REFINEMENT THE CRYSTAL STRUCTURE OF THE $Ga_{1-x}In_{1+x}S_3$

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The compounds of the Ga_2S_3-In_2S_3 system are well studied and the number of grown ternary crystalline phases with the general formula $Ga_{1-x}In_{1+x}S_3$ ($0 \le x \le 0.5$) is more than ten /1-8/. Most of them are characterized by a layered structure. It is known that layered chalcogenides mainly refer to the hexagonal system and are characterized by closely packed structures. The building blocks of such structures are two-dimensional infinite slabs consisting of several alternating anion (A)-cation (C) layers of the A-C-... -A type. Repetition of such slabs forms a three-dimensional structure. In this case, van der Waals (vdW) bonds form between the anions of the extreme atomic layers of the neighboring slabs (or packets). Also, in the mentioned Ga_2S_3-In_2S_3 system with the exception of one orthorhombic phase, all the other phases are belonging to rhombohedral or hexagonal crystal class.

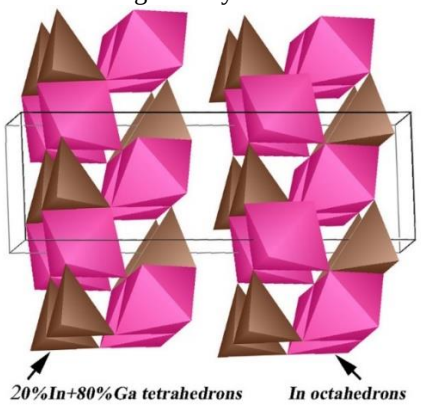

Fig 1. The crystal structure of $Ga_{0.8}In_{1.2}S_3$.

The orthorhombic phase was obtained by the chemical transport reaction from the pre-synthesized $Ga_{1-x}In_{1+x}S_3$ ($0.25 \le x \le 0.50$). The transporting agent was I_2. The crystal structure of orthorhombic $GaInS_3$ is presented in [3]. This structure is formed from articulated tetrahedral and octahedral fragments, with a ratio of 1: 1. Also, all tetrahedrons are occupied by Ga atoms, and the octahedrons are occupied by In atoms. The slabs of orthorhombic GaInS3 crystals consist of five atomic layers of S- (Ga, In) -S- (Ga, In) -S and the vdW space between them is in the form of a zigzag (Fig 1).

It was shown in [9,10] that these crystals are easily intercalated by 4-aminopyridine ($NC_5H_4NH_2$) molecules. They also found that deintercalation occurs in two stages, when about 15% of 4-AP molecules being removed in the first stage at 250ºC, and complete removal of organic molecules occur at 345C. Such a two-step decomposition of intercalate was difficult to harmonize with the crystal structure. Therefore, a need arose for a more detailed study of the crystal structure of the noted orthorhombic structure.

Obviously, octahedral positions can be populated only with indium atoms. However, tetrahedral positions can be inhabited not only by Ga atoms, but also by In atoms. Many sulfide compounds are known, where indium atoms have tetrahedral coordination. Therefore, we assumed that the stoichiometric formula of GaInS3 does not accurately describe the structure, but should have the form $Ga_{1-x}In_{1+x}S_3$. Therefore, we have refined the crystal structure of $Ga_{1-x}In_{1+x}S_3$. The refinement performed by Rietveld method on the basis of powder x-ray diffraction data (CuK_α, $5° \le 2\theta \le 120°$, D2 Phaser, Bruker), using the program TOPAS-4.2.

The XRD pattern of $Ga_{1-x}In_{1+x}S_3$ and the difference curve between the experimental and calculated intensities are shown in Fig 2. To refine the structure, the results of [3] were used. However, the positions of the gallium atoms were refined with the condition of the possibility of partial replacement by indium atoms. As a result, it turned out that these positions are populated as 20% In + 80% Ga. Therefore, the stoichiometric formula should be written as $Ga_{0.8}In_{1.2}S_3$.

Refined parameters of the unit cell, atomic positions, interatomic distances and characteristics of the experimental diffraction peaks are shown in tables 1-3. Fig 1 shows the projection on plane of the three-dimensional structure of $Ga_{0.8}In_{1.2}S_3$.

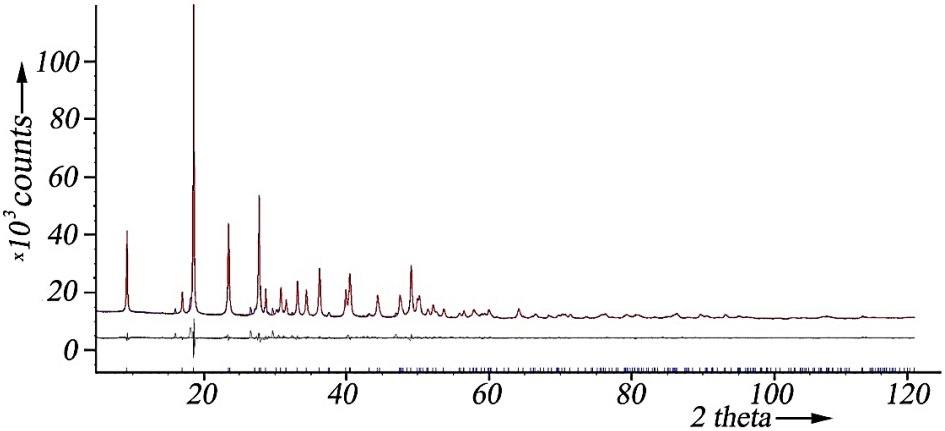

Fig 2. The XRD pattern of $Ga_{0.8}In_{1.2}S_3$

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Table 1. Refined parameters of the crystal lattice of the $Ga_{0.8}In_{1.2}S_3$ compound

Space group	A21ma
Lattice parameters at 298 K (A):	
a	6.2060(2)
b	19.0543(7)
c	3.8163(2)
Volume ($Å^3$)	451.27(3)
Density (g/cm^3)	4.26 (1)
R-Bregg (%)	1.032

Table 2. Atomic positional parameters of the $Ga_{0.8}In_{1.2}S_3$ crystals

Atom ident.	x	y	z	Atom type	Occupancy
Ga	0.05074(55)	0.0	0.11169(15)	Ga+3	0.80(1)
In	0.5	0.5	0.16679(10)	In+3	1
S(1)	0.2470(12)	0.0	0.22192(40)	S	1
S(2)	0.2133(16)	0.5	0.06556(45)	S	1
S(3)	0.1857(11)	0.5	0.39784(38)	S	1
Ga (In)	0.05074(55)	0.0	0.11169(15)	Ga+3,In+3	0.20(1)

Table 3. Interatomic distances in the $Ga_{0.8}In_{1.2}S_3$ compound

Атомы	S(1)	S(2)	S(3)
Ga (In)	2.428(8)	2.330(6) x 2	2.272(8)
In	2.685(5) x 2 2.616(8)	2.624(9)	2.547(5) x 2

As a result, it was established that the crystals of the orthorhombic phase are characterized by the composition $Ga_{0.8}In_{1.2}S_3$. By high-temperature x-ray diffraction, we studied the temperature dependence of the deintercalation of the mentioned in above intercalates $Ga_{0.8}In_{1.2}S_3$•4-AP. Now the two-step nature of deintercalation does not seem unexpected.

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