Chapter 7

EFFECT OF Bi SUBSTITUTION IN
Ba$_3$Ce$_{3-x}$Bi$_x$Ti$_5$Nb$_5$O$_{30}$ ($x = 0.5, 1.0, 2.0$ or $3.0$) (TUNGSTEN BRONZE TYPE) AND
Ca$_3$Ce$_{3-x}$RE$_x$Ti$_7$Nb$_2$O$_{26.5}$ ($x = 0, 1, 2$ or $3.0$) (PYROCHLORE TYPE) CERAMICS

The current chapter presents the results obtained from the investigations carried out on the Bi substitution for cerium in Ba$_3$Ce$_3$Ti$_5$Nb$_5$O$_{30}$ (tungsten bronze type) and Ca$_3$Ce$_3$Ti$_7$Nb$_2$O$_{26.5}$ (pyrochlore type) ceramics. Well grown microtubes have been observed during sintering of Ba$_3$Ce$_{3-x}$Bi$_x$Ti$_5$Nb$_5$O$_{30}$, whereas such microtubes are not seen during the sintering of pyrochlore type oxides: Ca$_3$Ce$_{3-x}$Bi$_x$Ti$_7$M$_2$O$_{26.5}$.
GRAIN GROWTH OF MICROTUBES DURING SINTERING IN SEMICONDUCTING \( \text{Ba}_3\text{Ce}_3-x\text{Bi}_x\text{Ti}_5\text{Nb}_5\text{O}_{30} \) \((x = 0.5, 1.0, 2.0 \text{ or } 3.0)\) CERAMICS

7.1 Introduction

In recent years, there has been intense research going on in microtubes and nanotubes, because of their exceptional physical properties and potential applications [Bachtold et al. 2001; Yin et al. 2004; Iijima 1991]. The preparation of such tubes is of great scientific and technological importance in applications such as photonic materials, microchip reactor, miniaturized sensor, separation technologies and non-linear optical apparatus [Taton et al 2001; Fendler 2001; Kityk 2001]. Recently, it was reported that inorganic microtubes in \( \text{MoS}_2 \) [Remskar et al. 1998(a)] and \( \text{WS}_2 \) [Remskar et al. 1998(b)] can grow during the chemical transport reactions. Earlier studies indicate that these microtubes have potential applications in biomedical drug delivery [Santini et al. 1999] biochips and microfluidic processes in microelectromechanical systems (MEMS) [Thorsen et al. 2002]. For the above applications, the microtubes should have the size range of a few micrometers with sufficient mechanical strength and chemical robustness. During our studies on semiconducting oxides of the type \( \text{Ba}_3\text{Ce}_3-x\text{Bi}_x\text{Ti}_5\text{Nb}_5\text{O}_{30} \), which has tungsten bronze type structure [Prabhakar Rao et al. 2003], we found that sintered pellets of \( \text{Ba}_3\text{Ce}_3-x\text{Bi}_x\text{Ti}_5\text{Nb}_5\text{O}_{30} \) \((x = 0.5, 1.0, 2.0 \text{ and } 3.0)\) mainly consists of well grown tubular grains, which might have potential applications in catalysis and other areas and the above results are reported here. This type of microtubes in a multicomponent system, we believe, has not been reported before.

7.1.2 Experimental Procedure

High purity (99.9%) chemicals \( \text{BaCO}_3 \), \( \text{Bi}_2\text{O}_3 \), \( \text{TiO}_2 \), \( \text{Nb}_2\text{O}_5 \) (Aldrich Chemicals) and \( \text{CeO}_2 \) (Indian rare earths limited) were weighed in stoichiometric amounts to get the formula \( \text{Ba}_3\text{Ce}_3-x\text{Bi}_x\text{Ti}_5\text{Nb}_5\text{O}_{30} \) with \( x = 0.5, 1.0, 2.0 \text{ and } 3.0 \). The powders were thoroughly wet mixed in agate mortar with acetone and dried in an air oven. This process of mixing and drying is repeated a few times to obtain homogeneous mixture. The dried unreacted powders were then calcined in air at 1200°C for 3 h in platinum crucibles. After calcination, it was ground into fine powder. The phase identification of the powder was done by powder x-ray diffraction analysis (XRD) with Ni filtered
CuKα1 radiation using Philips X'Pert diffractometer. The calcined powder was mixed well by adding 2 wt% polyvinyl alcohol (PVA) (binder) solution and dried. The dried product was powdered and formed into cylindrical pellets with a diameter of 10 mm and thickness of 1 to 2 mm applying a pressure of 250 MPa in a hydraulic press. These pellets were sintered at 1300°C for 3 hrs. For microstructural studies, the sintered pellets were polished first using emery papers, then using diamond paste. The polished pellets were cleaned using organic solvent in ultrasonic cleaner and were heated in air at 1250°C (below sintering temperature) for half an hour for the sake of thermal etching of polished surfaces. The surface morphology of the thermally etched samples was investigated using Scanning Electron Microscope, JEOL make JSM 5600LV and microchemical analysis of the samples was done by the energy dispersive spectrometer (EDS) attached to scanning electron microscope (SEM). The super ultra thin window (SUTW) detector Si(Li) is used in the EDS of EDAX Inc., NJ, USA for the elemental analysis of the samples. For electrical conductivity measurements, high temperature curing silver paste was applied to the circular faces of the pellet and long silver lead wires were attached on both sides. The pellets with silver wires were cured in a tube furnace for half an hour at 600°C. The dc conductivity of the pellet was recorded using Philips Digital Multimeter from 30° to 500°C.

7.1.3 Results and Discussion

The powder XRD patterns of Ba₃Ce₂.₅Bi₁₀.₅Ti₁₅Nb₅O₃₀, Ba₃Ce₂Bi₁Ti₃Nb₅O₃₀, Ba₃CeBi₂Ti₅Nb₅O₃₀ and Ba₃Bi₃Ti₁₅Nb₅O₃₀ are shown in Fig. 7.1 and they are very similar to the patterns reported earlier for Ba₃M₃Ti₁₅Nb₅O₃₀ (M = Sm or Y) [Prabhakar Rao et al. 2001], Ba₂Na₃RNb₁₀O₃₀ [Singh et al. 1992], Ba₄Nd₂Ti₄Ta₆O₃₀ [Wang et al. 2001], which are known to have tetragonal tungsten bronze (TTB) type structure. The powder XRD patterns of Ba₃Ce₂.₅Bi₁₀.₅Ti₁₅Nb₅O₃₀ and Ba₃Ce₂Bi₁Ti₁₅Nb₅O₃₀ in Fig. 7.1 are identical to JCPDS File No. 38-1331 and those of Ba₃CeBi₂Ti₁₅Nb₅O₃₀ and Ba₃Bi₃Ti₁₅Nb₅O₃₀ are identical to JCPD File No. 39-1445. Both these XRDs correspond to TTB type structure, with the latter having probably slight distortion in the structure due to large amount of Bi substitution in the lattice, which gives rise to
Figure 7.1 Powder X-ray diffraction patterns of Ba$_2$Ce$_x$BiTb$_{3-y}$O$_{9y}$

with $x = 0.5$, 1.0, 2.0 and 3.0.

$\theta$ (degrees)
splitting of $<330>$ and $<221>$ reflections. It should be mentioned here that SEM photographs of some of our samples (vide infra) show a hexagonal morphology (Figure 7.2d). This may be due to Bi substitution.

The SEM micrographs of all the three substitutions are presented in Figure 7.2a-h. The normal sintered grain morphology is observed in $\text{Ba}_3\text{Ce}_3\text{Ti}_3\text{Nb}_5\text{O}_{30}$ ceramics (Figure 7.2a). However, when Ce is partially replaced by Bi, the grains show tubular morphology (Figures 7.2b-f). The tubular grains have well defined edges. At the ends of the cylindrical tubes, they have octagonal shapes, hollow cores with diameters of 2-3 microns, lengths over a few tens of microns and wall thickness of 0.5 to 1.0 micron. The tubes are very straight and are apparently welded to each other on the sides. Also, at the ends of the tubes, growth spirals can be observed (Figure 7.2e) which resembles the features observed on single crystals during crystal growth experiments. It is known that such growth spirals would occur during solution growth or melt growth of single crystal materials [Goodman 1974]. This would indicate a mechanism of grain growth, in which growth takes place by packing of atoms on steps of screw dislocation like features as has been reported in crystal growth experiments earlier. Mass transport for such a process can not be accounted for by the usual mechanism of sintering by fusion of adjacent grains. Instead, we would propose that there is an initial partial melting of grains and nucleation of small grains takes place. These grains would grow into the tubes and mass transport necessary for this process can take place by diffusion of ions to the growing steps through the fluid phase that might prevail in the partial liquid conditions. This type of explanation would satisfy the observation of growth spirals at the ends of the tubes. The hollow tubes are not obtained when $x = 3$ i.e. Ce is completely substituted by Bi. In this case, the grains are grown into solid rods without hollowness (Figure 7.2g). The tubular growth as well as increase of wall thickness is observed to be more with greater Bi content until Bi$_2$ ($x = 2.0$) is reached. Thus, tube formation is more in $\text{Ba}_3\text{CeBi}_2\text{Ti}_5\text{Nb}_5\text{O}_{30}$ than in $\text{Ba}_3\text{Ce}_2\text{BiTi}_3\text{Nb}_5\text{O}_{30}$.

We tried to prepare the crystals of $\text{Ba}_3\text{Ce}_2\text{BiTi}_3\text{Nb}_5\text{O}_{30}$ from a potassium chloride (KCl) flux. 15 g of KCl was mixed with 2 g of the oxide and heated at 1100°C for several hours. KCl was slowly evaporated off. The SEM of the residue obtained is
shown in figure 8.2h. The crystals obtained have somewhat similar appearance to rod shaped grains found in Ba$_3$Bi$_3$Ti$_5$Nb$_5$O$_{30}$ (Figure 7.2g).

The microchemical analysis (cation content) of the Bi substituted Ba$_3$Ce$_{2.5}$Bi$_x$Ti$_5$Nb$_5$O$_{30}$ compounds was performed with energy dispersive spectrometer (EDS) attached to scanning electron microscope (SEM). EDS analysis was done on the calcined powder and the sintered tubular grains of the Ba$_3$Ce$_2$BiTi$_5$Nb$_5$O$_{30}$ ceramics. The analysis shows the presence of all the cations (Figure 7.3a and 7.3b) and also the stoichiometry obtained from the quantitative analysis is close to the theoretical one. This also confirms that Bi has gone into the lattice of the structure. It also reveals that Bi presence along with other elements causes the tube formation.
Figure 7.2a-h SEM photographs of Ba$_3$Ce$_{3-x}$Bi$_x$Ti$_6$Nb$_5$O$_{30}$ (a) $x = 0$, (b) and (c) $x = 0.5$, (d) $x = 1$, (e) and (f) $x = 2$, (g) $x = 3$ (h) $x = 1$ (KCl).
**Figure 7.3a** EDS analysis of the sintered Ba$_3$Ce$_2$BiTi$_6$Nb$_5$O$_{30}$ ceramics at 1300 °C.

<table>
<thead>
<tr>
<th>Element</th>
<th>Wt%</th>
<th>At%</th>
</tr>
</thead>
<tbody>
<tr>
<td>O</td>
<td>20.57</td>
<td>59.93</td>
</tr>
<tr>
<td>Nb</td>
<td>35.96</td>
<td>18.04</td>
</tr>
<tr>
<td>Bi</td>
<td>9.36</td>
<td>2.09</td>
</tr>
<tr>
<td>Ba</td>
<td>9.03</td>
<td>3.07</td>
</tr>
<tr>
<td>Ti</td>
<td>13.33</td>
<td>12.97</td>
</tr>
<tr>
<td>Ce</td>
<td>11.75</td>
<td>3.91</td>
</tr>
</tbody>
</table>
Figure 7.3b EDS analysis of the calcined powder of $\text{Ba}_3\text{Ce}_2\text{BiTi}_5\text{Nb}_5\text{O}_{30}$ ceramics.
The electrical resistivity ($\rho$) values at 300°C are listed in Table 7.1. It can be seen that the resistivity increases with Bi content. The variation of log conductivity ($\log \sigma$) versus 1000/T (K) is presented in Fig. 7.4. These curves resemble the results of our earlier work on cerium containing TTB type oxide $\text{Ba}_3\text{Ce}_3\text{Ti}_5\text{Nb}_5\text{O}_{30}$ [Prabhakar Rao et al. 2003]. The change of conductivity in $\text{Ba}_3\text{Ce}_{3-x}\text{Bi}_x\text{Ti}_5\text{Nb}_5\text{O}_{30}$ ($x = 0.5$, 1.0, 2.0 and 3.0) compounds may be attributed to change in carrier concentration due to the Bi substitution. Activation energy $E_a$ is obtained for all the Bi compositions and linearly increases with Bi content (Table 7.1). The conductivity in this material probably arises due to mobile electrons released by $\text{Ce}^{3+}$ as we have discussed earlier in chapter 6. Since $\text{CeO}_2$ (rather than $\text{Ce}_2\text{O}_3$) is used as a starting material in this preparation that would give more oxygen to the compound than necessary for the TTB structure. The ideal composition for TTB structure of these oxides is Metal:Oxygen ratio = 16:30. But, when $\text{CeO}_2$ is added, Ce is in $\text{Ce}^{4+}$ state and M:O ratio will become 16:31.5. To make M:O ratio 16:30, the extra oxygen will be ejected to the atmosphere and this will
reduce Ce$^{4+}$ to Ce$^{3+}$. Thus, Ce$^{3+}$ will be stabilized in the lattice even at 1300°C (Usually Ce$^{3+}$ in other compounds is unstable under these conditions and it will be converted to Ce$^{4+}$ in air at high temperature) and the compound obtained is black and semiconducting. Ba$_3$Bi$_3$Ti$_5$Nb$_5$O$_{30}$ is not black, since Ce is absent and the small conductivity obtained may be ionic. In this case, activation energy of conduction is also high as expected.

Table 7.1
Electrical Properties of Ba$_{3-x}$Bi$_x$Ti$_5$Nb$_5$O$_{30}$ (x = 0.5, 1.0, 2.0 and 3.0).

<table>
<thead>
<tr>
<th>Composition</th>
<th>Resistivity ohm.cm. at 300°C.</th>
<th>Activation Energy (E$_a$) eV</th>
</tr>
</thead>
<tbody>
<tr>
<td>x</td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.5</td>
<td>9.62x10$^3$</td>
<td>0.417</td>
</tr>
<tr>
<td>1.0</td>
<td>9.17x10$^3$</td>
<td>0.420</td>
</tr>
<tr>
<td>2.0</td>
<td>1.67x10$^5$</td>
<td>0.622</td>
</tr>
<tr>
<td>3.0</td>
<td>4.19 x10$^5$</td>
<td>0.893</td>
</tr>
</tbody>
</table>

7.1.4 Conclusions

Well grown microtubes of Ba$_3$Ce$_{3-x}$ Bi$_x$Ti$_5$Nb$_5$O$_{30}$ (x = 0.5, 1.0, 2.0 and 3.0) have been observed in the sintered ceramics. The microtubes have octagonal shapes at the cylindrical ends, hollow cores with diameters of 2-3 microns, lengths over a few tens of microns and wall thickness of 0.5 to 1.0 micron. In morphology, the tubes are very straight and are apparently welded to each other on the sides. The tubular growth as well as increase of wall thickness is observed to be more with greater Bi content, but when Ce is fully substituted by Bi, the tubes have grown into solid rods without hollowness. The growth spirals at the ends of tubes as seen by Scanning Electron Microscope (SEM) indicate that growth takes place in the longitudinal direction of the tubes. Observation of growth spirals on grains of a sintered ceramic is unusual. In fact, such features are usually seen in liquid phase growth and, therefore, we propose here grain growth in partially fluid conditions. The phase identification by XRD shows that the compound has a tetragonal tungsten bronze type (TTB) structure. The resistivity measurements above room temperature indicate that these compounds are semiconductors and both resistivity and activation energy increase with Bi content.
We could prepare ceramic microtubes having semiconductor behavior in the Ba-Ce(Bi)-Ti-Nb-O system. These microtubes might have potential applications in catalysis and other areas.

7.2 NEW PYROCHLORIE TYPE SEMICONDUCTING CERAMIC OXIDES: Ca$_3$Ce$_{3-x}$Bi$_x$Ti$_7$Nb$_2$O$_{26.5}$ (x = 0.5, 1.0, 2.0 or 3.0) - STRUCTURE, MICROSTRUCTURE AND ELECTRICAL PROPERTIES.

7.2.1 Introduction

Bismuth substitution for cerium in TTB type oxide: Ba$_3$Ce$_3$Ti$_7$Nb$_2$O$_{30}$ produced microtubes during sintering as seen in the above discussion. We could prepare cerium containing semiconducting oxide in pyrochlore type structure (Chapter 6). Effort has been made to see the effect of Bi substitution in Ca$_3$Ce$_3$Ti$_7$Nb$_2$O$_{26.5}$ for its microstructure, ceramic microstructure and electrical properties. As expected from TTB type oxide: Ba$_3$Ce$_3$Ti$_7$Nb$_2$O$_{30}$, the sintering of the pyrochlore ceramic did not yield any microtubes, but very crystalline grains in the shapes of rods for higher substitution of Bi has been observed.

In the present work preparation and characterization of new pyrochlore type semiconducting oxides: Ca$_3$Ce$_{3-x}$Bi$_x$Ti$_7$Nb$_2$O$_{26.5}$ (x = 0.5, 1.0, 2.0, 3.0) have been carried out and the results are given below.

7.2.2 Experimental

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$_2$O$_3$ (99.9%, Acros Organics), TiO$_2$ (99%, Acros Organics) and Nb$_2$O$_5$ (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 three hours in platinum crucible. The sample having fully Bi substituted composition was calcined at
a temperature of 1100°C for three hours. 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 three hours. The crystalline phases of the sintered samples were identified by X-ray powder diffraction method (XRD) with Ni- filtered Cu-Kα1 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 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.

7.2.3 Results and discussion

The X-ray powder diffraction patterns of the sintered compounds of Ca3Ce3-xBi2-xTi7-xNb2026 (x = 0.5, 1.0, 2.0, 3.0) are presented in figure 7.5. 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 A2B2O7 such as CaLnNb2O7 [Cann et al. 1996] and Bi2O3-ZnO-SnO2-Nb2O5 [Subramanian et al.1980], 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
Figure 7.5 Powder X-ray diffraction patterns of Ca$_3$Ce$_{3-x}$Bi$_x$Ti$_7$Nb$_2$O$_{28.5}$ ($x = 0.5, 1.0, 2.0, 3.0$) ceramics.
variation as given in Table 7.2. The ionic radius of $\text{Bi}^{3+}(1.20\text{Å})$ is greater than the ionic radius of $\text{Ce}^{3+}(1.11\text{ Å})$. Therefore progressive substitution of $\text{Ce}^{3+}$ by $\text{Bi}^{3+}$ ions causes an increase in the lattice parameter. (It is assumed that Ce occurs as $\text{Ce}^{3+}$ and not as $\text{Ce}^{4+}$ in these oxides). Such an increase is evident as shown in Table 7.2.

The SEM pictures obtained for all the four Bi incorporated samples are given in figure 7.6a-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 $\text{Ce}_{2.5}\text{Bi}_{1.5}$ is about 1-3μm where as that of $\text{Ce}_2\text{Bi}$ is of the order 1-5μm. The grain size of $\text{CeBi}_2$ is of the order 2-6μm while that of $\text{Bi}_3$ is in the range 5-20μm. Besides crystalline grains rod shaped grains are also visible in $\text{Bi}_3$ compound.

Figure 7.7 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 $\sigma_0$ 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 7.2. 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 $\text{Ce}^{3+}$ 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 $\text{CeO}_2$ is used in the experiment for the preparation of the compound, all the oxygen's in $\text{CeO}_2$ 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 colour. In the case of fully substituted compound $\text{Ca}_3\text{Bi}_3\text{Ti}_7\text{Nb}_2\text{O}_{26.5}$ (which does not contain any Ce) it also shows some conductivity. This may be the ionic conductivity due to $\text{O}^{2-}$ ions, not the conductivity due to
Figure 7.6a-d Scanning electron microscope photographs of $\text{Ca}_3\text{Ce}_{3-x}\text{Bi}_x\text{Ti}_7\text{Nb}_2\text{O}_{26.5}$ (a) $x = 0.5$, (b) $x = 1$, (c) $x = 2$ and (d) $x = 3$. 
Figure 7.7 Variation of electrical conductivity ($\sigma$) with temperature.

Figure 7.8 Variation of conductivity with Bi Concentration.
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 (Figure 7.8). Thus conductivity of \(\text{Ca}_3\text{Ce}_3\text{Ti}_7\text{Nb}_2\text{O}_{26.5}\) at 300°C is \(9.14 \times 10^3\) ohm\(^{-1}\)cm\(^{-1}\) where as the conductivity of \(\text{Ca}_3\text{Bi}_3\text{Ti}_7\text{Nb}_2\text{O}_{26.5}\) at 300°C is only \(2.257 \times 10^{-9}\) ohm\(^{-1}\)cm\(^{-1}\).

### Table 7.2

Crystal and electrical data on \(\text{Ca}_3\text{Ce}_{3-x}\text{Bi}_x\text{Ti}_7\text{Nb}_2\text{O}_{26.5}\) (\(x = 0.5, 1.0, 2.0\) or \(3.0\)) pyrochlores.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Phase</th>
<th>Lattice parameter, (Å)</th>
<th>Resistivity at 300 °C (ohm.cm)</th>
<th>Activation energy Ea (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\text{Ca}<em>3\text{Ce}</em>{2.5}\text{Bi}_{1.5}\text{Ti}_7\text{Nb}<em>2\text{O}</em>{26.5})</td>
<td>Pyrochlore</td>
<td>10.2245</td>
<td>3.58x10^4</td>
<td>0.496</td>
</tr>
<tr>
<td>(\text{Ca}_3\text{Ce}<em>2\text{Bi}</em>{2}\text{Ti}_7\text{Nb}<em>2\text{O}</em>{26.5})</td>
<td>Pyrochlore</td>
<td>10.2390</td>
<td>6.28x10^4</td>
<td>0.529</td>
</tr>
<tr>
<td>(\text{Ca}<em>3\text{Ce}</em>{1.8}\text{Bi}_{1}\text{Ti}_7\text{Nb}<em>2\text{O}</em>{26.5})</td>
<td>Pyrochlore</td>
<td>10.2688</td>
<td>1.82x10^7</td>
<td>0.556</td>
</tr>
<tr>
<td>(\text{Ca}<em>3\text{Bi}</em>{1.2}\text{Ti}_7\text{Nb}<em>2\text{O}</em>{26.5})</td>
<td>Pyrochlore</td>
<td>10.3041</td>
<td>4.43x10^8</td>
<td>1.190</td>
</tr>
</tbody>
</table>

#### 7.2.4 Conclusion

New pyrochlore type semiconducting oxides: \(\text{Ca}_3\text{Ce}_{3-x}\text{Bi}_x\text{Ti}_7\text{Nb}_2\text{O}_{26.5}\) (\(x = 0.5, 1.0, 2.0, 3.0\)) 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. Here Bi substitution did not yield any microtube formation during sintering, as seen in TTB type semiconducting oxides.