Structural and dielectric properties of ferroelectric $Sr_4R_2Ti_4Nb_6O_{30}$ ($R = Sm$ and Nd) ceramics

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Since the discovery of ferroelectricity and related properties in $BaTiO_3$ [1], a number of ferroelectric oxides of perovskite structure and tungsten bronze (TB) structure have been studied. Some niobates with the TB structure have attracted much attention due to their interesting ferroelectric, pyroelectric, piezoelectric, and nonlinear optic properties for applications in various electric devices, such as transducers, actuators, capacitors, and ferroelectric random access memory [2–7]. The TB structure consists of a complex array of distorted BO_6 octahedra sharing corners in such a way that three different types of interstices (A, B, and C) are available for a wide variety of cations giving the general formula $(A_1)_2(A_2)_4(C)_4(B_1)_2(B_2)_8O_{30}$. It has been found that the physical properties can be improved by different ionic substitutions at the above-mentioned sites. A number of compounds such as $Ba_5RTi_3Nb_7O_{30}$, $Ba_3R_3Ti_5Nb_5O_{30}$, and $Ba_4R_2Ti_4Nb_6O_{30}$ have been studied in BaO-R_2O_3-TiO_2-Nb_2O_5 (R = Dy, La, Nd, Sm, and Y) system in order to find new TB niobate ceramics [6–13]. However, very little data are available on the structure and dielectric properties of materials with the TB structure in the SrO-TiO_2-R_2O_3-Nb_2O_5 system. Thus, we report here the structural and dielectric properties of $Sr_4R_2Ti_4Nb_6O_{30}$ [R = Nd, and Sm].

Polycrystalline samples of $Sr_4Nd_2Ti_4Nb_6O_{30}$ and $Sr_4Sm_2Ti_4Nb_6O_{30}$ (referred to as SNTN and SSTN respectively) were prepared using high temperature solid-state reaction techniques. The stoichiometric mixtures of the high purity powders of $SrCO_3$ (>99.9%), R_2O_3[R = Nd and Sm] (>99.9%), TiO_2 (>99.95%), and Nb_2O_5 (>99.9%) were weighed and thoroughly ground in an agate mortar to obtain homogeneous mixtures and calcined at 1320 °C for 48 hrs. The calcined powders were reground into very fine powders and pelletized into disks of 11 mm diameter and about 2–4 mm thickness using a cold isostatic press at a pressure of 200 MPa, using polyvinyl alcohol as a binder. The pellets were sintered in air at 1370 °C for 4 hrs and cooled naturally to room temperature. The densities of the compacts were measured by the Archimedes method. The phase identification and microstructure characterization were done using a Rigaku D/MAX-RB powder X-ray diffractometer (XRD) using Cu K_α radiation ($\lambda = 0.154\,06$ nm) in a 2θ range from 10 to 70 ° and a Jeol JSM-5610LV scanning electron microscope (SEM). To study the dielectric properties, silver paste was applied to the circular surfaces of the samples, then heated at 600 °C for 1 hr and cooled naturally to room temperature. Temperature-dependent dielectric constant measurements were made, using a HP4284A LCR meter equipped with a thermostat, from room temperature (20 °C) to 400 °C at 10 kHz, 100 kHz, and 1 MHz.

The room temperature XRD patterns obtained using Cu K_α radiation are shown in Fig. 1a, and b. The two materials were found to exhibit single phase tetragonal TB structures in agreement with JCPDS file No. 34-409 for $Sr_3TiNb_4O_{15}$. The unit cell parameters of the ceramics refined by the least square method are as follows: $a = 1.22711(3)$ nm, $c = 0.38631(1)$ nm for SNTN; and $a = 1.22472(3)$ nm; $c = 0.38606(1)$ nm for SSTN. The replacement of Nd with the relatively smaller Sm leads to the unit cell parameters of SSTN compared to that of SNTN. The SNTN and SSTN ceramics show bulk densities of 5.129 $g \cdot cm^{-3}$ (96.2%) and 5.152 $g \cdot cm^{-3}$ (95.7%) respectively. Fig. 2 shows the SEM micrographs of the fracture surfaces of the SSTN and SNTN ceramics. The microstructure is monophasic with uniformly packed grains in the size range 2–7 μm for SSTN and 2–10 μm for SNTN.

The temperature-dependencies of the dielectric constants at frequencies of 10 kHz, 100 kHz, and 1 MHz for SSTN and SNTN are shown in Fig. 3. SSTN and SNTN exhibit room temperature dielectric constant of around 108 and 267 at 1 MHz respectively. As temperature increases, there is a sharp peak for both compounds in the dielectric constant corresponding to the ferroelectric-paraelectric phase transition from tetragonal 4 *mm*

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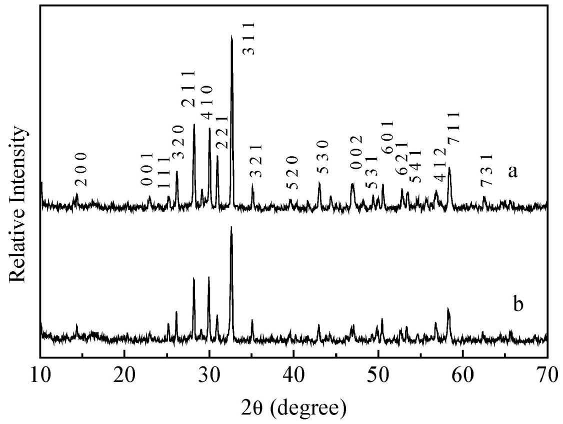
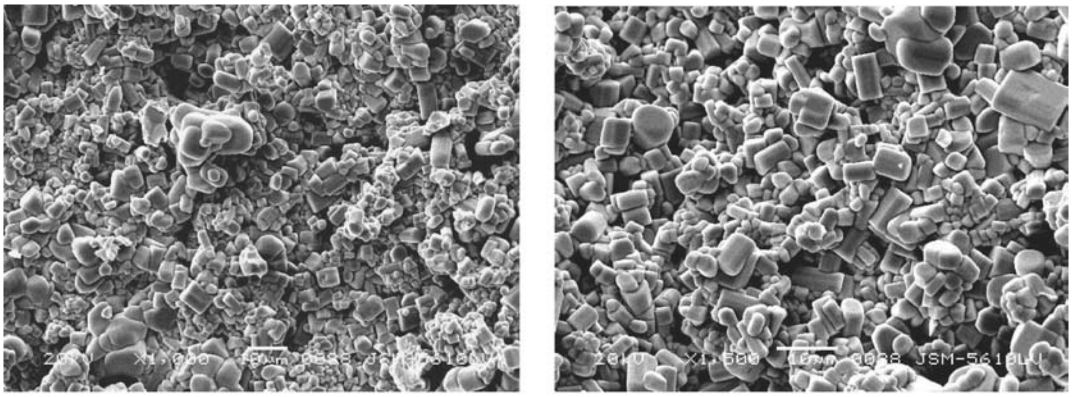


Figure 1 X-ray powder diffraction patterns of (a) SSTN and (b) SNTN.

symmetry to 4 *mmm* symmetry, which confirms that the two compounds belong to the ferroelectric TB phase with space group P4bm at room temperature [11,13]. The Curie temperature (T_C) is around 370 °C for SSTN and 260 °C for SNTN. The T_c of $Sr_4R_2Ti_4Nb_6O_{30}$ (R = Sm and Nd) decreases as the ionic radius of the R ion increases, and these results agree with the work of Bhanumathi *et al.* [14]. The T_c and dielectric constant for the three frequencies is almost constant for SSTN and SNTN in contrast to the characteristics of relaxor ferroelectrics with the TB structure such as $Sr_5NdTi_3Nb_7O_{30}$ and $Ba_5SmTi_3Nb_7O_{30}$, but similar to the situation in $Ba_4Nd_2Ti_4Nb_6O_{30}$ and $Ba_4Sm_2Ti_4Nb_6O_{30}$ reported by Chen *et al.* [11, 13, 15]. To some extent, this can be explained by the ordered-disordered state of A-sites ions in the TB structure. For $Sr_4Nd_2Ti_4Nb_6O_{30}$, the larger Sr^{2+} ions occupy A_2-sites and the smaller Nd^{3+} ions occupy A_1-sites; thus this phase more easily forms ordered state. In contrast in $Sr_5NdTi_3Nb_7O_{30}$ the number of the larger Sr^{2+} ions is not equal to the number of larger interstices A_2-sites, hence, the compound prefers to form the disordered state. In general, the ordered state is advantageous for ferroelectricity and the disordered state favors paraelectricity such that T_c of $Sr_4Nd_2Ti_4Nb_6O_{30}$ is higher than that of $Sr_5NdTi_3Nb_7O_{30}$ (180 °C) [15].

We conclude that the relaxor ferroelectric ceramics $Sr_4R_2Ti_4Nb_6O_{30}$ [R = Nd and Sm] have the tetragonal tungsten bronze structure at room temperature and undergo ferroelectric-paraelectric phase transitions around 260 and 370 °C for SNTN and SSTN, respectively. SNTN and SSTN compounds have room temperature dielectric constants of 267 and 108 at 1 MHz. The comparatively low room temperature dielectric constant indicates that these materials may have attractive benefits in electrooptic and infrared pyroelectric detector applications when grown in bulk single crystal or thin-film form [16].



(a) (b)

Figure 2 SEM micrographs of fracture surfaces of (a) SSTN and (b) SNTN.

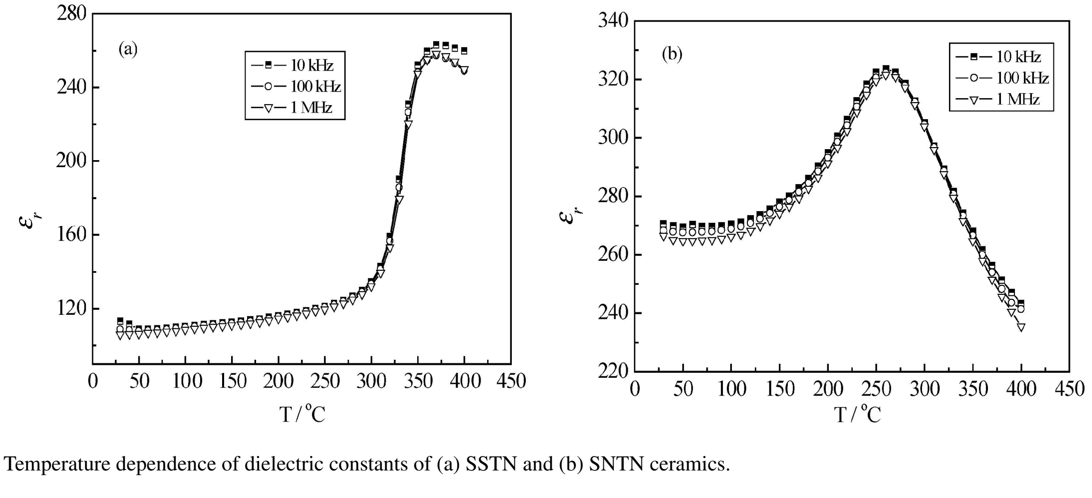


Figure 3 Temperature dependence of dielectric constants of (a) SSTN and (b) SNTN ceramics.

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