IJCRT.ORG ISSN : 2320-2882

INTERNATIONAL JOURNAL OF CREATIVE RESEARCH THOUGHTS (IJCRT)

An International Open Access, Peer-reviewed, Refereed Journal

Electrical Properties of Doped SbSI and SbTeI Compounds

Archana Singh[1], , D. E. Kshirsagar[2], Vijay S. Jadhav[2], Harish K. Dubey[2*]

[1]*Department of Chemistry, B. K. Birla College (Autonomous), Kalyan, India*
[2]*Department of Physics, B. K. Birla College (Autonomous), Kalyan, M.S., India*

Abstract:

The Chalcogenide compounds of group V-VI-VII have attracted the minds of researchers due to their multifunctional properties. They exhibit many rare combinations of strongly coupled photoconductive, semiconductive, Pyroelectric and ferroelectric properties which have been subjects of much recent interest. SbSI is one of most extensively studies compound of this series. It is expected that introduction of impurities may lead to some constructive changes in the properties of the compound. Therefore, synthesis of doped SbSI and SbTeI was carried with solid state thermal reaction technique. Tin and Indium were the two dopants introduced in place of Antimony and Sulfur. Composition of the elements present in each of these materials was examined by EDAX. The electrical conductivities of the doped materials were compared with the pure SbSI material. The dielectric constants of the samples were calculated using the capacitance of the material.

Keyword: SbSI, SbTeI, Tin, Indium, doped material, EDAX, Dielectric Constant.

1. Introduction:

The growth of $A^{V} B^{VI} C^{VII}$ [Where A= Sb, Bi; B= S, Se, Te and C= I, Cl, Br) compounds have been reported by various methods. Antimony sulphoiodide (SbSI) and Antimony Tellurium Iodide (SbTeI) are two of these ternary chalcogenide compounds of this group having unusually large number of interesting properties. They exhibit many rare combinations of strongly coupled photoconductive, semiconductive, Pyroelectric and ferroelectric properties which have been subjects of much recent interest. Furthermore, the crystal exhibits large electro-optical and electro-mechanical effects. Being a promising material with potential applications, SbSI was synthesized by many researchers in a variety of ways. For the first time SbSI was synthesized by Donges in 1950. Since then, a lot of techniques have been used to produce SbSI crystals. In most of the reported papers Sb_2S_3 and SbI_3 are used as the starting material to derive SbSI with the following chemical equation. The use of the elements Sb, S and I were avoided with a view that Sb, S and I unite exothermally generating a huge vapor pressure which may lead to explosion. To overcome the expected problem, it was thought to synthesis SbSI by a novel technique using Sb, S and I as the starting material. It was reported by us for the first time. SbTeI being the compound of the same family, later, its synthesis was also carried out with the similar technique. The electrical study of these compounds reveals some interesting results. However, it was also assumed to dope these materials with the elements from the neighbouring groups. Sn and In were chosen elements used for doping both SbSI and SbTeI. The comparison of the electrical properties of these doped materials are reported in this paper.

2. Experimental:

2.1 Developing SbSI and SbTeI Crystals:

In the present study initially needled shaped crystals of SbSI and SbTeI were developed. The AR grade powder of the constituent elements i. e. Sb, S/Te and I resublimed were weighted in the stoichiometric ratio. The elements were loaded in a quartz tube, evacuated to 10^{-5} Torr and sealed. The tube was then loaded in a programmable furnace. The furnace was programmed to achieve the 400 ^{o} C in 24 hrs and was retained at the same temperature for 480 hrs (20 days). The furnace was cooled @ 15 ^{o}C / hr. Temperature gradient was established at the growth end by inserting it inside a ceramic tube of diameter little higher than that of the quartz ampoule containing the mixture of Sb, S/Te and I. Figure 1 gives an experimental setup of the synthesis of pure and doped compounds. It was noticed that the dimensions of the crystal increases with the reaction Time.

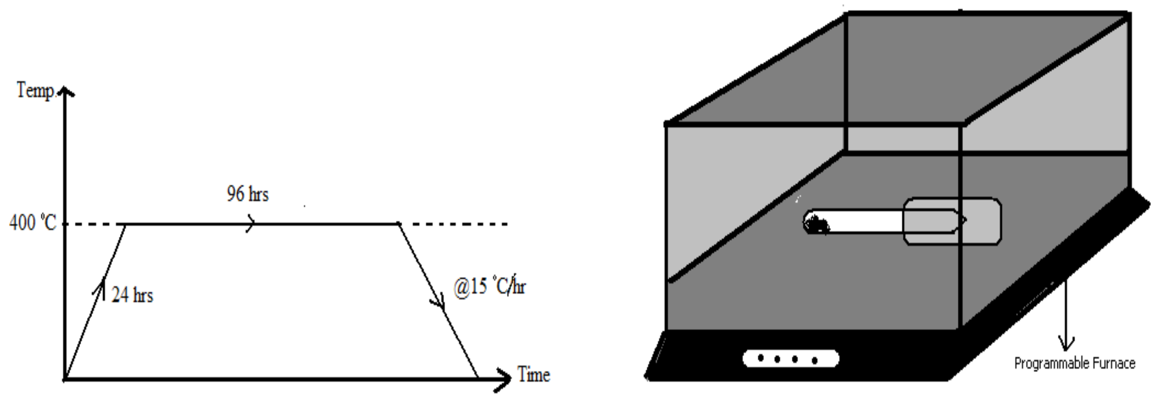

Fig. 1: Schematic diagram of the setup used to synthesize SbSI and SbTeI

Both the products were found in the form of the bundle of shiny needle shaped crystals oriented along c–axis at the bottom of the ampoule. When observed under microscope, the crystals looked reddish and transparent. Figure 2 shows some needle shaped crystals synthesised by Solid State Thermal reaction.

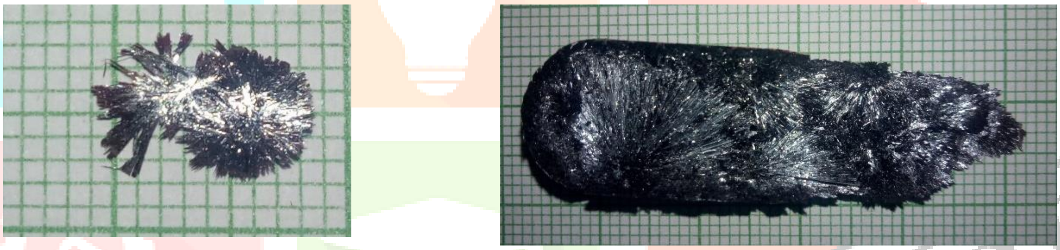

Fig. 2 : SbSI and SbTeI Crystals grown by Solid State Thermal Reaction

2.2 Growth of doped SbSI and SbTeI Crystals:

Doping of the two compounds was done by introducing Tin/Indium in place of Antimony and Sulfur in SbSI and Antimony and Tellurium in SbTeI. The composition of the doped compound was such that 50% of the weight of Sb/S/Te was replaced by Sn/In. The doped compound was also synthesised with the similar synthesis parameters as that of the pure SbSI and SbTeI compounds. As a result many quaternary compounds like $Sb_{1-x}Sn_xSI$, $Sb_{1-x}In_xSI$, $SbS_{1-x}Sn_{-x}I$, $SbS_{1-x}In_xI$, $Sb_{1-x}Sn_xTeI$, $Sb_{1-x}In_xTeI$, $SbTe_{1-x}Sn_xI$, $SbTe_{1-x}In_xI$ (where x = 0.5), etc were synthesized using the solid state thermal reaction technique. An abnormal behaviour is shown by $Sb_{1-x}In_xTeI$ sample. Firstly, this sample did not grow in the form of needle shaped crystal. Secondly, the sample got liquefied when kept in the air environment for 4-5 hrs. They again got solidified when heated to 100 ^{o}C.

2.3 Characterisation:

The SbSeI and SbTeI compounds were characterised by SEM, EDAX, XRD and Raman Spectroscopy. However, the doped compounds were just characterised by EDAX only to check the percentage composition of the doped quaternary compound.

2.4 Study of Electrical Properties:

The electrical resistivity and conductivity of the compounds were determined by indigenously developed Two Probe setup. Variation of resistance of SbSI sample at different temperature was studied for constant currents of 30 mA, 50 mA and 100 mA.. Knowing the dimensions of the sample, the electrical resistivity and hence the conductivity was found at different temperature. Fig. 3 shows the experimental setup of the Two Probe setup.

Fig. 3 The Two Probe setup

A circular pellet of 1 cm diameter of the compounds was made. Two parallel plates of the similar shape and dimension were used to construct a parallel plate capacitor. Two leads were taken out of these plates to connect to the capacitance measurement unit. To avoid the addition of the stray capacitance to the net capacitance of the material, initially the capacitance of the empty capacitor (without material) along with leads (without material) was measured. This value is subtracted from the net capacitance of the material.

We used Ablab LCR-Q meter to measure the capacitances of the SbSI, SbTeI and other materials by constructing a parallel plate capacitor as shown in the fig. 4.

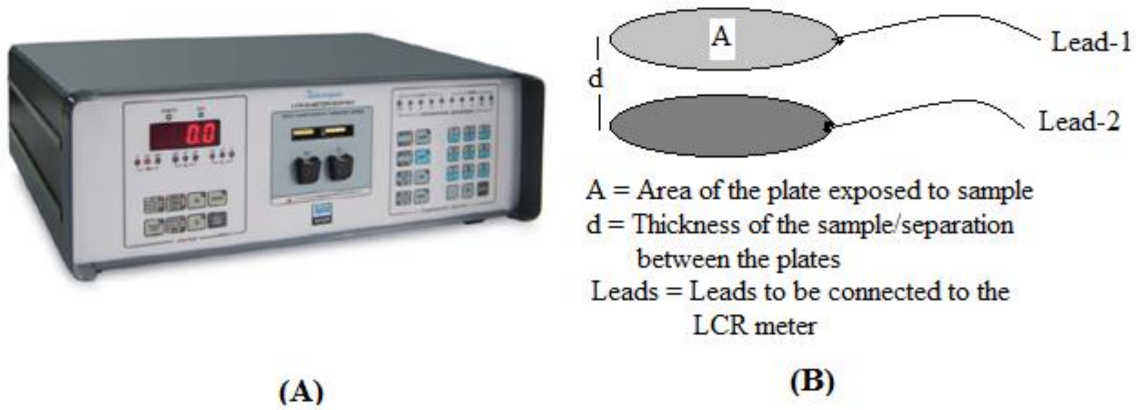

Fig. 4: Setup used in the measurement of dielectric constant.

For better accuracy, instead of taking the ratio of the two capacitances, we found only the capacitance of the capacitor with material and subtracted the stray capacitance from it. Hence the thickness of the sample (d) and the area of the surface exposed to the plates were also determined.

3. **Results and Discussion:**

It was noticed that the phase transition in the sealed ampule takes place at the varied temperatures. Although it was not possible to be observed physically in the closed furnace, but it is expected that the powdered mixtures of the constituent elements must have melted at their respective melting points. The vapours of these constituents must have reacted within the ampule to form the ternary and quaternary compound. It is revealed that the compound crystalises in the bunches of needles shaped predominant crystals observable by necked eye. The SEM images reveal its structure to be rod shaped orthorhombic crystal as seen in Fig 3. The lattice parameters calculated from the XRD data support the structure observed in the SEM images.

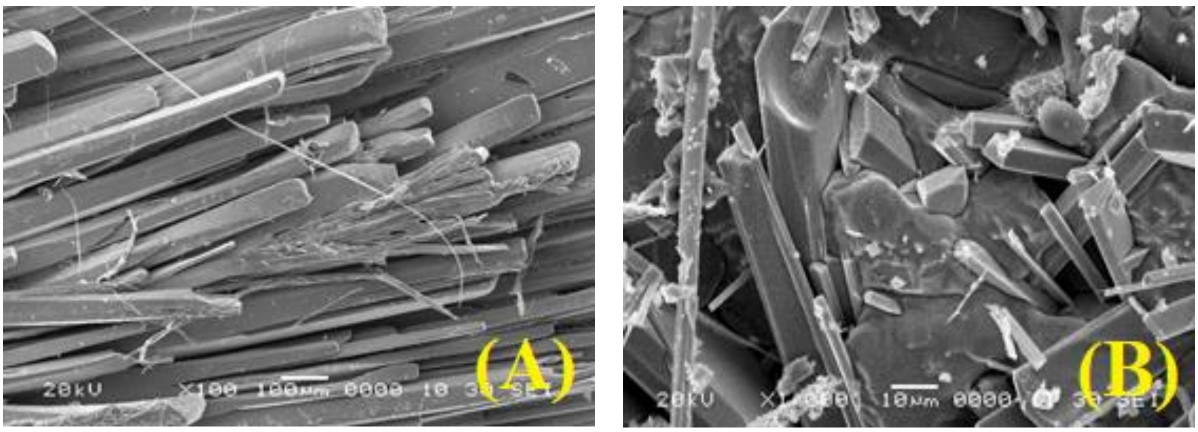

Fig. 5: SEM images of (A) SbSI Crystals and (B) SbTeI Crystals

As the crystals were not significantly large and no facility was available to analyze the available small single crystals, the crystals were powdered with the small hand grinders and pressed with 140 Kg/cm^3 pressure for 24 hrs with a 10 ton hydraulic to make pellet. The pellets were circular with 1 cm diameter and 0.5 to 1.5 mm thickness. Pellets were made without the use of any binder. To make the pellets strong, they were sintered for 90 min at 200 ^{o} C. Pellets of SbSI, SbTeI and doped materials were used to study the electrical and dielectric properties. It was evident that the resistance of the sample decreased from 60K to 20K, there after it remained constant up to about 7K (about 0.192 ohms) and then there was sudden decrease in the resistance at about 5K.There is some difference in the values of the resistance at 20K of SbSI (12µΩ) to that obtained with SbTeI (0.192 Ω).This suggests that though there is a transition at this temperature but is not due to superconductivity, because its resistance is still not equivalent to zero as was the case with SbSI. There is a need to establish whether there is any change in the structure of SbTeI at this temperature. Like SbSI the resistivity of SbTeI was also measured in the 300 K to 550 K range. The resistivity of SbSI was calculated to be 5.63 X 104 (Ω-cm) whereas the activation energy was found to be 1.04 eV.

Table 1 gives the values of the resistivity, conductivity, activation energy, band gap and dielectric constant of the samples prepared by doping SbSI and SbTeI by Sn and In. As the values of the resistances of the doped materials obtained by the two methods were found to be very high in the range to 2000.

Sample	**Resistivity (ρ) Ω-cm**	**Conductivity (σ) $(\Omega\text{-cm})^{-1}$**	**Activation Energy (E_a) eV**	**Band gap (E_g) eV**	**Dielectric Constant**
$SbS_{1-x}In_xI$ (x=0.5)	8 X 10^6	1.3 X 10^{-7}	0.33	0.66	738
$SbS_{1-x}Sn_xI$ (x=0.5)	3 x10^7	3 X 10^{-8}	0.42	0.83	2253
$Sb_{1-x}Sn_xSI$ (x=0.1)	3.96 X 10^4	2.52 X 10^{-5}	0.35	0.70	1390
$SbTe_{1-x}Sn_xI$ (x =0.5)	2 x 10^3	6 X 10^{-4}	0.20	0.38	1520

Table 1: Values of the typical characteristic of the Sn and In doped SbSI and SbTeI samples

4. Conclusion:

Electrical resistivity and conductivity of SbSI, SbTeI and doped compounds were calculated using two methods. The resistance of both the compounds in the temperature range from 4K to 300 K was determined. Although resistance vs. temperature profile shown by SbTeI is similar to SbSI, its resistance in the low temperature region is much higher compared to SbSI. On the other hand, its value in the high temperature range is lower compared to SbSI. The activation energy and band gap of SbSI is higher compared to SbTeI. This reveals that SbTeI is a better semiconductor in the higher temperature range. As far as dielectric properties are concerned, the dielectric constant of SbTeI is higher compared to SbSI. The electrical properties like resistivity, conductivity, activation energy of conduction and dielectric constants were found for the selected doped compounds. From the results obtained it revealed that the introduction of Sn and In at S site of SbSI decreased the resistivity and activation energy to a smaller extent. But doping of Sn at the Sb site in SbSI gives much better results compared to the earlier. Doping with In in SbTeI is not possible as the formed compound gets liquefied when kept in open environment whereas doping Sn forms a stable compound. The doping SbTeI with Sn at Te site depresses the resistivity and activation energy significantly. Thus, it can be concluded that Sn and In are the suitable dopants to improve the conductivity of the SbSI and SbTeI.

5. Reference:

1. Kichambare P., Sharon Maheshwar, Solid State Ionics, 62 (21), 1993.
2. Kichambare P., Sharon Maheshwar, Solid State Ionics, 101(155), 1997.
3. Wilayat Khan, Sajjad Hussain, Jan Minar and Sikander Azam. Journal of electronic materials, 47 (2): 1131–1139, 2017.
4. E. Fatuzzo, G. Harbete, W. J. Merz, R. NMerz, R. Nitsche, H. Roetschi, W. Ruppel. Physics Review. 127 (6): 2036, 1962.
5. R. Nitsche and W.J. Merz, Journal of Physical Chemistry Solids, 13: 154-155, 1960.
6. Arief C. Wibowo, Christos D. Malliakas, Zhifu Liu, John. A. Peters, Maria Sebastian, Duck Young Chung, Bruce W. Wessels, Mercouri G. Kanatzidis, norg. Chem. 52 (12): 7045-7050, 2013.
7. Ke Xu, Hao Zhang, Zeyu Ning, Hezhu Shao, Gang Ni, Jing Li,
8. Yongyuan Zhu, Heyuan Zhu, Costas M. Soukoulis, Wiley Online library,

2018.

9. Soonie J, Cho G, Kim WT, Kwun S. Solid State Communication, 8 (11): 1043-1046, 1988
10. Berlincourt D., Hans Jaffe, Merz W. J. and Nitsche R. (1964), Applied Physics letters, 4 (3): 61-63, 1964.
11. Dubey Harish K, Deshmukh L. P. , Khirsagar D. E. , Madhuri Sharon and Maheshwar Sharon. Advances in Physical Chemistry, 2014: 1-6, 2013.
12. Dubey Harish K., Deshmukh L.P., Kshirsagar D. E., Jadhav Vijay S. , Madhuri Sharon and Maheshwar Sharon, J. Nepal Chem. Soc. 30 (11) 2011.
13. M. Nowak, B. Kauch, P. Szperlich, M. Jesionek, M. Kepinska, L. Bober, J. Szala, G. Moskal, T. Rzychon, D. Stroz. Ultrasonics Sonochemistry, 16: 546-551, 2009.
14. Patidar D., Rathore K. S., Saxena N. S., Sharma Kananbala and Sharma T. P., Chalcogenide Letters, 5(2): 21, 2008.
15. Nkum R. K., Adimado A. A. and Totoe H.), Material Science and Engineering, B55:102, 1998.
16. Raciti1 R. , Bahariqushchi R. , Summonte C. , Aydinli A. , Terrasi1,and S. Mirabella1 A., Journal of Applied Physics 121, 115304, 2017.
17. G. P. Voutsas and P. J. Rentzeperis, Zeitschrift für Kristallographie- Crystalline Materials, 16, 1-2, 1982.