INTERCALATION OF ETHYLENEDIAMINE MOLECULES INTO ORTHORHOMBIC $In_{1.2}Ga_{0.8}S_3$ SINGLE CRYSTALS

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In recent years much interest has focused on the Intercalation of organic species into layered inorganic solids represents one of the useful approaches to create the ordered molecular-based materials with some novel properties.

A new intercalation compound, $In_{1.2}Ga_{0.8}S_3 \cdot 0.5(NH_2\text{-}C_5H_4N)$, is synthesized by the direct reaction of 4-aminopyridine with layered $InGaS_3$. By two-stage synthesis, more precisely, by substitution of 4-aminopyridine molecules with ethylenediamine molecules in the $In_{1.2}Ga_{0.8}S_3 \cdot 0.5(NH_2\text{-}C_5H_4N)$ intercalate, it was synthesized to intercalate with the composition $In_{1.2}Ga_{0.8}S_3 \cdot 0.5(NH_2\text{-}C_2H_4\text{-}NH_2)$. The structural parameters of intercalations and deintercalations of both the molecules were determined.

Keywords: intercalation, layered crystal; x-ray diffraction.
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INTERCALATION OF ORTHORHOMBIC $In_{1.2}Ga_{0.8}S_3$ WITH ETHYLENEDIAMINE MOLECULES

It would be noted that the intercalating of $In_{1.2}Ga_{0.8}S_3$ single crystals with 4-AP molecules under given conditions occurs naturally having preservation of crystallinity quality. However, our several attempts to synthesize analogous intercalation compounds with some similar organic molecules such as phenyldiamine, pyrazine, pipyrazine, and ethylenediamine, were unsuccessful means that the intercalation process of orthorhombic $In_{1.2}Ga_{0.8}S_3$ crystals is highly selective. We further investigated the interactions of the same molecules with the $In_{1.2}Ga_{0.8}S_3 \cdot 0.5(NH_2\text{-}C_5H_4N)$ intercalation compound where we tried to substitute 4-AP molecules with phenyldiamine, pyrazine and ethylenediamine molecules. Experiments with phenyldiamine and pyrazine molecules were unsuccessful, whereas the substitutions with ethylenediamine (EDA) molecules were accompanied by significant changes.

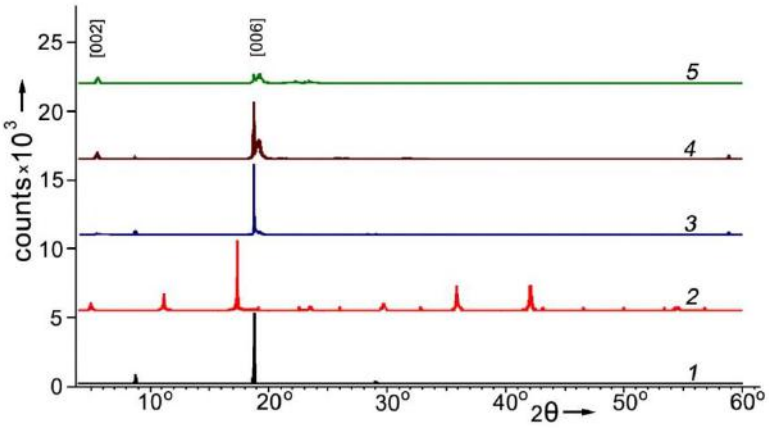

Fig. 1. XRD patterns for pristine orthorhombic $In_{1.2}Ga_{0.8}S_3$ crystal (*1*), $In_{1.2}Ga_{0.8}S_3 \cdot 0.5(NH_2\text{-}C_5H_4N)$ intercalation compound (*2*), and various samples obtained by the interaction of EDA molecules with $In_{1.2}Ga_{0.8}S_3 \cdot 0.5(NH_2\text{-}C_5H_4N)$ crystals (3)-(*5*).

Figure 1 represents the five XRD patterns for pristine orthorhombic $In_{1.2}Ga_{0.8}S_3$ crystal (*1*), $In_{1.2}Ga_{0.8}S_3 \cdot 0.5(NH_2\text{-}C_5H_4N)$ intercalation compound (*2*), and various samples obtained by the interaction of EDA molecules with $In_{1.2}Ga_{0.8}S_3 \cdot 0.5(NH_2\text{-}C_5H_4N)$ crystals (3)-(*5*). By comparing these diffraction patterns one can say that the intercalation of EDA into the $In_{1.2}Ga_{0.8}S_3 \cdot 0.5(NH_2\text{-}C_5H_4N)$ crystals accompanied by significant structural changes in the matrix intercalation crystals.

As can be seen, there is no any diffraction line in the diffractogram (*2*) that matches with patterns (3)-(5). This is in turn confirms that the complete extraction of 4AP molecules from $In_{1.2}Ga_{0.8}S_3 \cdot 0.5(NH_2\text{-}C_5H_4N)$ crystals occurs. Moreover, appearing typical diffraction lines for the orthorhombic $In_{1.2}Ga_{0.8}S_3$ in the diffraction patterns (*3*) and (*4*) means that the $In_{1.2}Ga_{0.8}S_3$ matrix crystals are partially recovered. The detection of new diffraction peaks in the patterns (3)-(4)-confirms that the EDA

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molecules substitute 4-AP molecules and a new intercalation compound with ethylenediamine is formed. A weak absolute value and relatively large width of the new peaks in patterns (3)-(5) indicate the possible exfoliation of the matrix crystal during the intercalation of EDA molecules into the layers.

The unit cell parameter *c* of the EDA intercalated crystals was calculated as ~13.975 Å from the diffraction patterns (*3*)-(*5*) within the 2θ range from~ 6.4 to 19.1 where the newly appeared peaks observed. In comparison with $In_{1.2}Ga_{0.8}S_3 \cdot 0.5(NH_2\text{-}C_5H_4N)$, the *c* parameter is decreased by ~1.9 Å. Such a change is quite expected since the molecular size of EDA is significantly smaller than 4-AP.

[1] *P. Trucano, R. Chen.* Structure of graphite by neutron diffraction Locality. Nature, 1975, 258, 136-137.

[2] *Ruge Quhe, Shenyan Feng, Jing Lubc and Ming Lei.* Electronic properties of layered phosphorus heterostructures. www.rsc.org/pccp.,(2016) DOI: 10.1039/c6cp06583j

[3] *Liangzhi Kou, Yandong Ma, Xin Tan, Thomas Frauenheim, Aijun Du, Sean Smith.* Structural and Electronic Properties of Layered Arsenic and Antimony Arsenide. *J. Phys. Chem. C* 2015, 119, 12, 6918–6922. https://doi.org/10.1021/acs.jpcc.5b02096

[4] *C.S. Barrett, P. Cucka, K. Haefner.* The Crystal Structure of Antimony at 4.2, 78 and 298 K. Acta Crystallographica (1,1948-23,1967), 1963, 16, 451-453.

[5] *Zheng Wei, Cristina Dubceac, Marina A. Petrukhina, Evgeny V. Dikarev.* From a volatile molecular precursor to twin-free single crystals of bismuth. Chem. Commun., 2019, 55, 5717. DOI: 10.1039/c9cc02820j

[6] *P. Joensen, R.F. Frindt, & S.R. Morrison.* Single-layer MoS2. *Mater. Res. Bull.* 21, 457–461 (1986).