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# STRUCTURAL STUDY INTERCALATES OF ORTHORHOMBIC GA0.8IN1.2S3 WITH 4-AMINOPYRIDINE MOLECULES

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## ABSTRACT

This paper presents new results of structural studies of orthorhombic Ga0.8In1.2S3 crystals and their intercalation with organic molecules. It is known that as a result of the interaction of these crystals with 4-Aminopyridine (4-AP) molecules, a new intercalated compound with the composition Ga0.8In1.2S3-0.5(4-AP) is formed. Attempts to obtain new Ga0.8In1.2S3 intercalate with phenyl diamine, pyrazine, and ethylene diamine molecules during their direct interaction have not yielded results. However, attempts to replace 4-AP molecules with Ethylene Diamine (EDA) in the pre-synthesized Ga0.8In1.2S30.54-AP intercalate led to strong changes. Layered materials due to the unique structural features and physico-chemical properties in the last few decades are widely studied. These materials can be single-element crystals, such as graphite, phosphorus, arsenic, antimony, bismuth, and inorganic compounds such as transition metal chalcogenides, many oxides, silicates, hydroxides, and so on.

**Keywords:** Crystal, Intercalation, Deintercalation, Ethylenediamine, Structure, Layered crystals.

## INTRODUCTION

As a rule, layered materials have a strong covalent bond in the plane and have weak Van der Waals forces between the layers. They are characterized by a wide range of electronic band structures, ranging from dielectrics, semiconductors, metals, superconductors to topological insulators. Intercalation is a reversible chemical process, the introduction of alien species into the crystalline gap. In condensed matter physics, the intercalation of transition metal dichalcogenides with ions leads to waves of charge density, two-dimensional superconductivity, and interesting phase transitions. The most famous electrochemical energy device using intercalation is a lithium-ion battery, in which Li ions are reversibly intercalated in the van der Waals gaps, for charging and discharging. The intercalation region in layered materials increased sharply with the advent of a large class of graphite intercalation compounds. Intercalation in transition metal dichalcogenides has been successfully achieved by chemical transport reaction, electrochemical, ion exchange and redox methods, in which atoms, ions or molecules can be embedded substances.

Depending on the growing conditions, in the Ga-In-S system they crystallize into several layered hexagonal phases with the composition Ga1-xIn1+xS3. All these phases belong to previously known structural types. In addition to the hexagonal phases, this compound crystallizes in the orthorhombic phase. This report presents the results of intercalation of the orthorhombic phase with organic molecules. This phase is also layered and is characterized by the first discovered original structure, where gallium atoms have tetrahedral and indium atoms an octahedral environment.

The papers 1,2 are devoted to the preparation of intercalates of layered compounds (Ga, In) 2S3 with 4-AP molecules and the modeling of their crystal structures. However, as a result of intercalation, the final product is highly dispersed. Therefore, an unambiguous determination of the unit cell parameters is encountered with certain difficulties and the structure of the intercalated.

## MATERIALS AND METHODS

Crystals has not yet been established. In this paper, we present new results regarding the structure of the mentioned orthorhombic phase, its intercalation and deintercalation with 4-AP, and also on the intercalation of ethylene diamine molecules.

It is known that crystals of most layered chalcogenides belong to the hexagonal syngony and are characterized by close packed type structures. The building blocks of such structures are two-dimensionally infinite packets consisting of several alternating anion-cation layers of the type A-C-A. Repetition of such packets along to c axis forms a three-dimensional structure. Moreover, the interaction between adjacent packets is Van der Waals, and they form between the anions of the outside layers. The packages of orthorhombic Ga0.8In1.2S3 crystals consist of five atomic layers S-(Ga, In)-S-(Ga, In)-S and it is interesting that, unlike most layered crystals, the inter-packet Van der Waals region is characterized by a complex corrugated (zigzag) architecture (Fig. 2). These crystals have a light yellow color and are transparent. The authors of/1,2/ note that the orthorhombic phase were grown by the Chemical Transport Reaction (CTR) from a pre-synthesized ingot with the composition $Ga_{1-x}In_{1+x}S_3$, where $0.25 \leq \times \leq 0.50$. In the literature for crystals of the orthorhombic phase, the formula Ga0.8In1.2S3 /1,2/ was usually used. It is in good agreement with the abstract structure of this phase, where the ratio of

Tetrahedrons to octahedrons are equal. In this case, it is believed that tetrahedrons are populated by gallium atoms and octahedrons by indium atoms. However, among sulfide compounds, there are cases when indium atoms are also localized in tetrahedron. To determine the actual composition, the structure of this phase was refined using powder diffraction data (Figure. 1). Diffraction data were obtained on a "D2 phaser" diffractometer $(5 \le 2-theta \le 120)$. Structural refinement was carried out by the Rietveld method using the EVA and TOPAS-4.2 programs (Bruker, Germany).

## RESULTS AND DISCUSSION

Analysis of the diffraction pattern showed that the investigated sample consists of two phases. That is, in addition to the main orthorhombic phase Ga1-xIn1+xS3, it also contains~2.45% crystals of the rhombohedral phase In2S3. Tables 1-3 below show the results of structure refinement only for the orthorhombic Ga1-xIn1+xS3. The refinement showed that the tetrahedrons in addition to gallium atoms are occupied by indium atoms on average by 20% (atomic). Thus, the studied orthorhombic crystals are characterized by the formula Ga0.8In1.2S3. Crystallographic characteristics, coordinates of independent atoms, and interatomic distances are given in the tables 1-3 respectively. In fig. 2 shows a three-dimensional projection of a crystal structure with polyhedrons (Tables 1-3).

Table. 1. Refined parameters of the unit cell of the Ga0.8In1.2S3 compound

| Space group | A21ma |
|---|---|
| Lattice parameters at 298 K (A ) : | |
| a | 6.2060(2) |
| b | 19.0543(7) |
| c | 3.8163(2) |
| Volume (A3) | 451.27(3) |
| Density (g/cm3) | 4.26 (1) |
| R-Bregg (%) | 1.032 |

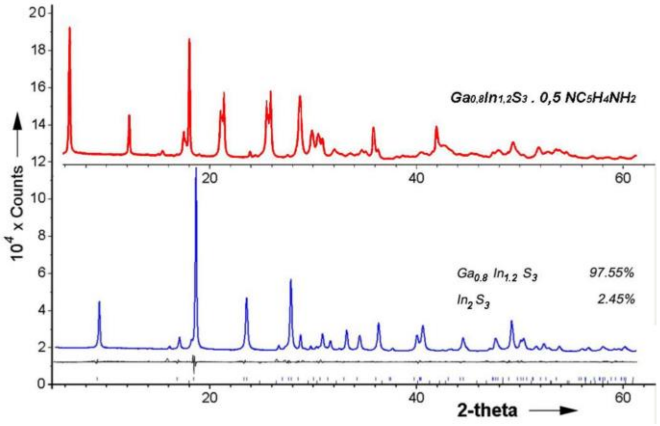

Fig 1. X-ray diffraction patterns of orthorhombic Ga0.8In1.2S3 and its intercalate with 4-AP

Table 2. Atomic positional parameters of the Ga0.8In1.2S3 crystals

| Atom | x | y | z | Atom type | Occupancy |
|---|---|---|---|---|---|
| Ga+In | 0.05074(55) | 0 | 0.11169(15) | Ga+3, In+3 | 0.80(1)+0.20(1) |
| In | 0.5 | 0.5 | 0.16679(10) | In+3 | 1 |
| S(1) | 0.2470(12) | 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 |

Table 3. Interatomic distances in the Ga0.8In1.2S3 crystals

| Atom | S(1) | S(2) | S(3) |
|---|---|---|---|
| Ga (In) | 2.428(8) | 2.330(6)x2 | 2.272(8) |
| In | 2.685(5)x2<br>2.616(8) | 2.624(9) | 2.547(5)x2 |

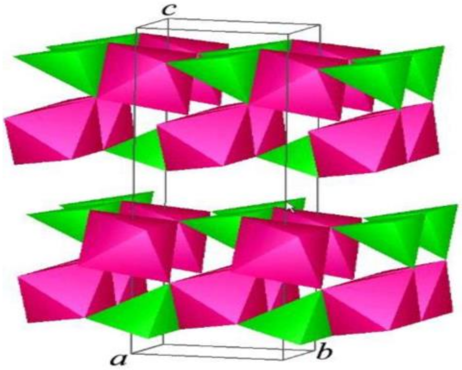

Fig 2. The structure of the orthorhombic phase of the Ga0.8In1.2S3 crystals

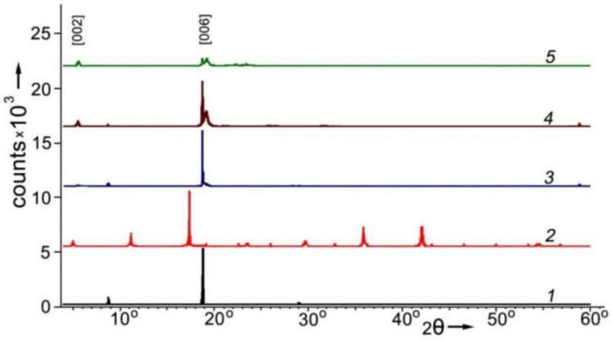

Fig 3. Diffraction patterns of crystals of the orthorhombic phase Ga0.8In1.2S3

Figure 3 shows five diffractograms. The first of them relates to crystals of the orthorhombic phase Ga0.8In1.2S3. The second diffraction pattern relates to Ga0.8In1.2S3 crystals intercalated with 4-AP. The remaining three diffraction patterns were taken from various samples obtained by the interaction of ethylene diamine with crystals previously intercalated with 4-AP. Comparison of these diffraction patterns clearly shows that, interaction with EDA led to strong structural changes. The following conclusions can be drawn:
-In diffraction patterns 3-5 no trace of the 2nd diffraction pattern. This suggests that there is a complete removal of 4AP molecules;
-Detection in the diffraction patterns of 3 and 4 lines of crystals of the original Ga0.8In1.2S3 shows a partial restoration of the Ga0.8In1.2S3 matrix crystal;
-The discovery of completely new peaks confirms the replacement of 4-AP molecules by EDA molecules; in other words, an intercalate of Ga0.8In1.2S3 crystals with ethylene diamine is formed.
-The low intensity and relatively large width of the new peaks suggests that the process is accompanied by exfoliation.

## CONCLUSION

Note that the formation of Ga0.8In1.2S3 0.5(4-AP) occurs naturally, without any particular difficulties and with the preservation of the single-crystal shape of the final product. However, our attempts to obtain analogous compounds with more symmetric analogs of 4-AP, such as phenyldiamine, pyrazine, pipyrazine, and ethylenediamine, were unsuccessful. That is, the intercalation process of orthorhombic Ga0.8In1.2S3 crystals is highly selective. The interaction of the abovementioned organic molecules with crystals that had previously been intercalated with 4-AP was also investigated.

That is, we tried to replace 4-AR molecules with phenyldiamine, pyrazine, ethylenediamine, and so on in the intercalate. Experiments with the aim of substitution with phenyldiamine and pyrazine molecules were unsuccessful, however, substitution with Ethylene Diamine (EDA) molecules led to dramatic changes, and the results of X-ray diffraction of the resulting product.

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