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Solid Solution Formation in Chalcopyrite Systems of the Type AgInX_2–Ag$M^{III}X_2$ Where M = Al, Ga, and X = S,Se

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Previous (*1*) work on ternary chalcopyrite solid solution formation has shown that the difference in end point axial ratios ($\Delta c/a$) is an important factor in determining the extent of mutual solubility. It was concluded that when $\Delta c/a > 0.13$ complete solid solubility will not occur. In this work it is shown that complete solid solution formation in the systems $AgAlS_2$–$AgInS_2$ ($\Delta c/a = 0.111$), $AgGaS_2$–$AgInS_2$ ($\Delta c/a = 0.11$) and $AgAlSe_2$–$AgInSe_2$ ($\Delta c/a = 0.112$) does occur. This shows that the value of $\Delta c/a = 0.13$ as an upper limit for solid solution formation can be approached closely.

Introduction

Materials of the type $M^{N-1}M^{N+1}X^{8-N}$, with the chalcopyrite structure (tetragonal $I\bar{4}2d$)^2 are related structually to zincblende compounds $M^N X^{8-N}$ (cubic $F\bar{4}3m$) (*2*) by doubling of the unit cell parameter along the c-axis. The metal atoms M^{N-1} and M^{N+1} are arranged in alternating, equally spaced x-y planes. The tetrahedral coordination of zincblende compounds is deformed in chalcopyrite compounds, as measured by the deviation of the axial ratio c/a from 2, $(2 - c/a)$, and by the atomic coordinate u. The axial ratio is a function of the difference between the average of M^{N-1}–M^{N-1} and M^{N+1}–M^{N+1} interactions in the a plane compared to the M^{N-1}–M^{N+1} interaction along the c-axis, while u is a function of the difference between M^{N-1}–X^{8-N} and M^{N+1}–X^{8-N} interactions.

In chalcopyrites where $N = III$ (phosphides and arsenides) Abrahams and Bernstein (*3*) have shown that the M^{IV} cations are almost perfectly tetrahedrally coordinated, whereas when $N = II$ (chalcogenides) there is greater distortion of the tetrahedron associated with large axial deviations of c/a from 2 (0 for $AgInSe_2$ to 0.12 for $AgGas_2$).

The mutual solubility of chalcogenide chalcopyrites has been found to be dependent on $\Delta(c/a)$ of the two ternary compounds involved. Systems of the type $M^I M^{III} S_2$–$M^I M^{III} Se_2$^{4} where $\Delta(c/a)$ varies from 0.0 to 0.02 form complete series of solid solutions. Studies (*1*) of the miscibility gaps in systems of the type Cu$M^{III}X_2$–Ag$M^{III}X_2$, where M^{III} = Al, Ga and X = S, Se, indicate that where $\Delta(c/a) \leqslant 0.13$ the systems will exhibit complete solid solubility as in $CuInS_2$–$AgInS_2$ ($\Delta c/a = 0.08$) and $CuInSe_2$–$AgInSe_2$ ($\Delta c/a = 0.08$). Where $\Delta(c/a) > 0.13$ the chalcopyrites are not completely miscible as in Cu(Al, Ga)Se_2–Ag(Al, Ga)Se_2 where $\Delta c/a = 0.14$ for both systems. Although the value of 0.13 was previously obtained from the trends in the miscibility gaps, it was not possible to firmly establish it as the upper limit for complete miscibility as only the In containing systems, where $\Delta c/a = 0.08$, which formed complete solid solutions, were investigated.

In this study, we report the results on chalcopyrite miscibility in systems of the type Cu$M_a^{III}X_2$–CuInX_2 (where M_a^{III} = Al, Ga) for which $\Delta(c/a)$ is close to but less than 0.13 ($\Delta = 0.110$, 0.112) in order to determine directly an upper value of $\Delta(c/a)$ for complete solid solution formation.

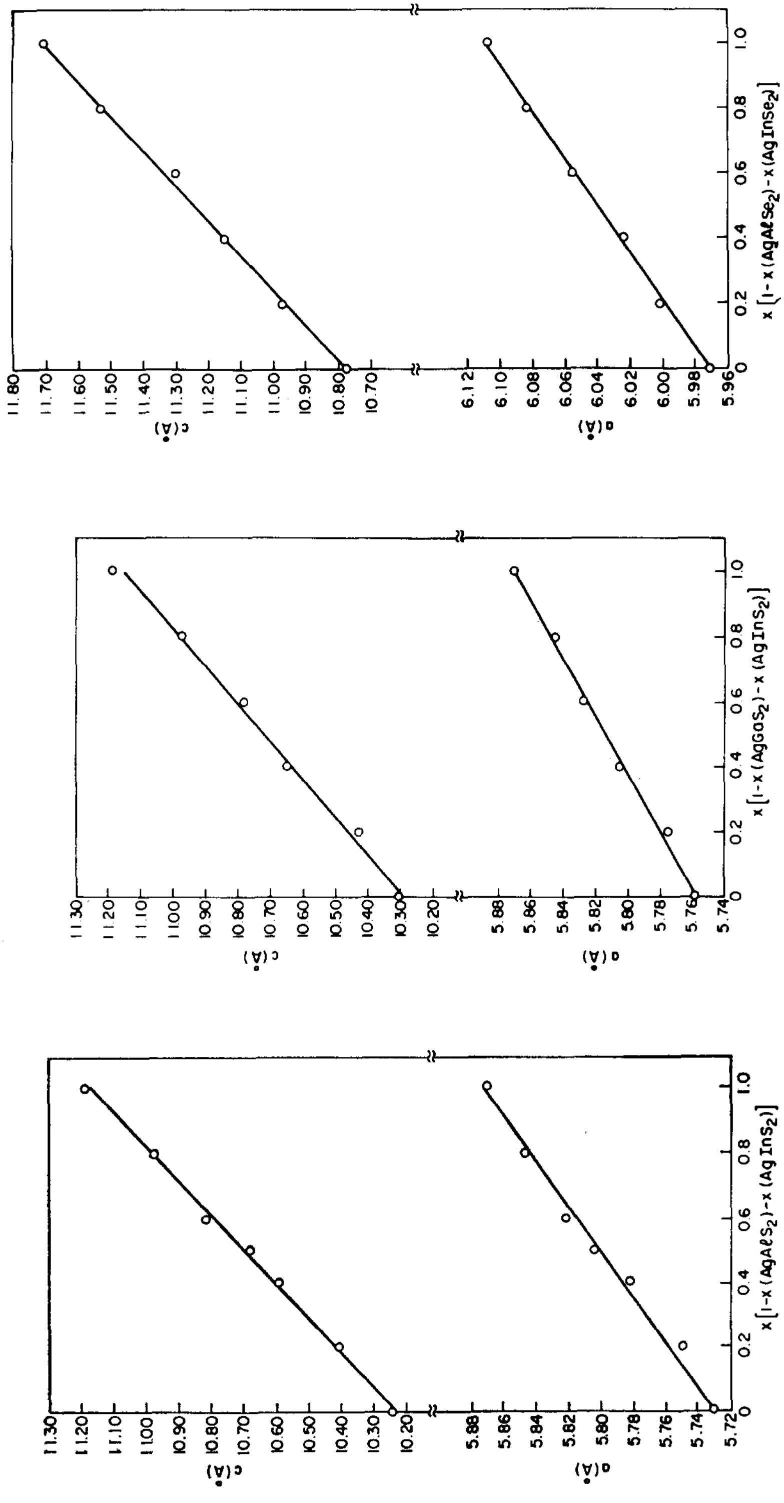

FIG. 1. Unit cell parameters versus composition in the systems $AgAlS_2$–$AgInS_2$, $AgGaS_2$–$AgInS_2$ and $AgAlSe_2$–$AgInSe_2$.

Experimental

All of the samples were prepared from mixtures of the elements (99.9% purity). The mixtures were sealed in evacuated silica tubes and heated at the rate of 10–15°C/hr to 800°C. The temperature was held at 800°C for 48 hr, at which time the samples were cooled by simply shutting off the furnace. In some cases, samples were refired by repeating the preceding procedure. The systems prepared in this manner were $AgAlS_2$–$AgInS_2$, $AgGaS_2$–$AgInS_2$, and $AgAlSe_2$–$AgInSe_2$.

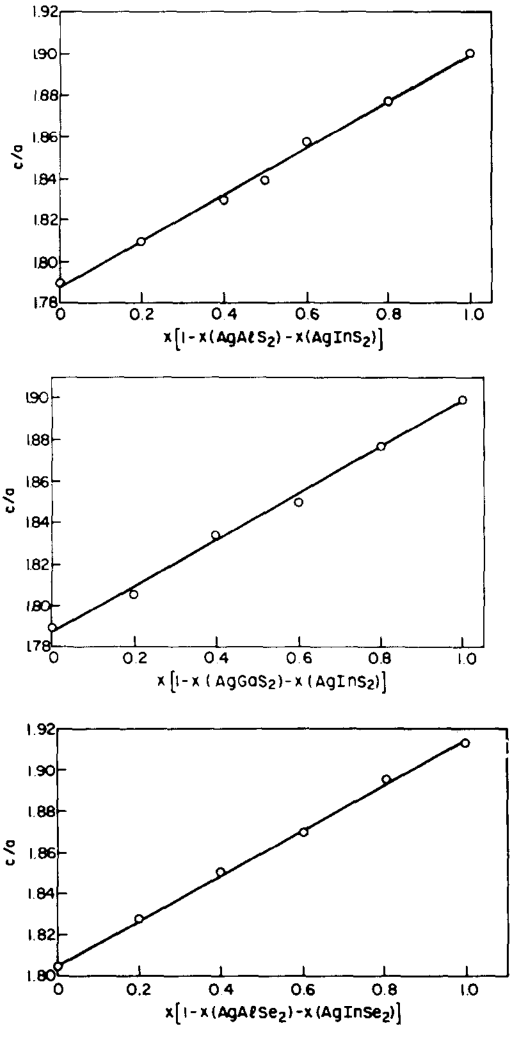

FIG. 2. c/a versus composition in the systems $AgAlS_2$–$AgInS_2$, $AgGaS_2$–$AgInS_2$, and $AgAlSe_2$–$AgInSe_2$.

All of the samples were analyzed by X-ray diffraction using a Norelco diffractometer and Cu*Kα* radiation. It was found that all of the systems formed with complete mutual solubility. Unit cell parameters and the axial ratios (c/a) vary linearly with composition (Figs. 1 and 2).

Al-rich samples for the system $AgAlSe_2$–$AgInSe_2$, did exhibit a tendency to hydrolyze in air when left exposed to it for any extended period of time.

Using unit cell parameters from this work, axial ratios of the ternary end-points were calculated. $\Delta c/a$ for the three systems investigated were found to be: 0.110 for the system $AgAlS_2$–$AgInS_2$, 0.110 for $AgGas_2$–$AgInS_2$, and 0.112 for $AgAlSe_2$–$AgInSe_2$.

Discussion

Although there is no combination of ternary chalcopyrites that would give a $\Delta c/a$ of 0.13, we have been able to show that for systems where $\Delta c/a$ is between 0.0 and 0.112 the systems will be completely miscible. As previously shown (*1*), when $\Delta c/a$ is 0.14 and greater, the systems do not exhibit complete mutual solubility.

The result of this and previous work has been to show that the value of 0.13 for $\Delta c/a$ is an accurate measure of the heats of mixing that determine solid solution formation in chalcopyrite mixtures. A short discussion showing that other factors would not be expected to contribute to the heat of mixing is given in the Appendix.

Appendix

In the text and in a previous paper (*1*) the solubility limits (and, by implication, the heats of mixing) of chalcopyrite compounds are related to the axial distortion factor $2 - c/a$. Other possible factors that might be considered are $2 + c/a$, a, or c separately, and the internal distortion parameter for the unit cell, denoted variously by u or x.

If a size factor (such as mismatch of covalent radii) were dominant, then $2 + c/a$, a, or c separately might be important factors. However, comparison of the lattice constants of $ZnGeP_2$, $ZnGeAs_2$, $CdSnP_2$, and $CdSnAs_2$ with the lattice constants of their isoelectric sphalerite analogues (GaP, GaAs, InP, and InAs, respectively) shows that in $M^{II}M^{IV}X^{V}{}_2$ chalcopyrite crystals, size factors do not exhibit consistent chemical trends. Because of the contribution of the *d*-electrons of Cu and Ag to cohesion, a similar comparison cannot be made for the $M^{I}M^{III}X_2^{VI}$ compounds, but because both structures are tetrahedrally coordinated, the conclusion should still be valid.

In the sphalerite pseudobinary alloys it has been shown by Van Vechten (*5*, *6*) that electronegativity differences are primarily responsible for heats of mixing and solubility limits. Phillips has shown (*7*) that the tetragonal distortion 2-c/a in $M^{II}M^{IV}X_2{}^{V}$ compounds can be predicted from dielectric (s–p) electronegativities. The internal strain parameter u or x can also be predicted (*8*) from electronegativity differences, both for $N = III$ and $N = II$ in $M^{N-1}M^{N+1}X_2^{8-N}$ compounds, although (because of *d*-electron effects), the errors are larger in the latter case.

One may conclude from the foregoing that 2-c/a is a good measure of that combination of electronegativity differences that determines strain energies and heats of mixing, so that the correlation between miscibility limits at 800°C and mismatch of 2-c/a noted here and previously (*1*) is a natural one. There is a small anomaly, however, which can be discussed here. From our previous data (*1*) it can be seen that the miscibility gap in $Cu_xAg_{1-x}GaS_2$ of about $\Delta x = 0.4$ is smaller than in $Cu_xAg_{1-x}AlS_2$, where $\Delta x = 0.7$, although $\Delta c/a$ is larger for the former (0.18) than for the latter (0.16). This small anomaly can be attributed to the peculiarly covalent character of Ga. Thus the largest anomalies in the internal strain parameters (*8*) are found in (Cu and Ag) GaS_2. Also, in elemental Ga the peculiar covalency is manifested in its crystal structure (one very near neighbor) and its very large entropy of melting (in cal/mole degree: Ga, 4.4; Al, 2.8; In, 1.8; and Ge, 7.3) which places it between normal metals and covalent crystals.

Acknowledgments

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