Structural and dielectric properties of $Ba_3R_3Ti_5Nb_5O_{30}$ (R = Pr or Ce) system

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Several dielectric systems have been extensively studied in recent years for various applications such as high dielectric constant capacitors both discrete and multiplayer [1–5], microwave telecommunication applications [6, 7] and low loss substrates for microwave integrated circuits [8]. Dielectric materials for temperature stable capacitor applications should have a reasonable dielectric constant with good thermal stability. The high dielectric constant materials are also very important in advanced microelectronics technologies such as dynamic random access memories (DRAM) [9]. These materials have to fulfill the requirements of a high dielectric constant (ε_r), low dielectric loss (high Q) and a small temperature coefficient of the dielectric constant (τ_ε). So far, dielectric materials with relative permittivity in the range 20 to 100 such as $BaO-TiO_2$ [10], $BaO-Nd_2O_3-TiO_2$ [11, 12] and $BaO-TiO_2-Nb_2O_5$ [13] have been investigated. However, these dielectric materials ($\varepsilon_r < 100$) are not sufficient to further decrease the size of microelectronic circuits. Hence, the search for new ceramics with dielectric constant in excess of 100 has become necessary. Studies of the structural and electrical properties of some ferroelectric oxides of TB structure [14, 15] have already been reported earlier. Rare earth ion substitutions influence the structure and dielectric properties of these ceramics and result in a broad or diffuse phase transition. In the present work, $Ba_3R_3Ti_5Nb_5O_{30}$ (R = Pr or Ce) ceramics were prepared and characterized to investigate the effects of Pr and Ce substitution on the structure and dielectric properties.

High quality and phase pure ceramics have been prepared by solid-state reaction, using the conventional mixed oxide technique. Ceramic powders used in this research work were 99.99% pure supplied by S.D. Fine Chemicals and Indian Rare Earths Limited. The constituent oxides (carbonate in the case of barium) were mixed in the required stochiometry in an agate mortar and ground for 24 h by ball milling in ethanol and then calcined at 1300 °C for 4 h. The powders were reground and then pressed into disks of 10 mm diameter and at about 1 mm thickness using a hydraulic press with a pressure of 150 MPa. The discs were sintered at 1275 °–1325 °C for 4 h in air. The true density or theoretical density is calculated from the molecular weight of the sample and unit cell volume. The density measurements were done employing the boiling water method using Archimedes' principle. Crystalline phases of the sintered samples were identified using a Philips
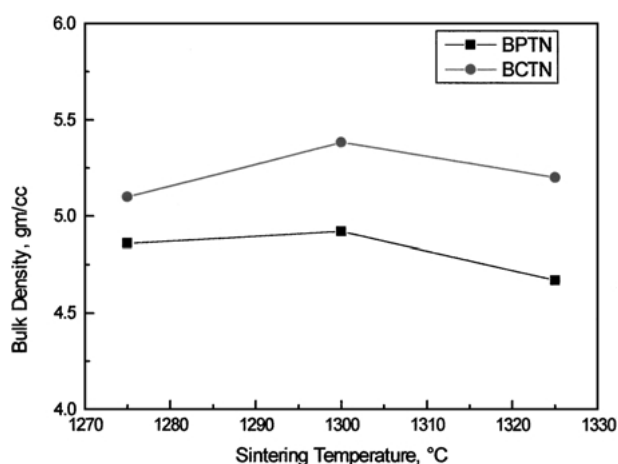

Figure 1 Bulk density of $Ba_3Re_3Ti_5Nb_5O_{30}$ (Re = Pr or Ce) ceramics as a function of sintering temperature.
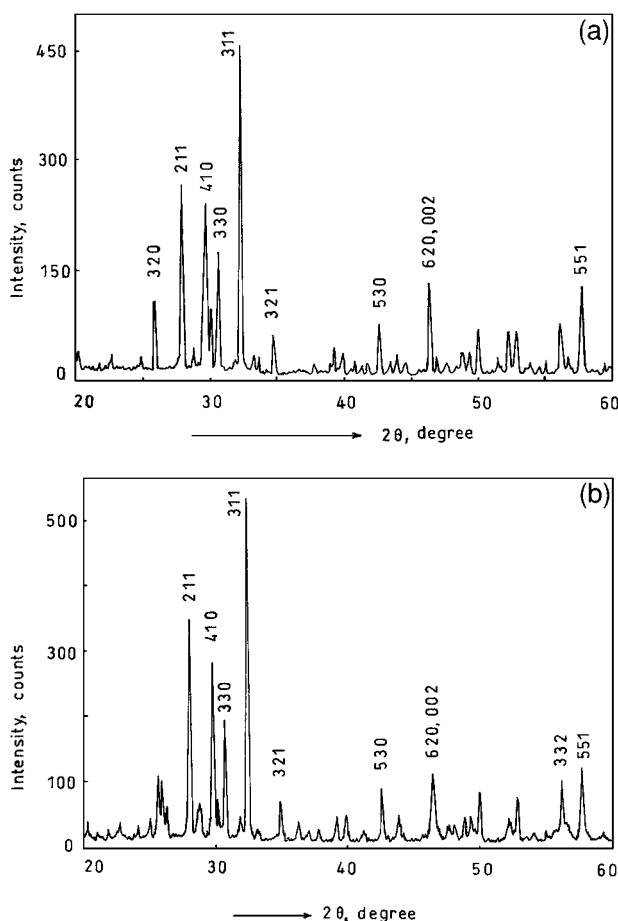
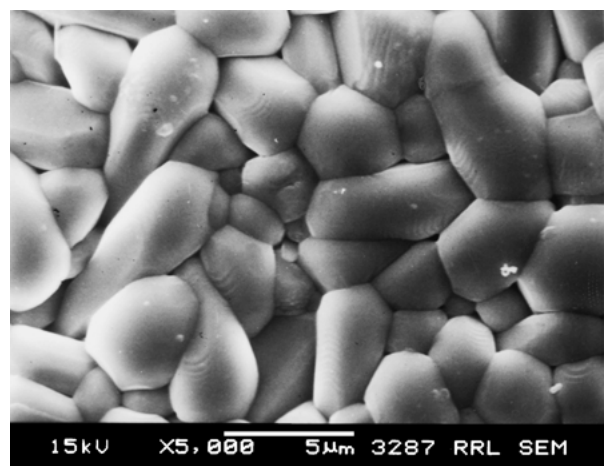*Figure 2* X-ray diffraction patterns of (a) $Ba_3Pr_3Ti_5Nb_5O_{30}$ and (b) $Ba_3Ce_3Ti_5Nb_5O_{30}$ ceramics.
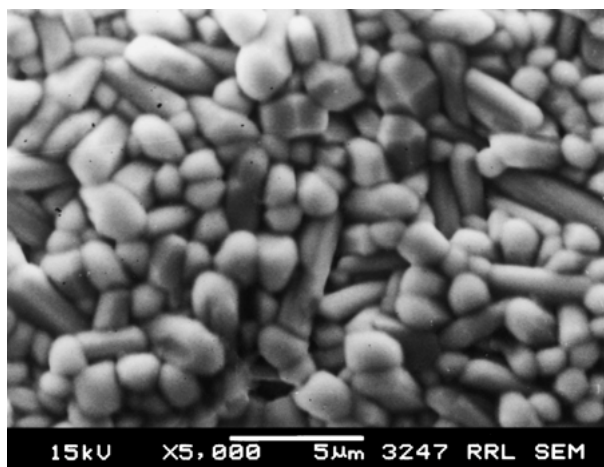
(a)
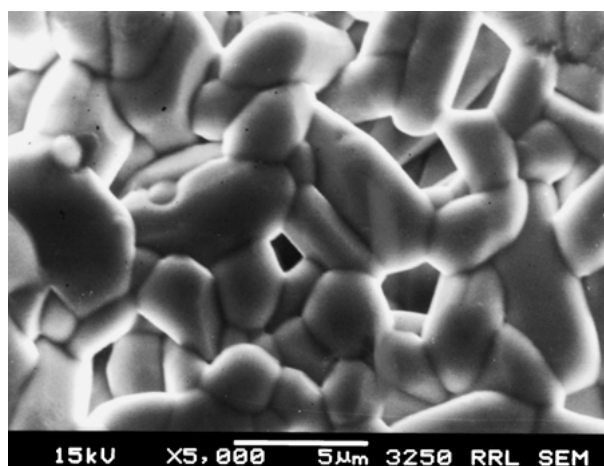
(b)


(c)

Figure 3 SEM micrographs recorded from thermally etched $Ba_3Pr_3Ti_5Nb_5O_{30}$ ceramics sintered at (a) 1275 °C, (b) 1300 °C and (c) 1325 °C.

1710 X-ray powder diffractometer utilizing Cu K_α radiation. For microstuctural studies, the sintered pellets were polished and thermally etched at 1275° for 1 h and then coated with gold by sputtering using a JFC Fine Coater. Micrographs of the samples were recorded at different magnifications with the help of Jeol JSM 5600 LV scanning electron microscope. For dielectric measurements of the pellets, silver paste was applied to the circular faces and electroded with copper leads on both sides. The electroded pellets were dried at

100 °C in an air oven. The capacitance and loss factor were measured in the frequency range from 100 Hz to 13 MHz using an impedance analyzer HP 4192A at room temperature while placing the electroded pellets in a moisture-free glass tube containing fused with $CaCl_2$ closed with a rubber cork. The Cu leads of the samples were taken out through the airtight cork.
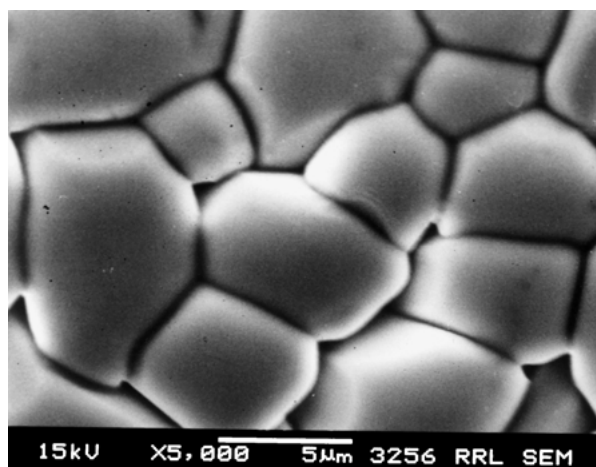
The $Ba_3R_3Ti_5Nb_5O_{30}$ (R = Pr or Ce) system had good sinterability in the temperature range 1275–1325 °C and resulted in a dense sintered product.
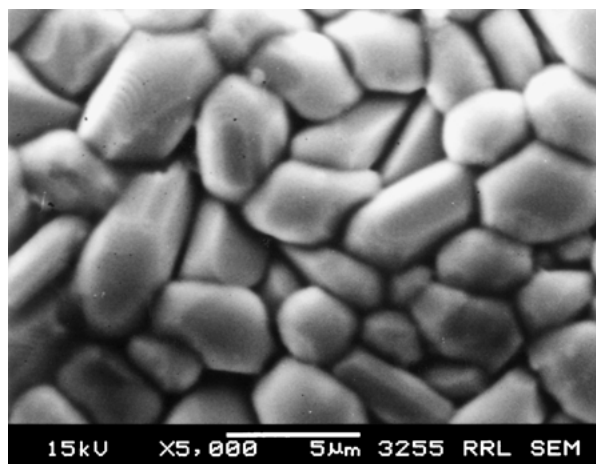
(a)
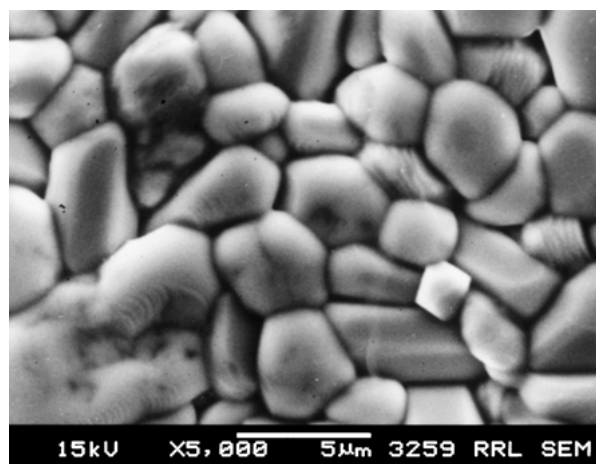
(b)

(c)

Figure 4 SEM photographs of $Ba_3Ce_3Ti_5Nb_5O_{30}$ ceramics sintered at (a) 1275 °C, (b) 1300 °C and (c) 1325 °C.

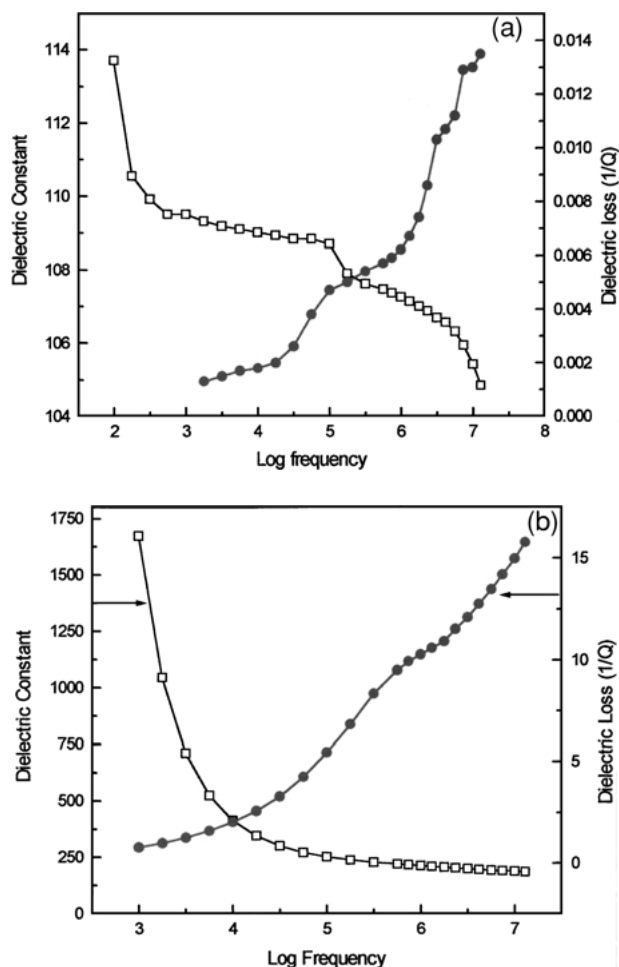*Figure 5* Variation of dielectric constant ε_r and loss of (a) $Ba_3Pr_3Ti_5Nb_5O_{30}$ and (b) $Ba_3Ce_3Ti_5Nb_5O_{30}$ ceramics.

The variation of bulk density with sintering temperature is given in Fig. 1. The density measured for $Ba_3Pr_3Ti_5Nb_5O_{30}$ is in the range 4.7 to 4.9 g/cc, whereas for $Ba_3Ce_3Ti_5Nb_5O_{30}$ it is in the range 5.1 to 5.4 g/cc. A higher density of cerium compound is due to the smaller cationic size of cerium oxide. As expected, this has affected significantly its dielectric properties. Fig. 2a and b shows the powder X-ray diffraction pattern of $Ba_3Pr_3Ti_5Nb_5O_{30}$ and $Ba_3Ce_3Ti_5Nb_5O_{30}$ ceramics. They are identical due to the similar chemical nature of Lanthanides (Pr and Ce). The sharp XRD peaks suggest the formation of well-crystallized single-phase tetragonal tungsten-bronze structure in agreement with the JCPDS file no. 38-1331. The five strong diffraction peaks correspond to 311, 221, 410, 211 and 320 planes. There is no indication of any secondary phases. The SEM micrographs recorded from Pr compound sintered at temperatures 1275 °C, 1300 °C and 1325 °C are shown in Fig. 3a–c. The grain size increases with sintering temperature in the range from 1–5 μm. Bigger grain formation is observed at higher sintering temperature. The SEM photograph of Pr compound at 1325 °C shows an elongated structure due to exaggerated grain growth. Fig. 4a–c shows the SEM micrographs of the Ce sample sintered in the same temperature range with grains from 2–6 μm. Typical cuboid grains with sharp crystalline edges are observed in both compositions at low sintering temperature (1275 °C). The micrographs for Pr as

well as Ce indicate no formation of secondary phase and are well supported by XRD (Fig. 2). The variation of dielectric constant (ε) and tangent loss with frequency (100 Hz–13 MHz) are shown for both Pr and Ce in Fig. 5a and b respectively. With Pr substitution, the dielectric constant is around 107. This is partly due to the lower density of the compact. On the other hand, the Ce based compound could increase the dielectric constant above 1673 at 1 KHz and 200 at 1 MHz with high dielectric loss. The higher value of dielectric constant at low frequency is due to the presence of all different types of polarization e.g. electronic, ionic, dipole and space charge. The increase in ε_r for the $Ba_3Ce_3Ti_5Nb_5O_{30}$ compound is largely attributed to the larger ion polarizability of Ce. The dielectric peaks of the compounds do not coincide with that of loss. The ε_r of both Pr and Ce compounds decreases with an increase in frequency. At 1 MHz both Pr and Ce compounds have dielectric constant of 107 and 213 respectively.

The compounds $Ba_3RE_3Ti_5Ta_5O_{30}$ (RE = Nd, Sm) have been synthesized and characterized and their dielectric properties have been studied. There is no change in the basic structure of the compound for substitution of different rare earth elements. Pr and Ce doped compounds show dielectric constants of around 123 and 117 (f = 1 MHz) respectively. These compounds having high dielectric constant ε_r and low loss (1/Q) are possible materials for practical applications in advanced microelectronics technology.

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