides and dichalcogenides, depending upon the divalent and tetravalent character of the group IV atoms. As the atomic number increases, the divalent character of the group IV atoms becomes more prominent (because of the increased stability of *s* subshell (*9*), resulting in the increased stability of monochalcogenides. Conversely, it can be argued that, if under some particular conditions monochalcogenides are found to be more stable, the divalent character of the group IV atoms should be considered more prominent as compared to its tetravalent character. Now to be able to participate in the formation of ternary tetrahedral phases the group IV element must exhibit tetravalency. It follows, therefore, that if a particular dichalcogenide is unstable, the ternary compound containing the two group IV and VI elements is also unstable, because the group IV atom does not show tetravalency in the presence of that particular group VI atom. The validity of this argument can be proved by taking Pb and Te as example.

No dichalcogenide of Pb is known (*10*), and therefore Pb does not participate in the formation of ternary tetrahedral compounds. The ditellurides of Ge and Sn are also not formed (*10*). Although ternary tellurides containing Ge and Sn have been reported in the literature, there are reports (*11*) indicating the presence of a second phase in these materials. Our own attempts to obtain these materials as single phases have failed. We always got a eutectic type of phase distribution in these materials, unlike in sulphides and selenides. A detailed account of this work on ternary tellurides will be published shortly.

Another important observation in this connection is the apparent dependence of lattice distortion on the valence state of the group IV atom. Most of the ternary tetrahedral compounds crystallize in slightly distorted sphalerite structure with a tetragonal unit cell. This tetragonal distortion has been attributed to the phenomenon of ordering in cation sites (*12*). This explanation is definitely not correct in case of $A_2^{I}B^{IV}C_3^{VI}$ groups of compounds.

In our earlier work on the temperature variation of lattice parameters of Cu_2GeSe_3 (*13*) and Cu_2GeS_3 (to be published) we found that the linear coefficient of thermal expansion along the *a* axis is larger than along the *c* axis. Since $a > c$, it means that the tetragonality parameter $(1 - c/a)$ increases with increasing temperature, that is, increasing disorder. That disproves the argument relating ordering to tetragonality.

Another explanation offered for tetragonal distortion in ternary tetrahedral compounds relates tetragonality to the relative bond polarization (ionicity) of the two cation–anion bonds (*12*). In the present case, the electronegativity difference between Cu and Ge atoms, a quantity that should determine the relative ionicity of the two bonds, is very small, accounting for less than 1% difference in their ionicities (*14*). Moreover, the same difference is present in Cu–Se and Sn–Se bonds but Cu_2SnSe_3 is not distorted.

It can, however, be seen that whenever the group IV atom has predominantly divalent character, the lattice distortion is reduced or removed altogether. As we have mentioned, the tetragonal compound Cu_2GeSe_3 gives $GeSe_2$ after decomposition while cubic $Cu_2Ge_2Se_3$ gives GeSe. If these dissociation products are taken as indications of the valence character of the group IV atom in the ternary compound, it is clear that the increase in Ge concentration in Cu_2GeSe_3 also increases its divalent character in the compound. In case of Sn, the divalent character is very prominent for reasons mentioned earlier (increased stability of *s* subshell) and all the ternary compounds containing Sn are cubic. Thus some relation between the valence character of the group IV atom and the lattice distortion seems to be there. The reason for this relation may be as follows:

It is known that the electronegativity of the group IV atoms decreases with decreasing participation of *s* subshell (*15*), or, in other words, tetravalent states are more electronegative than the divalent states. Therefore, ionicity of IV–VI bond,' or the difference in the electronegativities of IV and VI atoms, is more when the group IV atom is in the divalent state (in monochalcogenides) than when it is in the tetravalent state (in dichalcogenides). Increased ionicity of a bond should also make it less directional or more isotropic in character. The increased ionicity of IV–VI bonds thus seems to be responsible for making the structure more isotropic.

The increased ionic character of $Cu_2Ge_2Se_3$ over Cu_2GeSe_3 is also suggested by their thermal conductivity values, which are 24 and 8.4 mW/cm °C, respectively (*4*). It is known that thermal conductivity decreases with increase in ionicity (*16*). Here all other factors, like the atomic weights, coordination number, etc., remain the same; therefore only the increased ionicity can be associated with decrease in thermal conductivity.

To summarize the discussion we can state the following two conclusions.

1. The stability of ternary tetrahedral phase is governed by the capability of the group IV atom to exhibit tetravalency in the presence of the participating group VI atom.
2. The lattice distortion decreases with increased ionic character of the IV–VI bond.

The ideas expressed here are, obviously, qualitative in nature but seem to provide a basis for understanding the stability and structural distortion of $A_2^{I}B^{IV}C_3^{IV}$ group of compounds, in terms of the nature of interaction in the two basic binary systems A–C and B–C.

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References

1. N. A. GORYUNOVA, "The Chemistry of Diamond-like Semiconductors, p. 16, Chapman and Hall, London (1965).

2. G. K. Averkieva, A. A. Vaipolin, and N. A. Goryunova, *in* "Soviet Research in New Semiconductor Materials" (D. N. Nasledov and N. A. Goryunova, Eds.), p. 26, Consultants Bureau, New York (1965).
3. E. Parthe and J. Garin, *Montash für Chem.* 102, 1197 (1971).
4. D. P. Spitzer, *J. Phys. Chem. Solids* 31, 19 (1970).
5. R. E. Loehman, A. J. Armstrong, D. W. Firestone, and R. W. Gould, *in* "Amorphous and Liquid Semiconductors" (M. H. Cohen and G. Lucovsky, Eds.), p. 72, North Holland, Amsterdam (1972).
6. L. I. Berger and V. D. Prochukhan, "Ternary Diamond-like Semiconductors, p. 23, Consultants Bureau, New York (1969).
7. W. B. Pearson, *Acta Cryst.* 17, 1 (1964).
8. L. I. Berger and V. D. Prochukhan, "Ternary Diamond-like Semiconductors", p. 10, Consultants Bureau, New York (1969).
9. E. S. Gould, "Inorganic Reactions and Structures," p. 265, Holt, Rinehart & Winston, New York (1962).
10. N. K. Abrikosov, V. F. Bankina, L. V. Poretskaya, L. E. Shelimova, and E. V. Skudnova, "Semiconducting II–VI, IV–VI and V–VI Compounds" (translated from Russian by A. Tybulewicz) p. 65, Plenum, New York (1969).
11. K. Hirono and M. Kono, *Jap. J. Appl. Phys.* 7, 54 (1968).
12. L. I. Berger and V. D. Prochukhan, "Ternary Diamond-like Semiconductors," pp. 29–30, Consultants Bureau, New York (1969).
13. B. B. Sharma, *Phys. Status Solidi* (a) 2, K-13 (1970).
14. R. C. Evans, "Crystal Chemistry," p. 67, Cambridge Univ. Press, London (1964).
15. E. J. Huheey, "Inorganic Chemistry," p. 162, Harper and Row, London (1972).
16. J. P. Suchet, H. Rodot, P. Lerouxhugon, and M. Rodot, *Adv. Energy Conv.* 3, 569 (1963).