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SYNTHESIS AND PROPERTIES OF $AgGa_xIn_{1-x}Se_2$ SEMICONDUCTORS

ABSTRACT

For the first time the synthesis of the solid solutions $AgGa_xIn_{1-x}Se_2$ has been made successfully for various values of x. It has been found by X-ray diffraction that all samples have the chalcopyrite type crystal structure. The unit-cell parameters a and c and their ratio c/a vary linearly with x and that fact can be connected with the dimensions of atoms. The band width E_g increases linearly with x from 1.19 to 1.77 eV. The electric conductivity vary for several orders of magnitude with change of x from 0 to 1. Using thermoelectric probe it has been noticed that all compounds have n-type conductivity for x<1.

SYNTHESIS OF THE COMPOUNDS

The compounds $AgGa_xIn_{1-x}Se_2$ were synthesized for several values of x (x=0, 0.2, 0.4, 0.6, 0.7, 0.8, 1). The direct synthesis of pure elements (purity ≥ 5N) was made at 1170 K in evacuated and sealed silica tubes. The melting temperatures of $AgGaSe_2$ and $AgInSe_2$ are 1150 K and 1060 K, respectively. By slow cooling homogeneous polycrystalline samples were obtained with a gray metallic shine.

CRYSTAL STRUCTURE

It has been found[1] by X-ray diffraction that: a) all the samples are single-solid phases, b) they have the chalcopyrite-type crystal structure,

c) the unit-cell parameters a and c and their ratio c/a vary linearly with x. The results are given in Fig. 1.

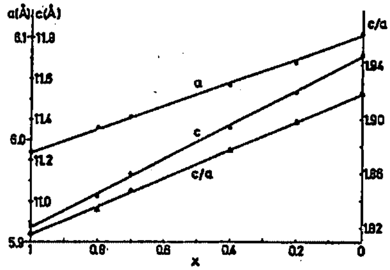

Fig. 1. Variation of the unit-cell parameters a and c and their ratio c/a with composition for solid solutions $AgGa_xIn_{1-x}Se_2$.

DISCUSSION

Owning to the same configuration of their outer shells the Ga atoms can be substituted by the In atoms (and vice versa) to give single-phase compounds, $AgGa_xIn_{1-x}Se_2$. The linear dependence of the unit-cell parameters and their ratio c/a with x can be explained with a simple model, in which the atoms are represented as spheres. It may be expected that the building of the same crystal structure with bigger or smaller atoms will produce a bigger or a smaller unit-cell, and this can be seen from the change of the unit-cell parameters. Also, a bigger difference between the dimensions of the constituent atoms will produce a bigger disortion of thetetrahedra which are elementary motifs in the chalcopyrite-type structures. This simple model can qualitatively describe variations of the unit-cell parameters and their ratio for various $A^{I}B^{III}C_2^{VI}$ chalcopyrite-type compounds. The Pauling covalent atomic radius can be used for estimation of the atom dimensions(2) (in Å units):

Cu (1.35)	Al (1.26)	S (1.04)
Ag (1.52)	Ga (1.26)	Se (1.14)
	In (1.44)	Te (1.32)

The substitution of Cu with Ag in the $A^{I}B^{III}C_2^{VI}$ chalcopyrite-type structures produces the same type of structure with bigger unit-cell parameters (see table I). The same happens with substitution of Al with Ga, Ga with In, S with Se, and Se with Te. Changes in the unit-cell parameters are proportional to the changes in dimensions of substituted atoms. The tetrahedral disortion described as (2-c/a) is proportional to the difference between dimensions of atoms A and B in the $A^{I}B^{III}C_2^{VI}$ compounds. Using different sources[1,2,4] the following table can be constructed:

Table I	a(Å)	c(Å)	2-c/a
$AgAlS_2$	5.707	10.28	0.20
$AgGaS_2$	5.757	10.305	0.21
$AgInS_2$	5.829	11.19	0.08
$AgAlSe_2$	5.968	10.77	0.20
$AgGaSe_2$	5.988	10.880	0.18
$AgInSe_2$	6.104	11.714	0.08
$AgAlTe_2$	6.309	11.85	0.12
$AgGaTe_2$	6.301	11.96	0.10
$AgInTe_2$	6.419	12.58	0.04
$CuAlS_2$	5.323	10.44	0.04
$CuGaS_2$	5.347	10.474	0.04
$CuInS_2$	5.52	11.08	-0.01
$CuAlSe_2$	5.604	10.977	0.04
$CuGaSe_2$	5.618	11.01	0.04
$CuInSe_2$	5.77	11.55	-0.008
$CuAlTe_2$	5.967	11.80	0.03
$CuGaTe_2$	5.99	11.90	0.01
$CuInTe_2$	6.179	12.36	-0.003

BAND GAP WIDTH

The investigation of the spectral dependence of transparency showed that the band gap width E_g changes continuously with x from 1.19 eV to 1.77 eV. The results are given in Fig. 2.

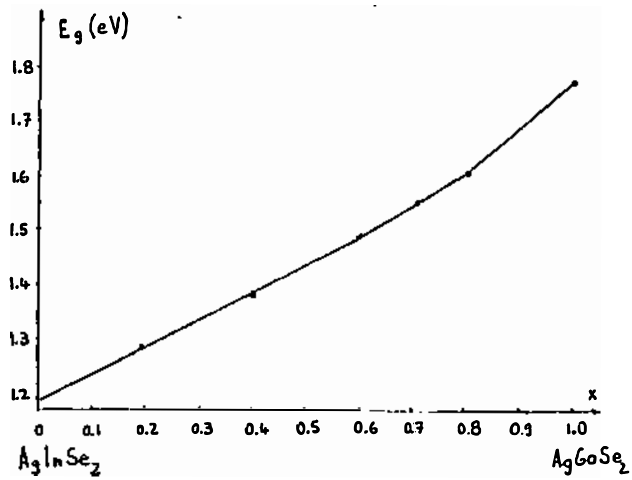

Fig. 2. Dependence of E_g on x in the $AgGa_xIn_{1-x}Se_2$ compounds

ELECTRICAL PROPERTIES

Conductivity of $AgGaSe_2$ is low, as it was also observed by the other authors(6,7). For the polycrystalline samples it has been found that the conductivity for $AgGaSe_2$ amounst $\approx 10^{-7}$ $Ohm^{-1}m^{-1}$, while for $AgInSe_2$ is $\approx 10^{-1}$ $Ohm^{-1}m^{-1}$. For the solid solutions $AgGa_xIn_{1-x}Se_2$ conductivity changes continuously with x between two values.

Using thermoelectric probe it has been noticed that all the compounds are of n-type for $x<1$. In the case of $AgGaSe_2$ it was impossible to determine the type because of the very low conductivity.

REFERENCES

1) B. Gržeta-Plenković, S. Popović, B. Čelustka, B. Šantić J. Appl. Cryst. (1980.) 13 311-315

2) C. Kittel Introduction to Solid State Physics 3th ed. John Wilwy, New York 1966.

3) G.B. Bokiy, ed., Kristallokhimicheskie fiziko-khimicheskie svoystva poluprovodnikovykh veshchestv, Izdatel'stvo standartov, Moskva, 1973.

4) B. Tell, H.M. Kasper: Phys. Rev. B 4 (1971) 4467

5) A. Shaukat, R.D. Sing: J. Phys. Chem. Solids 39 (1978) 1

6) B. Tell, J.L. Shay, H.M. Kasper: J. Appl. Phys., 43 (1972) 2469

7) B. Tell, H.M. Kasper: J. Appl. Phys. 45 (1974) 5367