

## Investigation of Phase Diagrams of In<sub>2</sub>Se<sub>3</sub>–Sb<sub>2</sub>Se<sub>3</sub> and In<sub>2</sub>Se<sub>3</sub>–Bi<sub>2</sub>Se<sub>3</sub> Binary Systems

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**Abstract:** Phase diagrams of In<sub>2</sub>Se<sub>3</sub>–Sb<sub>2</sub>Se<sub>3</sub> and In<sub>2</sub>Se<sub>3</sub>–Bi<sub>2</sub>Se<sub>3</sub> binary systems were constructed based on DTA and X-ray diffraction analysis data. There are no intermediate compounds in the In<sub>2</sub>Se<sub>3</sub>–Sb<sub>2</sub>Se<sub>3</sub> system but two finite regions of In<sub>2</sub>Se<sub>3</sub>-based solid solutions were found: the first one, called β' (from 11 to 3.6 mol% Sb<sub>2</sub>Se<sub>3</sub>), of the tetradymite structure, and the second (from 3.6 to 0 mol% Sb<sub>2</sub>Se<sub>3</sub>) being the β-In<sub>2</sub>Se<sub>3</sub> stabilized form, these results are nearly same obtained by D. Eddike work (5). Also, there are no intermediate compounds in the In<sub>2</sub>Se<sub>3</sub>–Bi<sub>2</sub>Se<sub>3</sub> system but there are wide ranges of solid solutions based on the terminal compounds and an intermediate range of de-mixing. The solid solutions are of tetradymite type. Their limits are related to the substitution of the bismuth-indium atoms in the layers. Electrical conductivity and thermoelectric power measurements confirm the boundaries of the solid solution regions deduced based on the thermal and X-ray diffraction data analyze.

**Keywords:** Chalcogenides, Crystal growth, Differential scanning calorimeter, X-ray diffraction, Phaseequilibria, Electronic materials

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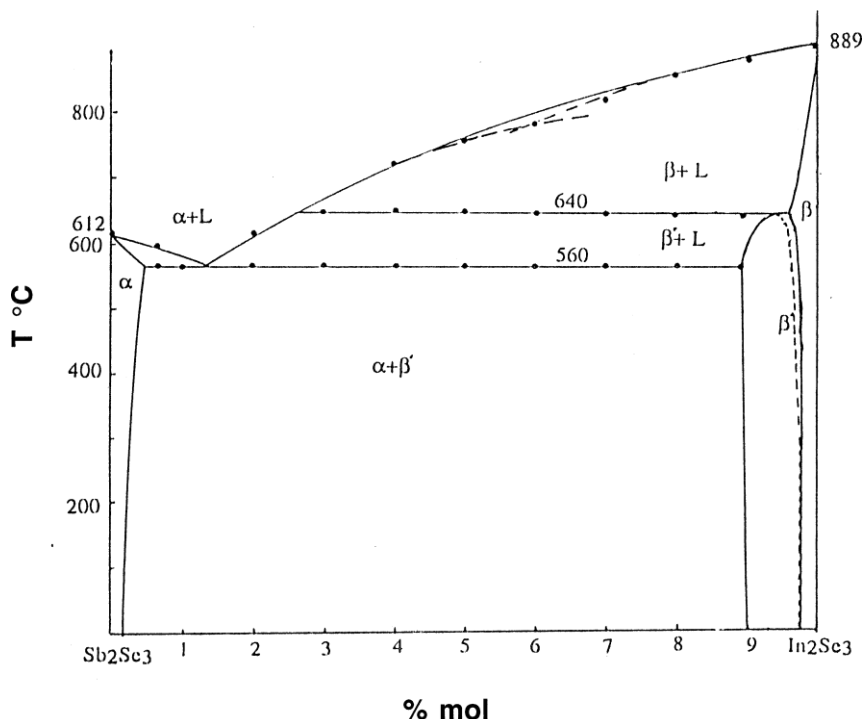
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### I. Introduction

The indium selenide compound In<sub>2</sub>Se<sub>3</sub> is interesting for its semiconducting properties [1], mainly in thermoelectric applications. Phase diagram of Bi<sub>2</sub>Se<sub>3</sub>–In<sub>2</sub>Se<sub>3</sub>, show that the only bismuth-doped In<sub>2</sub>Se<sub>3</sub> form encountered is the β-In<sub>2</sub>Se<sub>3</sub> form, which is unstable at room temperature. The Bi<sub>2</sub>Se<sub>3</sub> structure is isomorphous with smaller cell parameters ( $a = 4.13 \text{ \AA}$ ,  $c = 28.7 \text{ \AA}$ ) and smaller bond lengths (Bi–Se' = 2.99 Å, Bi–Se<sub>2</sub> = 3.05 Å, and Se'–Se<sub>2</sub> = 3.30 Å) [2]. At room temperature, In<sub>2</sub>Se<sub>3</sub> can crystallize in several different structures depending on synthesis conditions [6]. We have pointed out that the substitution of the indium atoms by bismuth (or antimony) atoms, even in very low quantity (< 1%), results in the formation of the tetradymite-type rhombohedral structure (R3m) isomorphous. The cell parameters for the (In<sub>0.98</sub>Bi<sub>0.02</sub>)<sub>2</sub>Se<sub>3</sub> composition are  $a = 3.972(2) \text{ \AA}$  and  $c = 28.15(3) \text{ \AA}$ , the In–Se octahedral bond length being about 2.95 Å with a Se'–Se' distance of 3.55 Å between adjacent layers.

### II. Results and Discussion

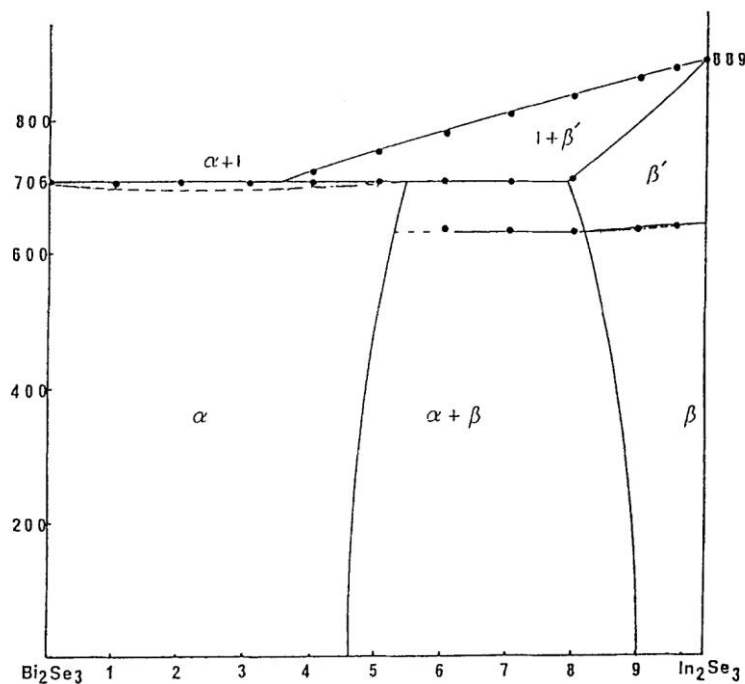
The alloys were synthesized at 10 mol% Sb<sub>2</sub>Se<sub>3</sub> intervals from the elements in evacuated quartz ampoules. All the samples were synthesized from a stoichiometric mixture at 970°C and kept at this temperature for 3 hours, then cooled to 490°C and annealed for 8 days. The phase diagram was constructed based on DTA and X-ray diffraction (XRD) analysis data. Neither a finite compound like InSbSe<sub>3</sub> nor the polymorphic transitions based on In<sub>2</sub>Se<sub>3</sub> are observed. On the other hand, a narrow range of solid solution based on In<sub>2</sub>Se<sub>3</sub> is determined from 92 to 97 In<sub>2</sub>Se<sub>3</sub> mol% (called β'). Its structure is isomorphous of the tetradymite, rhombohedral R3<sup>-</sup>m. The unit cell for the composition 10mol% Sb<sub>2</sub>Se<sub>3</sub> has the dimensions  $a = 395.6(4) \text{ pm}$ ,  $c = 2810 \text{ pm}$  (refer to work at 5). With less than 3 mol% Sb<sub>2</sub>Se<sub>3</sub>, the solid solution is still rhombohedral but the XRD lines have different relative intensities, indicating small shifts of either the atoms in the layers or the whole layers one to the other. The XRD pattern corresponds to that of the Popovic β-In<sub>2</sub>Se<sub>3</sub> phase with the cell parameters  $a = 397.2(4) \text{ pm}$ ,  $c = 2827(2) \text{ pm}$ . β has a volume roughly 1.5% greater than that of β'. β' is formed peritectic at 640°C: β + L = β'. The concentration of the Sb<sub>2</sub>Se<sub>3</sub>- based solid solution a reach less than 3 mol% In<sub>2</sub>Se<sub>3</sub> at room temperature. The eutectic between a and β' contains 86 mol% Sb<sub>2</sub>Se<sub>3</sub> and has a melting point of 560°C. In the diffraction patterns of alloys containing from 97 to 10 mol% Sb<sub>2</sub>Se<sub>3</sub>, the intensity of the lines typical of Sb<sub>2</sub>Se<sub>3</sub> (orthorhombic structure) decreases and new lines confirming the presence of the β' phase appear.



**% mol**  
**Phase diagram of the  $\text{Sb}_2\text{Se}_3\text{-In}_2\text{Se}_3$  system.**  
**FIG 1**

The liquidus line is much different from that gained by P.G. Rustanov(3), even for the small inflection at 60 mol%  $\text{In}_2\text{Se}_3$  that could correspond to a de-mixing tendency in the liquid state as shown in fig 1.

Preparation of  $\text{In}_2\text{Se}_3$  by melting of the elements (from 610° to 820° C) with rapid cooling, without any special conditions, one always obtains a phase, which is considered the stable phase at high temperature(according to work at 4). This phase has two different polytypic structures: hexagonal,  $a = 4.02 \text{ \AA}$ ,  $c = 19.12 \text{ \AA}$ ; and rhombohedral,  $a = 4.02 \text{ \AA}$ ,  $c = 28.76 \text{ \AA}$ .



**Mole%**  
**Phase diagram of the  $\text{Bi}_2\text{Se}_3\text{-In}_2\text{Se}_3$  system.**  
**FIG2**

The substitution of indium by bismuth atoms, even in very low quantity stabilizes the rhombohedral form, isomorphous with tetradymite, therefore isomorphous with the Bi<sub>2</sub>Se<sub>3</sub> structure [7,8]. Two compounds form a continuous solid solution as shown in fig2.

### III. Conclusions

In the Bi<sub>2</sub>Se<sub>3</sub>-In<sub>2</sub>Se<sub>3</sub> system, there is only one symmetry site for the metal (Bi or In) and the substitution occurs preferentially either in the bismuth layers on the Bi<sub>2</sub>Se<sub>3</sub> side or in the indium layer on the In<sub>2</sub>Se<sub>3</sub> side.

From In<sub>1.8</sub>Sb<sub>0.2</sub>Se<sub>3</sub> to In<sub>1.93</sub>Sb<sub>0.07</sub>Se<sub>3</sub>, we found finite solid solution  $\beta'$  with the tetradymite structure, and from In<sub>1.93</sub>Sb<sub>0.07</sub>Se<sub>3</sub> to In<sub>2</sub>Se<sub>3</sub>, a solid solution of substitution based on the binary  $\beta$ -In<sub>2</sub>Se<sub>3</sub> phase, the structure of which is similar. The addition of antimony atoms stabilized the  $\beta$ -In<sub>2</sub>Se<sub>3</sub> phase but not a phase, as was determined earlier [4,5]. Hexagonal parameters correspond to the trigonal ones we found [ $a' = 397$ ,  $c' = 1887$  pm vs.  $a = 397$ ,  $c = 2827$  ( $3/2c'$ ) pm]. The electrical conductivity values of single crystals of that  $\beta$ -In<sub>2</sub>Se<sub>3</sub> phase (In<sub>1.94</sub>Sb<sub>0.06</sub>Se<sub>3</sub>) collected at room temperature were found to agree with those in the literature. Overall the results show that, in both systems (In<sub>2</sub>Se<sub>3</sub>–Sb<sub>2</sub>Se<sub>3</sub> and In<sub>2</sub>Se<sub>3</sub>–Bi<sub>2</sub>Se<sub>3</sub>) no stable compounds observed but only finite regions exist.

### References

- [1]. Мирзоева Р.Д. Аллазов М.Р. Шихалибеги Ш.Ш. Бабанлы М.Б. Международный журнал прикладных и фундаментальных исследований. – 2014. – № 8 (часть 1) – С. 35-39.
- [2]. Qianfan Zhang,† Zhiyong Zhang,‡ Zhiyong Zhu,§ Udo Schwingenschloß,§ and Yi Cui†,^,\* VOL 6 ' NO. 3 ' 2345–2352 ' 2012, American Chemical Society.
- [3]. T.N. Guliev, E.V. Magerramov, and P.G. Rustanov, Izv. Akad. Nauk SSSR, Neorg. Mat. 13 (4), 627 (1977).
- [4]. H. Ghoumari Bouanani, D. Eddike, B. Liautard and G. Brun, Materials Research Bulletin, Vol. 31, No. 2, pp. 177-187, 1996.
- [5]. D. Eddike1, A. Ramdani1, G. Brun2, J.C. Tdenac2, and B. Liautard2, Materials Research Bulletin, Vol. 33, No. 3, pp. 519 –523, 1998.
- [6]. Ye,J.;Soeda,S.;Nakamura,Y.;Nittono,O.Crystal Structures and Phase Transformation in In<sub>2</sub>Se<sub>3</sub> Compound Semiconductor. Jpn. J. Appl. Phys. 1998, 37, 4264–4271.
- [7]. Zhang, Y.;He,K.;Chang,C.Z.;Song,C.L.;Wang,L.L.;Chen, X.; Jia, J. F.; Fang, Z.; Dai, X.; Shan, W. X.; et al. Crossover of the Three-Dimensional Topological Insulator Bi<sub>2</sub>Se<sub>3</sub> to the Two-Dimensional Limit. Nat. Phys. 2010, 6, 584–588.
- [8]. Zhang, H.J.;Liu,C.X.; Qi,X.L.;Dai,X.; Fang,Z.;Zhang,S.C. Topological Insulators in Bi<sub>2</sub>Se<sub>3</sub>, Bi<sub>2</sub>Te<sub>3</sub> and Sb<sub>2</sub>Te<sub>3</sub> with a Single Dirac Cone on the Surface. Nat. Phys. 2009, 5, 438–442.

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