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DETERMINATION OF PHASE TRANSITION ENTHALPIES OF $A^{I}B^{III}C_2^{VI}$-TYPE COMPOUNDS

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ABSTRACT

$A^{I}B^{III}C_2^{VI}$-type compounds have been synthesised.Melting and phase transition temperatures, heats and entropies of $CuAlSe_2$, $CuInS_2$, $CuInSe_2$, $CuInTe_2$, $AgGaS_2$, $AgGaSe_2$ and other compounds have been determined by the quantitative differential thermal analysis method. Phase transition nature in these compounds is discussed.

$A^{I}B^{III}C_2^{VI}$ compounds take a separate place among multiple diamond-like semiconductors . These compounds are the nearest electronic, chemical and crystallochemical analogs of $A^{II}B^{VI}$compounds,that are broadly used at present. $A^{I}B^{III}C_2^{VI}$-type compounds are promising as nonlinear optic materials as well as materials for solar elements with high efficiency (ref.1-3). In order to grow the perfect crystals of this compound class we must have exact data on thermodynamic characteristics of the process of transition from solid state into liquid. However literature gives controversary information regarding temperatures, heats and melting character for these compounds. Works (ref.4-6) state that $CuGaSe_2$, $CuInSe_2$, $CuInTe_2$ compounds form as a result of peritectical reaction. Authors of the above mentioned works come to such a conclusion on the basis that DTA curves contain peaks corresponding to additional heat effects. Works (ref.7,8)contain T-x diagrams of Cu_2Se-InSe, CuTe-In_2Te_3 cut states,and the authors consider that additional DTA curve peaks correspond to cation-cation disordering. Literature data on melting temperatures and phase transition temperatures also differ substantially. Thus,melting point for $CuInS_2$ 1273K (ref.9) and 1388K (ref.10) and for $CuInSe_2$ 1259K (ref.11) and 1285K(ref.12) are given respectively.

The resalts of $A^{I}B^{III}C_2^{VI}$-type compounds phase transition thermodynamic characteristics measured by the quantitative DTA method are provided. We used crystals grown by two-temperatures method

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($CuInS_2$, $AgInS_2$, $AgGaSe_2$) or Bridgeman-Stockbarger method. Two temperature synthesis was conducted as follows. Metallic components of stoichiometric quantities were loaded into a boat and placed into one end of the ampoule. Chalcogene, taken in excess relative to compound stoichiometric composition, was placed at the opposite end of the ampoule. The ampoules were vacuumed to residual pressure 10^{-3} Pa and sealed. An ampoule was placed into a horisontal doublezone furnace in such a way that a boat with the metallic component occured in the hot zone, where temperature was 20-40K higher than the melting point of the compound. The cold zone temperature containing chalcogene was increased slowly up to 683-723K and endured for 2-3 hours. In order to finish the reaction completely the cold zone was heated to 823-843K and lefted for 3 hours. After that hot zone temperature was decreased to 1073-1173K and 5-7 day annealing took place. Part of two temperatures method grown crystals were used to grow monocrystals by Bridgeman method. Double cone ampoules were used. The temperature gradient of the crystallization zone was 20-40 K/cm and the ampoule lowering rate was 0-0.6 mm/hr. $AgGaS_2$, $CuInSe_2$, $CuInTe_2$ monocrystals 12-16 mm in diameter and 50 mm long were grown under these conditions.

The individual characteristics of the compounds obtained were studied by the chemical, X-ray and differential thermal analyses. X-ray results showed one line system corresponding to the chalcopyrite structure. Compound crystals were rubbed to powder and loaded into Stepanov's containers to take DTA curves and measure phase transition heats. The free space of containers was filled with quartz ballast for preventing sample decomposition and after that containers were evacuated and sealed. The DTA device was calibrated on tin, tellurium, antimony, germanium and silver. Samples for calibration coefficient K determination were prepared in the same way as the samples of $A^{I}B^{III}C_2^{VI}$ compounds. Sample mass for DTA curves determination was 1.5g, heat rate - 6 K/min. Phase transition heats was determined according to equation $m\Delta H = K\cdot A$, where ΔH - phase transition heat, m - sample mass, K - calibration coefficient, A - curve peak area (ref.13).

Experimental data on unit cell dimensions, phase transition temperatures, heats and entropies for a number of $A^{I}B^{III}C_2^{VI}$ compounds is given in the table. Temperature error is not more than

2-4K, phase transition heat error - 6-8% under reliability 0.95.

Table. Unit cell dimensions a and c, phase transitions temperatures, heats and entropies of $A^{I}B^{III}C_2^{VI}$ ternary compounds

Compound	Dimensions		T_{c-c},K	T_{c-a},K	T_{melt},K	ΔH_{melt} kJ/mol	ΔS_{melt} J/molK
	a, A	c, A					
$CuAlSe_2$	5.607	10.98			1336		
$CuGaS_2$	5.348	10.48			1515		
$CuGaSe_2$	5.616	11.02	1040		1361		
$CuGaTe_2$	5.994	11.91			1145		
$CuInS_2$	5.523	11.13	1248	1313	1363	66.8	49.0
$CuInSe_2$	5.782	11.62	1083		1259	83.6	66.4
$CuInTe_2$	6.179	12.36	940		1058	96.0	90.7
$AgGaS_2$	5.754	10.30			1268	53.6	42.3
$AgGaSe_2$	5.985	10.90			1123	58.6	52.0
$AgInS_2$	5.880	11.20	958		1145		

DTA curves for $CuGaSe_2$, $CuInSe_2$, $CuInTe_2$, $AgInS_2$ compounds besides melting peaks contain also endopeaks at 1040K, 1083K, 940K and 958K respectively. DTA curve for $CuInS_2$ compound has three endopeaks. It is seen from the table that existense of two and more thermal effects is characteristic for those compounds, where c/a ratio equals 2 or near 2, i.e. for such compounds where tetragonal compression ($\delta = 2-c/a$) is wery small or absent at all.

The nature of compounds thermal effects fixed on DTA curves may be explained on the basis of ideas expressed by Palatnik et al (ref.14). They showed (ref.14) that in the process of ternary semiconductor compound heating two disorder effects can be observed. If a crystal consists of three atom types they are located in the crystal matrix knotes in order or in disorder. If ordering energy of A and B atoms will be smaller than the energy of each of them relative to C atom, then while heating of an ordered crystal disordering of A atoms relative B atoms (cation-cation disordering) at a certain temperature T_1 will first take place, afterwords A and B atoms will disorder relative C atom (cation-anion disordering) at a certain temperature T_2 ($T_2 > T_1$).

On the basis of the above results we may suppose that melting of the compounds studied goes as follows. While ternary $A^{I}B^{III}C_2^{VI}$ compounds are heated chalcopyrite structure is first disordered at T_{c-c} temperature into zinc blende structure (cation-cation disordering); then at T_{c-a} temperature (in analogy with ZnS) further disordering of zinc blende structure into vurcite structure (cation-anion disordering) occurs and then at T_{melt} congruent or incongruent melting takes plase.

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