THE ROENTGENOGRAPHIC STUDY OF LAYERED SEMICONDUCTORS OF $Ga_{0,5-x}Sn_xIn_{1,5}S_3$ TYPE

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For the first time the phase-formation in the system $Ga_{0,5-x}Sn_xIn_{1,5}S_3$ was investigated in details by the method of the thermal, roentgenographic, microstructural analysis. Their monocrystals are obtained by the method of the direct crystallization. It was established, that they belong to the initial stage of the ordered polytype series of the structure of the layered type on the vourcite base.

Introduction

The significance of the physical-chemical and structural study of substance with semiconductive properties is obvious. The synthesis, the monocrystals growth, the study of their physical-chemical and structural peculiarities, phase-formation regularities and the mechanism of structural phase transition have a great scientific-practical mean. In this aspect Ga_2S_3-In_2S_3 system compounds are perspective objects for the solution of questions of the structurization, polymorphy, polytype, methods of the phase stabilization and the clarification of characteristics physical-chemical properties.

The phase equilibrium in Ga_2S_3-In_2S_3 quasi-binary cut of the triple system Ga-In-S were for the first time studied by authors [1,2], where the formation of just one triple phase GaInS, melting uncongradually, was established. It should be noted, that in these papers there is a visible discrepancy in the state diagram and values of hexagonal cell parameters. Neither was determined the crystal structure of the compound.

Judging from experimental facts on the presence of some polymorphy modifications in sesqui chalcogenide of A_2S_3 (A-Al, Ga, In) type, authors [3,9] investigated in details the phase-formation in the given system.

Applying the method of chemical transport reaction (CTR), the presence of polymorphy phases line, polytype forms and three independent compounds (table 1) was established as result of roentgenostructural study of monocrystals, obtained from before synthesized contents $Ga_{0,5}In_{1,5}S_3$ and $GaInS_3$ in various temperature gradients.

To reveal the influence of multivalent tetrahedral atoms on the stabilization of polymorphy modifications $(GaIn)_2S_3$, partially substituting tetrahedral placed atoms Ga and In by atoms Cu and Mn (conserving the total balance of the valency) by the method of direct synthesis, authors [10,11] realized 2H and 3R polytypes, having the layered structure of polytype line a= 3,82 Å, c 15Å· n (n = 2,3) and a = 3,82Å, c 18 Å· n (n = 2).

Experimental part

The objective of the present work is to receive the monocrystals on the base of $Ga_{0,5}In_{1,5}S_3$ with the partial substitution of tetrahedral coordinate atoms In(Ga) by atoms Sn and the study of their structure and phases stabilization .

The synthesis was conducted in pumped-out quartz ampoules (10^{-2} Pa) in the one-temperature furnace at 1223-1273 K (the heat rate is 100 grade/hour). After half an hour keeping at this mode the ampoule was slowly cooled up to the temperature 673-693 K and was held at the given temperature during 72 hours, As a result samples from yellow ($Gà_{0,17}Sn_{0,5}In_{1,5}S_3$) to red ($Gà_{0,33}Sn_{0,25}In_{1,5}S_3$) colors, lightly cracked on the fine plate-layered crystals, were obtained.

Table 1

Crystallographic data of polymorphic phases and polytype forms of compounds of $(GaIn)_2S_3$ content.

The content of the phase	Sp.gr.	à, Å	â, Å	Ñ, Å	Z
$GaInS_3$	Ð3ml	3,81		18,19	2
$GaInS_3$	P3ml	3,81		54,61	6
$GaInS_3$	$P6_1$	6,65		17,92	6
$GaInS_3$	$P6_3mc$	3,81		30,62	10/3
$GaInS_3$	P3m	3,81		45,89	5
$GaInS_3$	$Bb2_1m$	19,06	6,19	3,81	4
$Ga_{0,5}In_{1,5}S_3$	P3ml	3,84		12,33	1
$Ga_{0,5}In_{1,5}S_3$	R3m	3,81		100,04	11
$Ga_{0,67}In_{1,33}S_3$	2H	7,64		74,00	8
$GaInS_3$	R3m	3,82		63,41	6
$Ga_{0,25}In_{1,75}S_3$	C2/m	6,55	3,72	12,62 â=100°	4
$GaInS_3$	Shpinell str. Type	10,79			8

It should be noted, that temperature conditions at the initial stage of the synthesis were chosen by the experimental way with the involvement of the literature data analysis on the receipt of binary compounds In_2S_3, $Gà_2S_3$, SnS and the thermographic record of synthesis process of each content. By this it was supposed, that the fusing temperature grows almost in a linear fashion with the content change. Though the obtained material has the crystal-mosaic nature, the method is reliable and may be successfully applied to obtain many sulphides, having the layered structure.

The roentgenographic study showed, that all synthesized samples are homogeneous and applicable for the detailed roentgenographic analysis. The diffractograms were obtained on the device DRCI (the roentgen diffractogram of common use) (the radiation Cu-K_α). The analysis of calculated inteplane distances (d) showed, that investigated contents are isostructural and formed on the base of the ordered phase $GaInS_3$, realized in the temperature gradient 873-973 K with the part of crystal J_α (CTR). The indexing of interplane distances allowed to reveal, that both contents are isostructural and crystallized, unlike the ordered modification $GaInS_3$, in the

rhombohedral lattice with parameters: a=6,500 Å; c= 18,685 Å, V=684,13Å^3, Z=6, sp.gr. $P6_2$, V_s= 38,45 Å^3 and a=6,485 Å; c= 18,653 Å^3, V=679,81Å^3, Z=6, V_s= 37,77 Å^3; for $Gà_{0,17}Sn_{0,5}In_{1,5}S_3$ and $Gà_{0,33}Sn_{0,25}In_{1,5}S_3$ respectively. Roengenographic data of the samples under investigation are presented in table 2.

Synthesized compounds with regard to various solvents are mainly stable (concentrational mineral acids dilute them with the hydrogen sulphide emission), and keep the primary characteristics fore a long time.

Microhardenesses were determined on polished semicrystalline samples. The research showed, that the microhardeness of samples under investigation depends on the orientation of fine-crystalline faces of the surface for $Gà_{0,33}Sn_{0,25}In_{1,5}S_3$ and $Gà_{0,17}Sn_{0,5}In_{1,5}S_3$ respectively.

Table 2

Roentgenographic data of phases $Gà_{0,17}Sn_{0,5}In_{1,5}S_3$ and $Gà_{0,33}Sn_{0,25}In_{1,5}S_3$

$Gà_{0,17}Sn_{0,5}In_{1,5}S_3$			$Gà_{0,33}Sn_{0,25}In_{1,5}S_3$		
d_{exp}	I/I_0	HKL	d_{exp}	I/I_0	HKL
6,2282	55	003	6,2195	45	003
3,2503	100	110	3,2433	100	110
3,1146	15	006	3,1104	10	006
2,8810	20	113	2,9159	10	113
2,8053	15	200	2,8070	10	200
2,7352	15	106	2,7565	10	106
2,6984	80	202	2,6952	70	202
2,2936	10	116	2,2325	12	116
2,0767	60	009	2,0731	50	009
1,9489	12	109	1,9411	10	109
1,9058	90	118	1,9018	80	118
1,8413	10	302	1,8289	10	302
1,6260	10	220	1,6218	8	220
1,5856	10	223	1,5713	8	223
1,5564	12	0012	1,5531	10	0012

Discussion

Results of the experimental study on the synthesis and roentgenographic analysis of polytype forms of compounds of $Gà_{0,5-X}Sn_XIn_{1,5}S_3$ type were described above. It was established, that they are individual compounds and isostructural with the ordered structure on the base of vourcite, and are photosensitive in visible region of the spectrum. Certainly, the presence of experimental data on the transmission, absorption, voltamperic characteristics is necessary for the discussion of optic and electrooptic properties of materials under investigation. These works are still underway and it is planed to report on results in the nearest future. We should note only the fact, that the width of the forbidden band of investigated samples is visibly reduced in comparison with the ordered phase $GaInS_3$, for which F_g makes 2.84 eV.

In the present paper we found that it is necessary to discuss experimental facts of the phase-formation and the influence of various cations on the stabilization of polymorphic modifications. $Gà_2Sn_3 – In_2S_3$ system phases, realized to the present time, are assembled in table 1. Their structural data are described in papers [3-9,12]. It should be noted, that three stable polymorphy varieties of $(GaIn)_2S_3$ type-monoclinic, rhombohedral, cubic and five polytype lines, the line beginning from structural variant ã – In_2S_3, i.e. c 9 Å· n, the line with period c 12 Å· n; c 15 Å· n ; c 18Å· n, with the constant value a 3,8 Å and the ordered line with the constant a 6,5 Å, c 18 Å are distinguished among revealed phases.

The preliminary crystal-chemical analysis of indicated structural facts allows to reveal, that unlike the influence of copper atoms, where the polytype line

c 15 Å· n and Mn-Ohm polytype line with c 12 Å· n are mainly stabilized, at the tin part, as a stabilizing atom, the ordered phase, realized in limits of the spatial group of $P6_2$ symmetry and non $P6_1$ for the ordered phases $GaInS_2$, is formed. Such situation allows to conclude, that, except the valency of “elements-stabilizers”, ion radii and Jn and Ga atoms ratio have the essential part for the phase stabilization.

Conclusion

Therefore, crystallographic and physical-chemical properties of crystals $Gà_{0,17}Sn_{0,5}In_{1,5}S_3$ and $Gà_{0,33}Sn_{0,25}In_{1,5}S_3$ are for the first time synthesized and investigated. It was established, that these crystals are wide band semiconductors and form the ordered structure of the layered nature.

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Received: 10.05.02