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New pyrochlore type semiconducting ceramic oxides: $Ca_3Ce_{3-x}Bi_xTi_7Nb_2O_{26.5}$ ($x = 0.5, 1.0, 2.0$, or 3.0)—structure, microstructure and electrical properties

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Oxides of the pyrochlore family have a general formula $A_2B_2O_7$ and they have been extensively studied because of their wide spectrum of physical properties including electrical, magnetic, optical, dielectric, and catalytic behavior [1–5]. The host lattice of this structure allows a wide variety of chemical substitutions at the A and B sites, which is responsible for their exhibiting a variety of properties. The unit cell of this structure is usually face centered cubic with space group Fd3m with eight molecules per unit cell ($Z = 8$) [6]. The A site cation with higher ionic radius is in eight fold coordination, with oxygen anions, while the smaller B cation resides in six fold coordination forming a (BO_6) oxygen octahedra. Of the seven oxygen anions, one is separate from the (BO_6) octahedra and its only bond is to the A cations, located in the voids between the (BO_6) octahedra. The larger A sites can accommodate rare earths and other trivalent cations such as Sc, In, Sb, Bi, while the B sites can be occupied by tetravalent elements i.e. Ti, Zr, Si, and Sn. For the formation of any pyrochlore compound, there are two criteria: (1) the ratio of the ionic radius of the cation at the A site to that at the B site must be between 1.46 and 1.80 and (2) the chemical valences of various ions must make the compound neutral [6, 7].

Recently, during our investigation, we could prepare pyrochlore type oxides in the quarternary Ca-R-Ti-Nb-O oxide system [8, 9]. $Ca_3Y_3Ti_7Nb_2O_{26.5}$ is colorless and insulating, but when Y^{3+} is completely replaced by Ce^{4+},the compound retains the pyrochlore structure, but is black and semiconducting. Electrical conductivity in this compound is probably due to the presence of Ce^{3+}, which remains in the reduced state without being oxidized to Ce^{4+} by structural stabilization (Ce^{4+}will hold more oxygen than can be accommodated by the structure).

Semiconducting oxides have been extensively studied for various applications such as thermistors, PTCR materials, sensors, catalysts for reactions in organic chemistry, and photoelectrolysis of water. In the present work preparation and characterization of new pyrochlore type semiconducting oxides $Ca_3Ce_{3-x}Bi_xTi_7Nb_2O_{26.5}$ ($x = 0.5, 1.0, 2.0, 3.0$) have been carried out and the results are given below.

Phase pure samples have been prepared by the conventional solid state ceramic route. The samples were prepared by mixing the stoichiometric proportions of raw materials in the solid state followed by heating. The raw materials used in the preparation of samples are $CaCO_3$ (99+%, Acros Organics), CeO_2 (99.9%, Acros Organics), Bi_2O_3 (99.9%, Acros Organics), TiO_2 (99%, Acros Organics), and Nb_2O_5 (99.9%, Aldrich Chemicals). These materials were taken in required ratio, then were mixed thoroughly in agate mortar. Acetone was added into the powder for proper mixing. The mixture was then dried by keeping in a hot air oven at 100 °C. The process of mixing and drying was repeated three times to get a homogeneous mixture. The dried unreacted powder was calcined at a temperature of 1200 °C for 3 hr in platinum crucible. The sample having fully Bi substituted composition was calcined at a temperature of 1100 °C for 3 hr. The calcined powder after cooling to room temperature is transferred to an agate mortar and ground well until a fine powder is obtained. To this powder 4 wt% poly vinyl alcohol (PVA) solution is added and again mixed well. PVA acts as the binder. The binder does not affect the chemical properties of the sample because it burns off during sintering. The powder is then pelletized into cylindrical pellets with diameter of 10 mm and thickness of 2 mm using a hydraulic press by applying a pressure of 250 Mpa. The pellets were then sintered at 1300 °C for 3 hr. The crystalline phases of the sintered samples were identified by X-ray powder diffraction method (XRD) with Ni-filtered Cu-Kα_1 radiation using a Philips X'pert Pro Diffractometer

The surface morphology of the pellets was investigated using scanning electron microscope. The SEM photographs were taken from polished and thermally etched samples using JEOL instrument JSM-5600 LV. The grain size and porosity can be obtained from SEM. Electrical resistivity was measured as follows. High temperature curing silver paste was applied to both faces of the pellet and electroded with long silver wires

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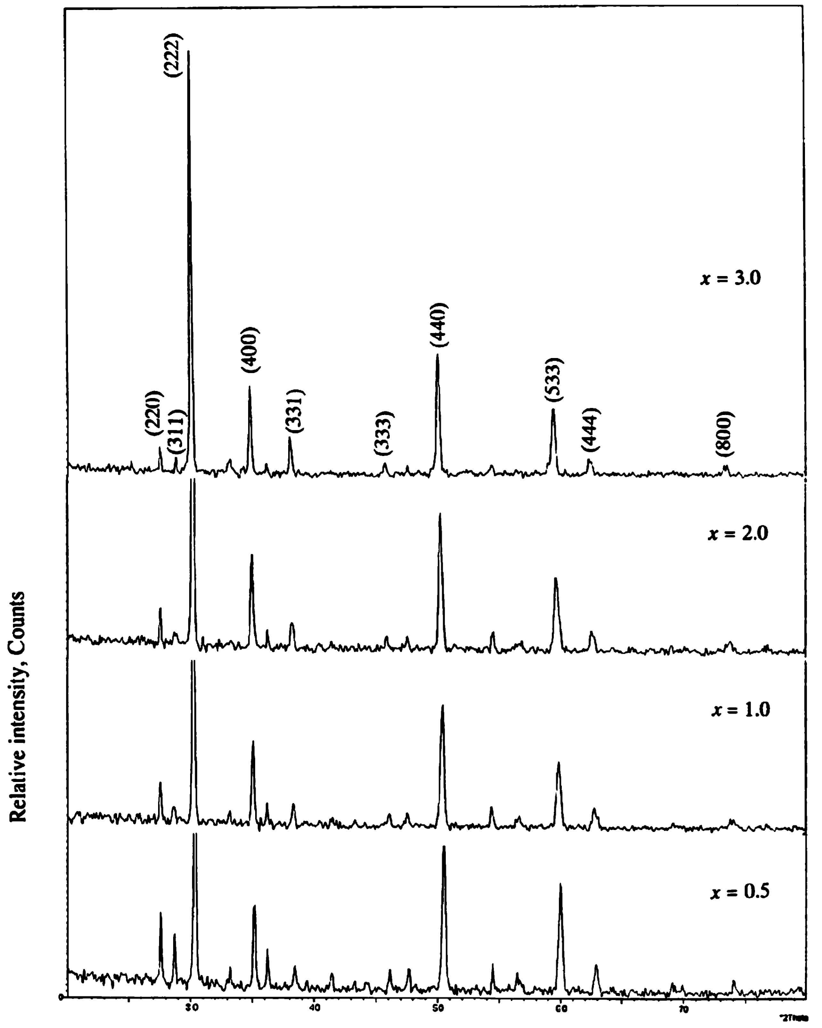

Figure 1 Powder X-ray diffraction patterns of $Ca_3Ce_{3-x}Bi_xTi_7Nb_2O_{26.5}$ ($x = 0.5, 1.0, 2.0$, or 3.0).

on both sides. The electroded pellets were cured in the tube furnace for half an hour at 600 °C. The DC conductivity of the pellet was recorded from 30 °C to 600 °C using a digital multimeter.

The X-ray powder diffraction patterns of the sintered compounds of $Ca_3Ce_{3-x}Bi_xTi_7Nb_2O_{26.5}$ ($x = 0.5, 1.0, 2.0, 3.0$) are presented in Fig. 1. The very sharp and high intensity peaks in the XRD pattern reveal the crystalline nature of the product. All the reflections were assigned to the cubic pyrochlore phase of space group Fd3m. The patterns are similar to earlier reported compounds of the formula $A_2B_2O_7$ such as $CaLnNb_2O_7$ [10] and Bi_2O_3-ZnO-SnO_2-Nb_2O_5 [11], except slight variation in 2θ values for various substitutions of Bi. The d-spacing corresponds to stronger X-ray reflections from (220), (222), (400), (440), (622) and (444) planes of the pyrochlore structure. It indicates the compound obtained is pure pyrochlore type phase without any impurities. The unit cell parameter of these compounds show the variation as given in Table I. The ionic radius of Bi^{3+}(1.20 Å) is greater than the ionic radius of Ce^{3+}(1.11 Å). Therefore progressive substitution of Ce^{3+} by Bi^{3+} ions causes an increase in the lattice parameter. (It is assumed that Ce occurs as Ce^{3+} and not as Ce^{4+} in these oxides). Such an increase is evident as shown in Table I.

The SEM pictures obtained for all the four Bi incorporated samples are given in Fig. 2a–d. All the sintered compounds reveal well-grown grains. Bi incorporation results in the appearance of growth steps in the grains. As the amount of Bi is increased steps on grains become deeper and deeper. There is a variation in grain size with the amount of Bi incorporated. The grain size of $Ce_{2.5}Bi_{.5}$ is about 1–3 μm whereas that of Ce_2Bi is of the order 1–5 μm. The grain size of $CeBi_2$ is of the order 2–6 μm while that of Bi_3 is in the range

TABLE I Crystal and electrical data on $Ca_3Ce_{3-x}Bi_xTi_7Nb_2O_{26.5}$ ($x = 0.5, 1.0, 2.0$, or 3.0) pyrochlores

Compound	Phase	Lattice parameter (Å)	Resistvity at 300 °C (ohm.cm)	Activation energy E_a (eV)
$Ca_3Ce_{2.5}Bi_{.5}Ti_7Nb_2O_{26.5}$	Pyrochlore	10.2245	3.58×10^4	0.496
$Ca_3Ce_2BiTi_7Nb_2O_{26.5}$	Pyrochlore	10.23908	6.28×10^4	0.529
$Ca_3CeBi_2Ti_7Nb_2O_{26.5}$	Pyrochlore	10.26885	1.82×10^7	0.556
$Ca_3BiTi_7Nb_2O_{26.5}$	Pyrochlore	10.3041	4.43×10^8	1.190

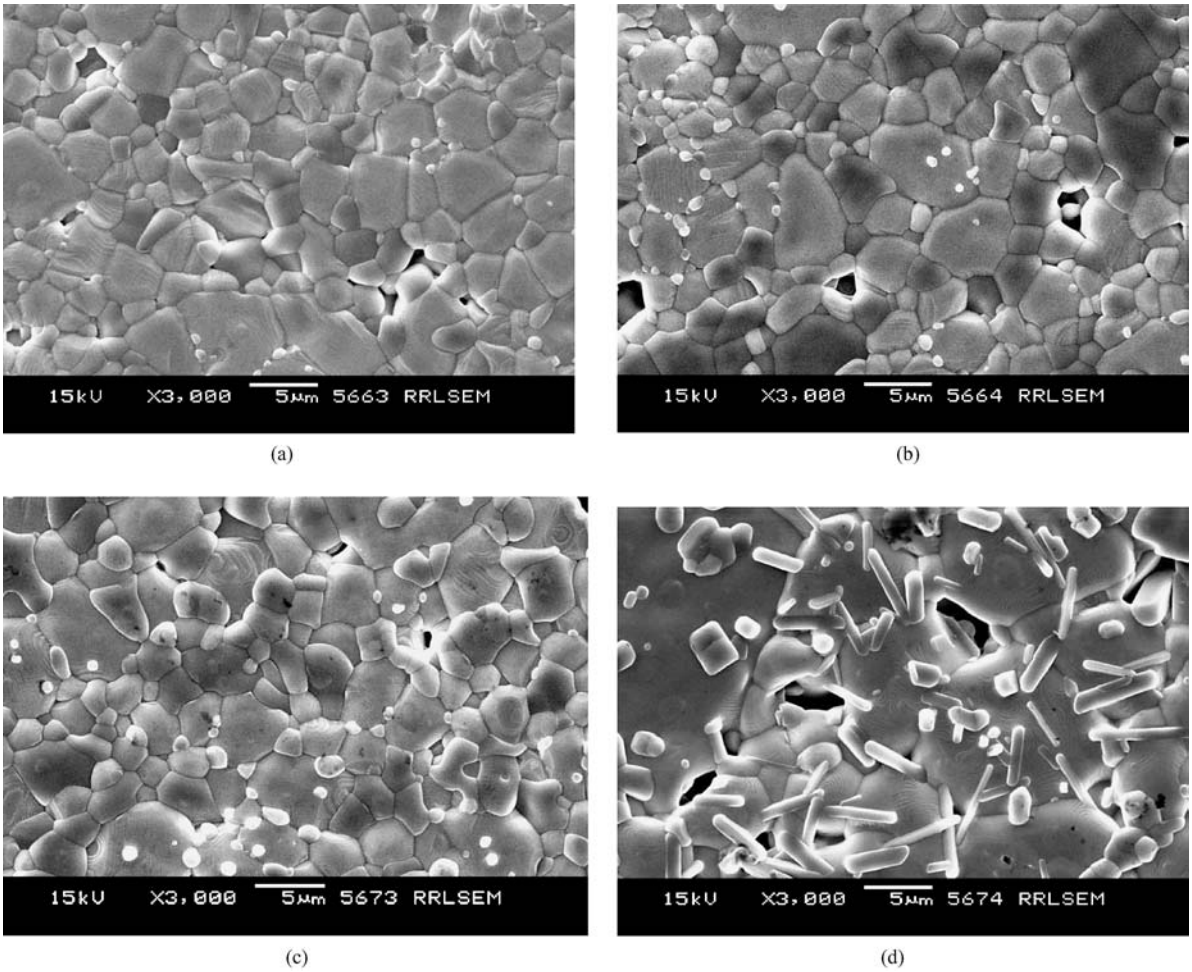

Figure 2 Scanning electron microscope photographs of $Ca_3Ce_{3-x}Bi_xTi_7Nb_2O_{26.5}$ (a) $x = 0.5$, (b) $x = 1$, (c) $x = 2$, and (d) $x = 3$.

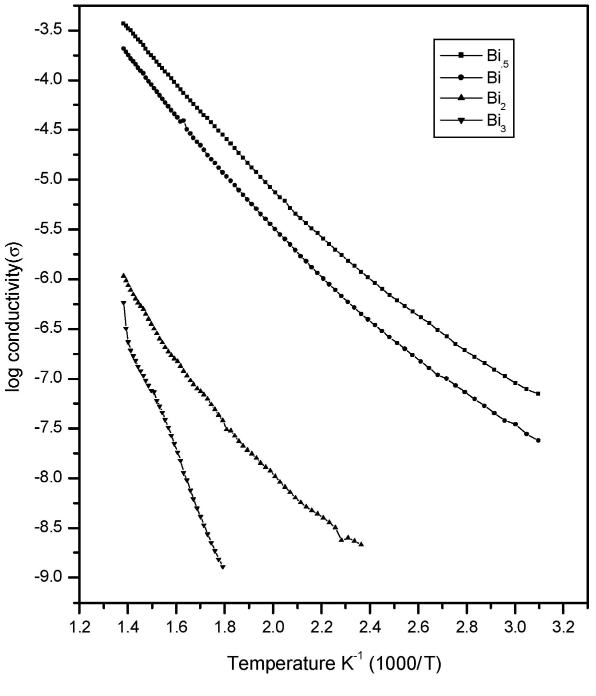

Figure 3 Variation of log conductivity (σ) vs. reciprocal of temperature.

5–20 μm. Besides crystalline grains rod shaped grains are also visible in Bi_3 compound.

Fig. 3 illustrates the electrical conductivity as a function of temperature for all compounds. The relation $\sigma = \sigma_0 \exp(-E_a/kT)$ is used to calculate the activation energy for the current carriers. In this relation σ_0 represents the pre exponential factor, E_a is the apparent activation of conduction process, k is the Boltzman constant, T is the absolute temperature. The activation energy of the carriers of the conduction process is calculated using the above equation and are listed in Table I. When Ce is partially substituted by Bi, both resistivity and activation energy are found to increase. This could be explained as follows. As conducting electrons probably arise from Ce^{3+} in the lattice, substitution of Ce by Bi would reduce the number of current carrying electrons. Therefore, resistivity will increase with substitution and the activation energy of current carriers will increase.

In the present compound though CeO_2 is used in the experiment for the preparation of the compound, all the oxygens in CeO_2 cannot be incorporated in the oxygen lattice of the structure (because pyrochlore structure can have only seven oxygens for every four metal atoms) and, therefore, the extra oxygen probably escapes leaving behind electrons in the lattice. These free electrons will remain in the conduction band and render the solid electrically conducting and black in color. In the case of fully substituted compound $Ca_3Bi_3Ti_7Nb_2O_{26.5}$ (which does not contain any Ce) it also shows some conductivity. This may be the ionic conductivity due to O^{2-} ions, not the conductivity due

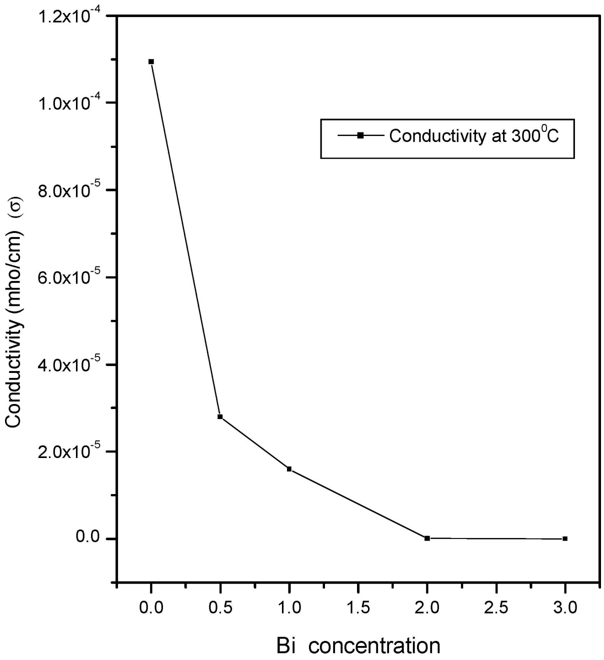

Figure 4 Variation of conductivity with Bi concentration.

to electrons. In other compounds where part of Ce is substituted by Bi the total conductivity may be a sum of electrical conductivity due to electrons from Ce^{3+} and also oxygen ions. Usually ionic conductivity is much less than electronic conductivity and probably due to this reason there is a very large decrease in conductivity with progressive substitution of Ce by Bi (Fig. 4). Thus conductivity of $Ca_3Ce_3Ti_7Nb_2O_{26.5}$ at 300 °C is 9.14×10^3 $ohm^{-1}cm^{-1}$ whereas the conductivity of $Ca_3Bi_3Ti_7Nb_2O_{26.5}$ at 300 °C is only 2.257×10^{-9} $ohm^{-1}cm^{-1}$.

The compounds $Ca_3Ce_{3-x}Bi_xTi_7Nb_2O_{26.5}(x = 0.5, 1.0, 2.0, 3.0)$ have been synthesized and characterized. The XRD patterns show the formation of pyrochlore structure. SEM pictures reveal well-grown grain structures. The electrical conductivity studies on these compounds indicate that Bi incorporation decreases the conductivity and also increases the activation energy of the conduction process. These semiconducting oxides may be useful in active and passive electronic applications.

References

1. J. ISASI, M. L. LOPEZ, M. L. VEIGA and C. PICO, *Solid State Ionics* **89** (1996) 321.
2. X. WANG, HONG WANG and XI YAO, *J. Amer. Ceram. Soc.* **80** (1997) 2745.
3. M. A. SUBRAMANIAN and A. W. SLEIGHT, in "Handbook on the Physics and Chemistry of Rare Earths," Vol. 8, edited by K. A. SCHNEIDER and L. EYRING (Elsevier, Amsterdam, 1993) p. 642.
4. C. BANSAL, H. KAWANAKA, H. BANDO and Y. NISHIHARA, *Physica B* **329–333**(2) (2003) 1034.
5. D. P. CANN, C. A. RANDALL and T. R. SHROUT, *Solid State Commun.* **100**(7) (1996) 529.
6. M. A. SUBRAMANIAN, G. ARAVAMUDAN and G. V. SUBBA RAO, *Prog. Solid State Chem.* **15** (1983) 55.
7. R. A. MCCAULEY and F. A. HUMMEL, *J. Solid State Chem.* **33** (1980) 99.
8. P. PRABHAKAR RAO, S. J. LIJI, K. RAVINDRAN NAIR and PETER KOSHY, *Physica B* **349** (2004) 115.
9. *Idem.*, *Mater. Lett.* **58** (2004) 1924.
10. S. YA ISTOMIN, O. G. D'YACHENKO and E. V. ANTIPOV, *Mater. Res. Bull.* **32**(4) (1997) 421.
11. H. DU, X. YAO and L. ZHANG, *Ceram. Int.* **28** (2002) 231.

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