

Electrical properties of $\text{Bi}_{1.5}\text{ZnSb}_{1.5}\text{O}_7$ pyrochlore ceramics

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$\text{Bi}_{1.5}\text{ZnSb}_{1.5}\text{O}_7$ pyrochlore samples were prepared by solid state reaction method. They were examined by x-ray diffraction and scanning electron microscopy. Single phase, belongs to the cubic pyrochlore structure, with a lattice parameter of 10.442 Å and grain size that varies from 16 to 20 μm was obtained. The electrical properties were measured at different temperatures in the range 15–330 K under different applied magnetic fields up to 1.4 T. In our measurements for Hall coefficient, Hall resistivity, and mobility; we noticed an anomalous behavior at two temperatures (around 250 and 310 K) which was supported by the I-V measurements (double transition of the slope of I-V characteristics (β) at the same temperatures). This was discussed in terms of polarization phenomenon and mixed ionic-electronic conduction.

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1 Introduction

Pyrochlore type compounds have many potential application areas due to their wide spectrum of properties such as electrical, magnetic, dielectric, optical and catalytic properties [1]. Pyrochlores are widely used in active and passive electronic applications such as thermistors, gas sensors, switching elements, thick film resistors and material for screen printing. Pyrochlore compounds have also different possible application areas such as oxygen electrode, semiconductor electrode for solar energy conversion, solid electrolytes, high temperature electrodes, heating elements, and fixation for radioactive waste [1].

Pyrochlore compounds are represented in general by $\text{A}_2\text{B}_2\text{X}_6\text{Z}$, where A and B are different cation species with different oxidation states (e.g. A^{3+} B^{4+} or A^{2+} B^{5+}) and X and Z are anions, generally oxygen. The ionic radius (r) of the A and B cations should lie within the 0.0087–0.151 and 0.04–0.078 nm ranges, respectively. In addition, the r_A/r_B ratio should be between 1.29 and 2.30 nm [1, 2]. The cubic pyrochlore structure belongs to the space group Fd3m (No. 227, $Z = 8$) and can be regarded as an anion-deficient fluorite, which retains the face centered cubic lattice [1, 3]. In a stoichiometric pyrochlore structure ($\text{A}_2\text{B}_2\text{X}_6\text{Z}$), there are 88 atoms in a unit cell (origin selected at the A cation site): 16 A in 16 (c), 16 B in 16 (d), 8 Z in 8 (a) and 48 X in 48 (f). Symmetry fixes the coordinates of all the ions except for those in position 48 (f). This position contains one unknown coordinate, x . In the pyrochlore structure, the A cations are eight coordinated and are located within scalenohedra (distorted cubes) and the smaller B cations are six coordinated and are located within trigonal antiprism (distorted octahedra).

$\text{Bi}_{1.5}\text{ZnSb}_{1.5}\text{O}_7$ compound has the pyrochlore structure and forms in ZnO-based varistors. The pyrochlore phase does not generally make up the varistor microstructure because after its formation at around 700 °C, it reacts with ZnO between 950 and 1050 °C forming the spinel ($\text{Zn}_7\text{Sb}_2\text{O}_{12}$) and Bi_2O_3 [4]. However, in some cases pyrochlore phase may be reproduced on slow cooling with reaction of spinel and bismuth oxide [4]. Pyrochlore phase plays no role in the nonohmic behavior of the ZnO varistors which has been confirmed by the

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direct measurements of the current-voltage (I-V) characteristics of the individual interfaces combined with determination of their chemistry and phase composition [5]. Nevertheless, the breakdown field of ZnO varistors decreases as the amount of pyrochlore phase in ZnO varistors increases [6].

Dielectric and electrical properties of $\text{Bi}_{1.5}\text{ZnSb}_{1.5}\text{O}_7$ pyrochlore were investigated by several researchers. Mergen and Lee [7] determined that $\text{Bi}_{1.5}\text{ZnSb}_{1.5}\text{O}_7$ has a dielectric constant of around 32 with a dielectric loss of about 0.005 at 20 °C and weakly temperature dependent between 20 and 120 °C [7]. The dielectric permittivity measured by impedance spectroscopy in the frequency range from 5 Hz to 13 MHz between 100 and 500 °C gave values in the range 40–48 exhibiting slight dependence of dielectric losses with temperature up to 400 °C [8]. The electrical conductivity of $\text{Bi}_{1.5}\text{ZnSb}_{1.5}\text{O}_7$ studied as a function of temperature and partial pressure of oxygen showed that the $\text{Bi}_{1.5}\text{ZnSb}_{1.5}\text{O}_7$ was a mixed ionic-electronic conductor with an energy gap of 3.15 ± 0.9 eV [9].

The present study deals with the electrical properties of $\text{Bi}_{1.5}\text{ZnSb}_{1.5}\text{O}_7$ pyrochlore ceramic between 15 and 330 K under different applied magnetic fields (B) up to 1.4 T. The electrical properties of this pyrochlore are important because of its presence at interfaces in varistor ceramics. Single phase $\text{Bi}_{1.5}\text{ZnSb}_{1.5}\text{O}_7$ ceramic was produced by solid state reaction of mixed oxides powders. The sintered pellets were characterized by x-ray diffraction (XRD) and scanning electron microscopy (SEM). The electrical properties were examined by I-V characteristics and Hall effect measurements.

2 Experimental

Reagent grade Bi_2O_3 (99.9%), Sb_2O_3 (99.5%) and ZnO (99.9%) (supplied by Aldrich Chemical Company Ltd., UK) were weighed according to the stoichiometric $\text{Bi}_{1.5}\text{ZnSb}_{1.5}\text{O}_7$ pyrochlore composition and wet mixed and milled in ethanol for 4 h in a polyethylene bottle using zirconia milling media. The resultant wet slurry was then dried for 24 h at 130 °C. The mixture was then placed in an alumina crucible and calcined at 700 °C for 4 h. Following grinding, two separate pellets were uniaxially pressed at 250 MPa in a 10 mm diameter die and fired at 1200 °C for 5 hours. Sintered samples were examined by powder x-ray diffractometer (Philips 1710, Cu K_α , $1^\circ/\text{min}$) and scanning electron microscope (JEOL 6400).

The electrical measurements were achieved using two different techniques. The first sample was used for I-V measurements by the two probe method. Using silver paste, we fixed two probes on either sides of the sample whose thickness is approximately 1 mm. Currents in the range from 1 pA to 1 μA were applied with a current source (Keithley 220) and the voltage drops were measured with a nanovoltmeter (Keithley 2182). I-V data at zero applied magnetic field were taken at different temperatures in the range 15–330 K. The same measurements were also performed under 1.4 T magnetic field applied perpendicularly to the surface of the sample.

The other sample was used for Hall effect measurements using the van-der-Pauw technique. Four point contacts forming the shape of a square were fixed on the top surface of the sample. Lake Shore 7507 Hall-effect measurements system was used to measure the Hall parameters at different temperatures and magnetic fields. Hall-effect data were collected using an IEEE computer interface and IDEAS software provided by Lake Shore. Cooling of the sample was achieved using a closed cycle cryostat (Advanced Research Systems) and Lake Shore 340 temperature controller. Measurements were done under magnetic fields up to 1.4 T, using a 7 inch variable gap electromagnet, applied perpendicular to the current direction.

3 Results and discussion

The results of the X-ray analysis presented in fig 1 indicated that the fired (1200 °C, 5 hours) composition was single phase and belongs to the cubic pyrochlore structure with a lattice parameter of 10.442 Å. The density measurements with a mercury densitometer revealed that the sintered pellets had a relative density of around 96% which was calculated from the theoretical density of $\text{Bi}_{1.5}\text{ZnSb}_{1.5}\text{O}_7$ which is 7.86 g/cm^3 . The grain size of the densely sintered ceramic body of the pyrochlore (obtained from scanning electron micrographs) was found to vary from 16 to 20 μm .

Fig. 1 X-ray diffraction pattern of $\text{Bi}_{1.5}\text{ZnSb}_{1.5}\text{O}_7$ pyrochlore produced by solid state sintering at 1200 °C. Peaks are labeled by its Miller indices (hkl).

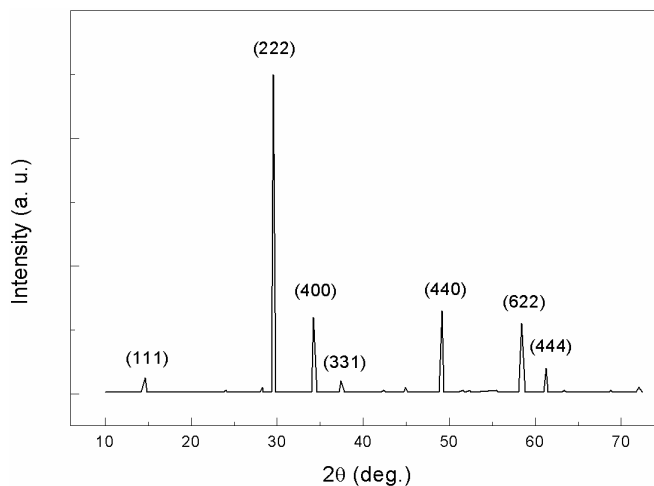


Fig. 2 I-V characteristics of $\text{Bi}_{1.5}\text{ZnSb}_{1.5}\text{O}_7$ pyrochlore at different temperatures under zero applied magnetic field.

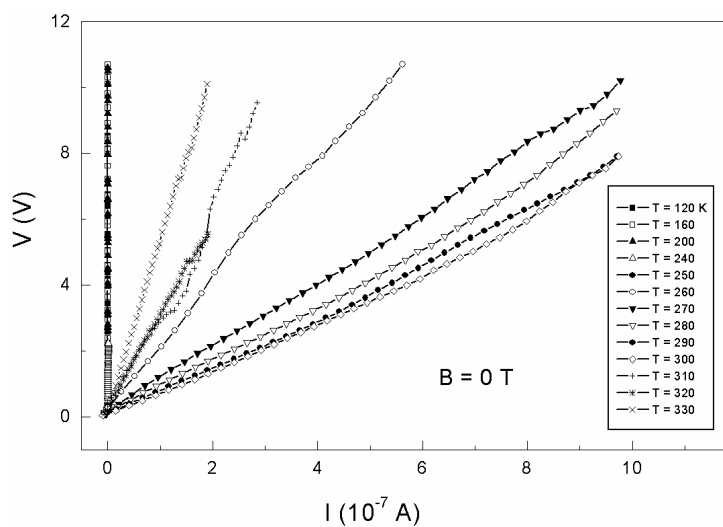
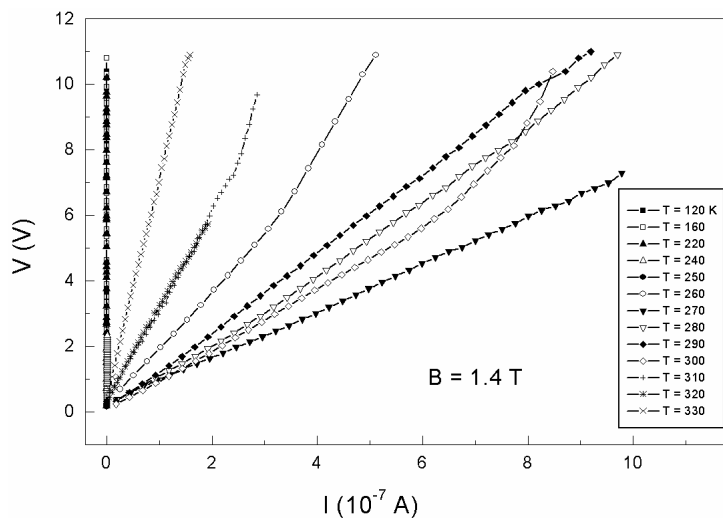


Fig. 3 I-V characteristics of $\text{Bi}_{1.5}\text{ZnSb}_{1.5}\text{O}_7$ pyrochlore at different temperatures under 1.4 T applied magnetic field.



The I-V characteristics were measured at different temperatures in the range from 15 to 330 K under zero applied magnetic field. Due to the similarity of I-V curves at low temperatures, we only show the results of I-V

measurements between 120 and 330 K. These are presented in fig 2. The I-V data sets measured under 1.4 T magnetic field in the same temperature range are shown in fig 3. Our I-V data (with and without applied magnetic field) were fitted to the expression $V = I^{\beta(T)}$ where β is the slope of the log V versus log I plot. β values fluctuate around 1 up to 220 K showing an ohmic behavior in this region. After this, sudden drop of β from 1 to 0.4 occurs at 250 K which is attributed to a change in the conduction mechanism at this temperature. Between 260 and 300 K, β takes values around 0.9 after which it drops to 0.8 up to 330 K. Here we notice that there is some kind of double transition at 250 and 310 K. This behavior will be supported by the Hall effect data given below.

The magnitude of the Hall coefficient $|R_H|$ measured at different temperatures in the range 15–330 K under different applied magnetic fields up to 1.4 T is shown in fig 4. R_H is negative, indicating that conduction is done by electrons and not by holes; and takes values in the order of magnitude of $10^{14} \text{ cm}^3/\text{C}$. It is quite interesting to notice here also the double transition mentioned before in the discussion of I-V characteristics at approximately 250 and 310 K. A peak value of $|R_H|$ ($|R_H| \approx 20 \times 10^{14}$) occurs at 240 K and 0.1 T after which it drops to smaller values of the order of magnitude of 10^{12} for temperatures in the range 260–300 K. $|R_H|$ starts to increase again at temperatures more than 300 K. We can also notice the sensitivity of R_H to very small magnetic fields where $|R_H|$ drops significantly under applied magnetic fields in the range 0.1–0.4 T.

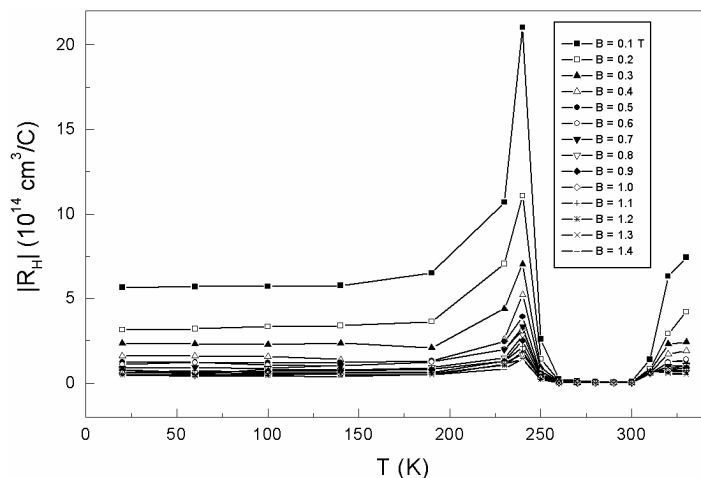


Fig. 4 The temperature dependency of $|R_H|$ at different applied magnetic fields up to 1.4 T for $\text{Bi}_{1.5}\text{ZnSb}_{1.5}\text{O}_7$ pyrochlore.

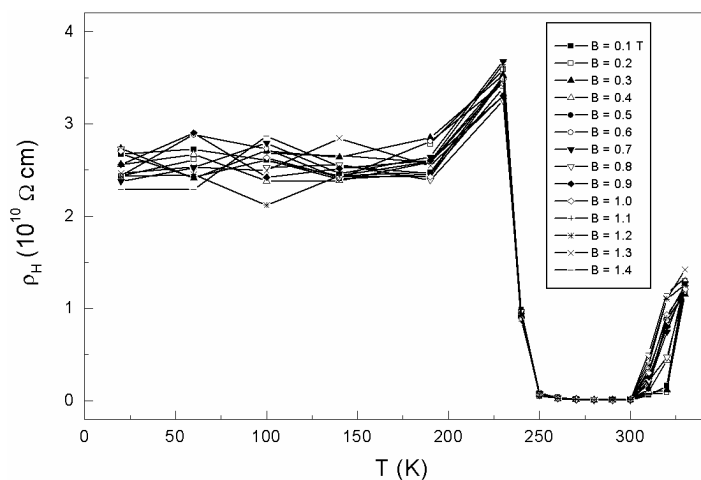


Fig. 5 The temperature dependency of Hall resistivity ρ_H at different applied magnetic fields up to 1.4 T for $\text{Bi}_{1.5}\text{ZnSb}_{1.5}\text{O}_7$ pyrochlore.

The Hall resistivity ρ_H was also measured at different temperatures in the range from 15 to 330 K under different applied magnetic fields up to 1.4 T. The representative curves are shown in fig 5. The ρ_H versus T

behavior is almost the same for all applied magnetic fields where ρ_H fluctuates around $2.5 \times 10^{10} \Omega \text{ cm}$ up to 190 K followed by an increase and a peak value of approximately $3.5 \times 10^{10} \Omega \text{ cm}$ at 230 K. ρ_H drops to small values of the order of $10^7 \Omega \text{ cm}$ in the temperature range 250–300 K after which it starts to increase again at 310 K. The temperature dependencies of mobility at different magnetic fields up to 1.4 T are shown in fig 6. Mobility values of the order of $10^4 \text{ cm}^2/\text{Vs}$ were measured at temperatures up to 230 K; after which a sudden increase of mobility to a peak value of approximately $3.5 \times 10^5 \text{ cm}^2/\text{Vs}$ is observed at 250 K. Mobility decreases again between 260 and 300 K followed by a second peak of approximately $4 \times 10^5 \text{ cm}^2/\text{Vs}$ at 320 K.

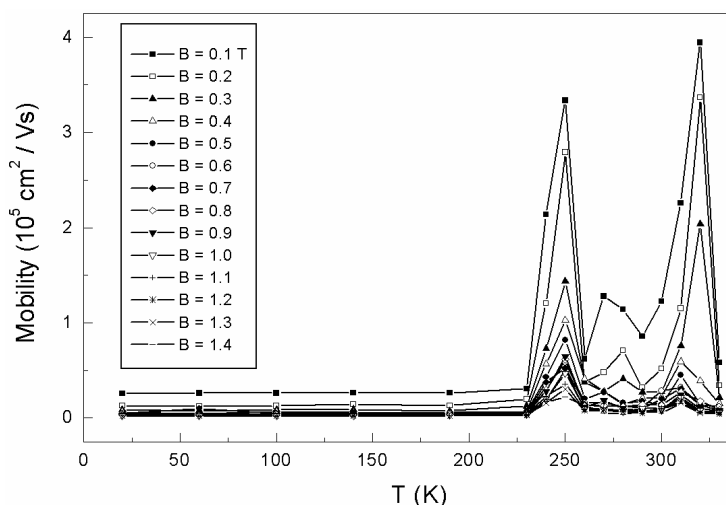


Fig. 6 The temperature dependency of mobility at different magnetic fields for $\text{Bi}_{1.5}\text{ZnSb}_{1.5}\text{O}_7$ pyrochlore.

Some pyrochlores showed a significant levels of ionic conductivity because of intrinsic Frenkel disorder or acceptor doping [10, 11]. The conductivity of $\text{Bi}_{1.5}\text{ZnSb}_{1.5}\text{O}_7$ pyrochlore has been discussed by several authors [8, 9]. They considered the material to be a mixed ionic-electronic conductor. A considerable ionic contribution to the conductivity was monitored by the shallow minimum in their conductivity measurements [9]. This material can have a p-type or n-type semiconductor characteristics, depending on the balancing of defects [8]. But, its high resistivity makes it a poor semiconductor. A transition from n-type to p-type conductivity was achieved by increasing the partial pressure of oxygen [9]. So the ionic conduction here is mainly due to oxygen ions. In our measurements for Hall coefficient, Hall resistivity, and mobility; we noticed an anomalous behavior at two temperatures (around 250 and 310 K) which was supported by the I-V measurements of the first sample (double transition of the slope of I-V characteristics (β) at the same temperatures). Nobre and Lanfredi [8] observed two anomalies in the permittivity curve for $\text{Bi}_{1.5}\text{ZnSb}_{1.5}\text{O}_7$ as a function of temperature at 200 and 320 °C. They suggested the presence of a polarization phenomenon associated to the charge carriers (electrons). This may be the reason for the observed double transition and peak effect in our measurements.

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