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Ferroelectric SbSI-Crystals Exhibiting Dual Electrical Nature

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ABSTRACT

We report synthesis and characterization of rod shaped SbSI crystals that exhibit semiconducting and metallic properties as well. The shiny crystals of SbSI were synthesized using powders of antimony, sulphur and iodine as the precursors by an indigenously developed chemical vapour deposition (CVD) technique. The as-obtained crystals were characterized through the SEM, EDS, XRD, micro Raman analysis and electrical conductivity techniques. The crystal composition was determined by an EDS technique and is found to be very nearly stoichiometric. Surface morphology by SEM showed needle shaped crystallites of 50-100 µm in size. The X-ray diffraction studies gave crystalline nature with a good match of interplaner distances (d), reflected intensities (I/Imax) and lattice constants revealing orthorhombic phase structure of SbSI. Micro- Raman analysis showed characteristics peaks at 12 cm-1, 70 cm-1, 81 cm-1, 90 cm-1, 118 cm-1, 151 cm-1, 226 cm-1 and 331 cm-1 confirming the crystal to be SbSI. SbSI showed semiconducting behaviour in the range of temperature from 300K to 525K whereas it behaves as Metallic in the 300K to 4K temperature range.

Keywords: Orthorhombic, SbSI, CVD, electrical conductivity, semiconductor to superconductivity transition.

I. INTRODUCTION

SbSI is a ferroelectric material with the Curie point at about 20^{o}C and has the highest Curie temperature in the class of compounds of V-VI-VII series. It crystallizes in orthorhombic rod like structure with the lattice constants: a = 8.49 Å, b = 10.1 Å and c = 4.16 Å [1,2]. The typical crystal structure of SbSI is shown in fig. 1.

Its rod shaped crystals are composed of double chains of $(Sb_2S_2I_2)n$ (fig. 1A) having covalent bonds and weak Vander Waals forces between the neighbouring chains. These rods are usually grown in bunches along c- axis coinciding with the ferroelectric (polar) c-axis (fig. 1B) [2].

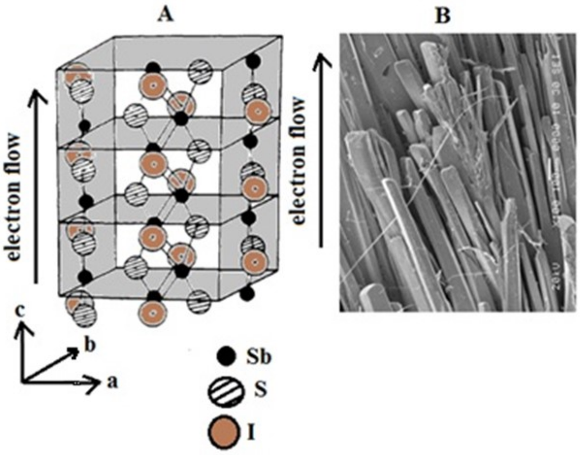

Fig. 1 (A) Orthorhombic structure of SbSI showing the proposed direction of flow of electron in c-

direction and (B) SEM Image of SbSI obtained by a CVD method.

This structure has some similarity with bismuth and thallium based superconductors. SbSI is a ferroelectric semiconductor [3-6] and has attracted the attention of physicists for its large number of interesting properties such as pyroelectric [7-9], photoconductive [10-11], piezoelectric [12-14], electro-optic [15] and other nonlinear dielectric effects [16-17]. However, to the best of our knowledge no study has been reported with SbSI for its electrical conductivity properties in the temperature range below 300K. In the present paper, we report our efforts on the synthesis of SbSI by an indigenously developed chemical vapor deposition method and its characteristic properties thorough the XRD, SEM, micro Raman analysis and electrical conductivity measurements in the 4K to 550K temperature range.

II. METHODS AND MATERIAL

II.1 Synthesis of SbSI by a chemical vapour deposition technique

In a CVD setup, vapours of the three constituent elements (antimony, sulphur and iodine) are to be produced at some suitable temperature and transported to one place where recombination reaction takes place to form SbSI. This requirement needs a provision to interconnect three furnaces such that, from each furnace, the vapours of the individual element are transported to one common place for reaction to take place. A CVD unit consisting of three furnaces each controlled with a separate temperature controller, three quartz tubes containing three constituents (i.e. Sb, S and I), Ar gas to carry the vapours of elements into the quartz tube containing Sb and a gas flow controller was developed in our laboratory [18]. Fig. 2 shows its block diagram .

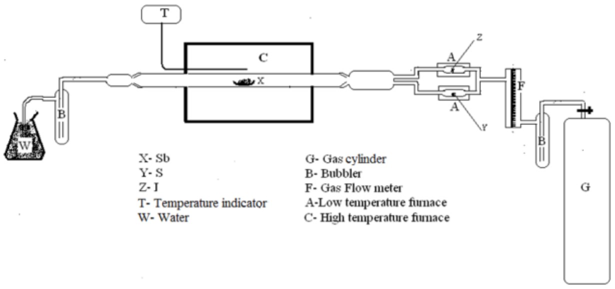

Fig. 2. Block diagram of a CVD unit

Known quantity of powdered Sb (2 gm) was kept in a quartz boat (X) and was placed inside the quartz tube having two inlets and one outlet openings. Powders of other two elements were placed in the two interconnected quartz tubes having two openings placed in two furnaces (A). The known quantities of sulfur (Y) (2 gm) and iodine (Z) (2 gm) were kept in the respective quartz tubes. To carry the vapours of sulfur and iodine, Ar gas was allowed to carry the vapours from two quartz tubes (A) to quartz tube (X) which contains Sb. Flow rate (0.5 cc/min) of carrier gas was controlled by a flow meter (F). Care was taken to allow equal flow rate of carrier gas into the two quartz tubes (A). A gas bubbler (B) was also introduced at the outlet of the quartz tube. The gas coming out of the reaction tube was bubbled into flask (W) containing water. Initially the quartz tube was flushed with Ar to make entire tube free of oxygen. Thereafter, the furnace (C) was switched ON to attain the set temperature. Two quartz tubes containing Sulfur and iodine were heated to attain the melting points of the respective elements. Care was taken so that the carrier gas from furnace (A) could flow to furnace (C) only when the temperatures of the furnaces (A) and (C) had attained the melting point of the respective materials kept in each furnace. Thus, vapours of S and I were transported by the Ar gas to the quartz tube containing molten Sb. The reaction time of the process was optimized to 6 hrs. The reaction amongst these three elements takes place in the quartz tube (X) at its set temperature. We tried three temperatures typically, 650oC, 750^{o}C and 850^{o}C. It was observed that crystals were grown nicely at 650°C. At the end of the experiment, rod shaped SbSI was taken out and characterized by the XRD, Raman, surface morphology and electrical conductivity measurement techniques.

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II.2. Characterization of SbSI crystals

The SbSI crystals were analysed compositionally by an EDAX attached to the SEM. A JEOL-6360 SEM with a probe current of 1 nA was used for this purpose. The SEM images were also obtained by this machine. The energy range for sample scanning was 0-20 KeV. The XRD was recorded for a good quality sample by Phillips PW 3710 X-ray diffractometer using CuKα line. The range of 2θ values was from 10o to 80o. The Raman spectrum was also obtained using Horiba Jobin-Yvon Lab Raman spectrophotometer for the powdered sample. He-Ne laser source (632.88 nm wavelength) was used for this purpose. The electrical conductivity was measured for a pallet sample in the temperature range from 4K to 300K by a four probe method and a two probe method was also used to measure the resistivity in the 300K to 550K temperature range.

III. RESULTS AND DISCUSSION

The chemical composition of the as-synthesized SbSI crystal was determined by the EDAX technique. The as-grown crystal had 1:1.04:1.5 stoichiometry. Iodine was found to be in little higher percentage compared to other two elements. This may be because the quantity of vapours of iodine carried by the Ar gas was in slightly excess due to its high vapour pressure. The X-ray diffraction pattern was obtained for this powdered sample in the 2θ range from 100 to 800 and is shown in fig. 3. It appears that the sample is crystalline with sharp and highly intense peaks. All the reflections matched with the orthorhombic phase for SbSI and the cell constants are found to be: a=0.851 nm, b=1.015 nm and c=0.424 nm.

Figure 3. X-ray diffractogram of SbSI powder

The micro Raman spectrum of powdered SbSI was obtained in the 0 to 500 cm-1 range [19]. The measurements were performed using a 50X objective lens, D 0.3 filter and randomly at 10 different positions. The spectrum was taken at room temperature (27^{0}C) i.e. in paraelectric phase and is shown in fig. 4. SbSI is known to undergo phase transition from ferroelectric to paraelectric at 200C. The characteristic peaks (fig. 4) obtained at 12 cm^{-1}, 70 cm^{-1}, 81 cm^{-1}, 90 cm^{-1}, 118 cm^{-1}, 151 cm^{-1}, 226 cm^{-1} and 331 cm^{-1} are in good consonance with the results reported by Agrawal (1971) [20] and Gommonai (2003) [21] confirming the crystal to be SbSI. Since no peaks have been reported beyond 500 cm-1, no spectrum was taken for higher wave numbers.

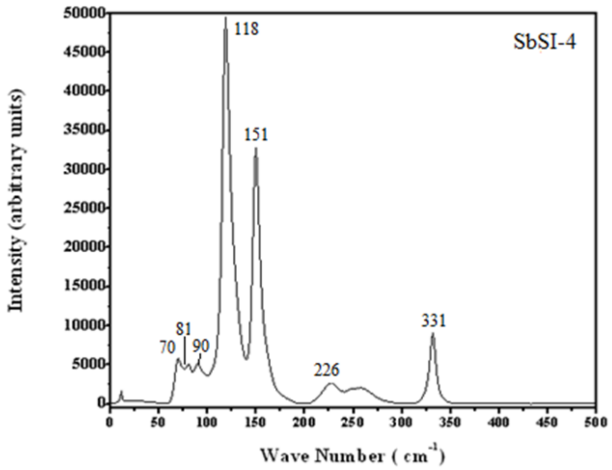

Figure 4. Raman spectrum of the SbSI crystal (at R.T.)

The electrical conductivity was measured for the pellets of this crystal by a four probe method. The range of temperature was from 4K to 300K. Figure 5 shows variation of electrical resistance as a function of temperature.

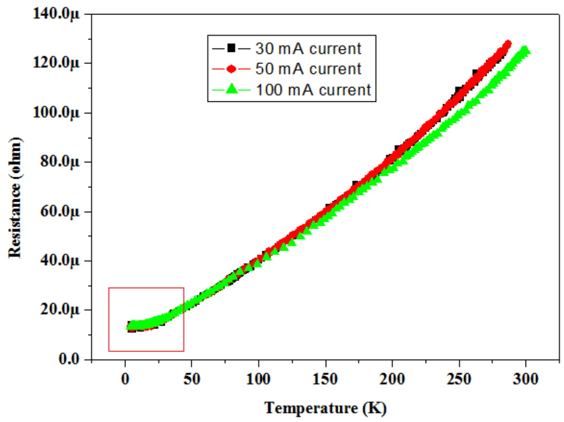

Figure 5 (A). Resistivity of SbSI versus temperature in the temperature range of 0K to 300K [19]

SbSI shows a transition temperature at 20K where its resistance falls down to almost zero i.e. 1.3 X 10-4 Ω. The resistance remains constant thereafter. To the best of our knowledge no efforts have been made till today to study the resistivity of this material below 300K. Resistance of this pellet sample was also measured by a two probe technique in the 300K-525K temperature range. This is shown in fig. 6 .

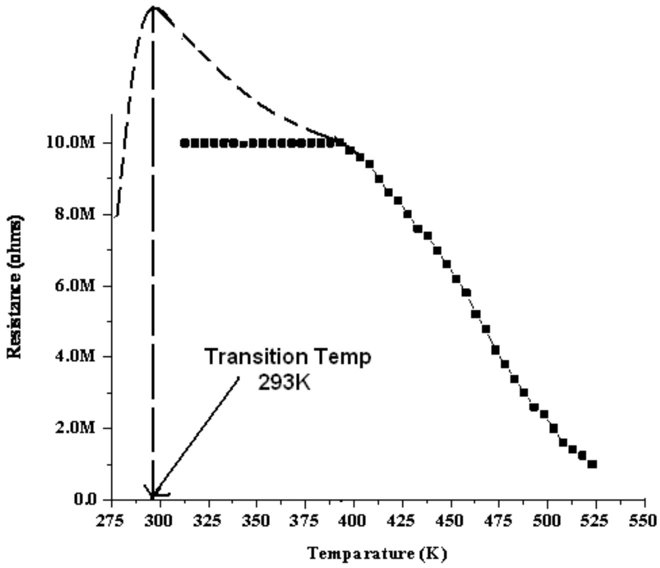

Figure 6 Electrical resistance of SbSI in the 300K to 525K temperature range.

When the nature of plots of electrical resistivity vs temperature in the 4K to 300K and 300K to 550 K temperature ranges are examined, it suggests that the ferroelectric phase of SbSI is metallic below 300K whereas paraelectric phase is semiconducting in 300K to 525K temperature range, because it is reported that below 220C it shows ferroelectric and above this temperature it is pyroelectric [22-24].

To the best of our knowledge, we have not come across any report on SbSI showing phase transition from metallic to semiconducting behaviour. Such behaviour needs in-depth studies as to why transition from metallic to semiconducting behaviour occurs in SbSI crystals.

We believe that there may be structural changes occurring in SbSI at different temperatures those need to be examined below 20K, above 50K, below 293K and around 500K and clarified. The structural changes at this temperature may be able to throw some light on its special behaviour at 20K, phase transition at 293K and reasons for transition from metallic to semiconducting behaviour.

IV. CONCLUSION

SbSI crystals were grown by utilizing elemental components of the compound and using a simple chemical vapour deposition technique designed and developed in our laboratory. The material is characterized to be of the composition equal to 1:1.04:1.5. Iodine content is observed to be slightly higher in the material. The material was characterized by the XRD, Raman and surface morphology and has been observed to be rod shaped. Electrical conductivity was measured by the four probe technique in the temperature range of 4K to 300K and by the two probe technique in the temperature range of 300K to 525K. SbSI crystals exhibit metallic properties in 4K to 300K range and semiconducting 300K to 525K range, that is a dual electrical nature. The transition of metallic to semiconducting behaviour takes place at around room temperature.

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