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Preparation, characterization and dielectric properties of $Sr_4Ln_2Ti_4Ta_6O_{30}$ (Ln = Nd and Sm) ceramics

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Materials of tungsten-bronze (TB) structure belong to an important family of dielectric materials, which display interesting ferroelectric, pyroelectric, piezoelectric, and nonlinear optic properties for applications in various electric devices, such as transducers, actuators, capacitors, and ferroelectric random access memory [1–3]. The TB structure consists of a frame work 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 occupying in the general formula $(A_1)_2(A_2)_4(C)_4(B_1)_2(B_2)_8O_{30}$. It has been found that different ionic substitutions at the above-mentioned sites can play an important role in tailoring their physical properties [2–4]. In previous investigations, the ferroelectric nature of TB compounds has been especially emphasized, and less attention has been focused on those compounds with paraelectric nature which occur in the TB family. Recently, owing to the rapid progress in microwave telecommunications, satellite broadcasting and other related technologies, a number of paraelectric TB compounds such as $Ba_5RTi_3Ta_7O_{30}$, $Sr_5RTi_3Ta_7O_{30}$, $Ba_4R_2Ti_4Ta_6O_{30}$, $Ba_5RZnM_9O_{30}$ and $Ba_3R_3Ti_5M_5O_{30}$ (R = La, Nd, Sm; M = Nb, Ta) with high dielectric constant have attracted much attention because of being important in the miniaturization of microelectronic devices [5–19]. An extensive literature survey on TB compounds reveals that, even though a lot of work has been done on the compounds of this family, there is no report on the presence or the dielectric properties of titled compounds. This paper presents the preparation, characterization and dielectric properties of two new compounds $Sr_4Ln_2Ti_4Ta_6O_{30}$ (Ln = Nd, Sm), for the first time.

Polycrystalline samples of $Sr_4Nd_2Ti_4Ta_6O_{30}$ and $Sr_4Sm_2Ti_4Ta_6O_{30}$ [referred to as SNTT and SSTT, respectively] were prepared using high temperature solid-state reaction techniques. The stoichiometric mixtures of the high purity powders of $SrCO_3$ (>99.9%), Ln_2O_3 (Ln = Nd, Sm) (>99.9%), TiO_2 (>99.95%) and Ta_2O_5 (>99.9%) were weighed and thoroughly ground in an agate mortar to obtain homogeneous mixtures and calcined at 1380 °C for 48 hrs. The calcined powders were reground into very fine powders and pressed into disks of 11 mm diameter and about 2–4 mm thickness at a pressure of 200 MPa, using polyvinyl alcohol as a binder. The pellets were sintered in air at 1450 °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 ($\lambda = 0.15406$ 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 measurement 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.

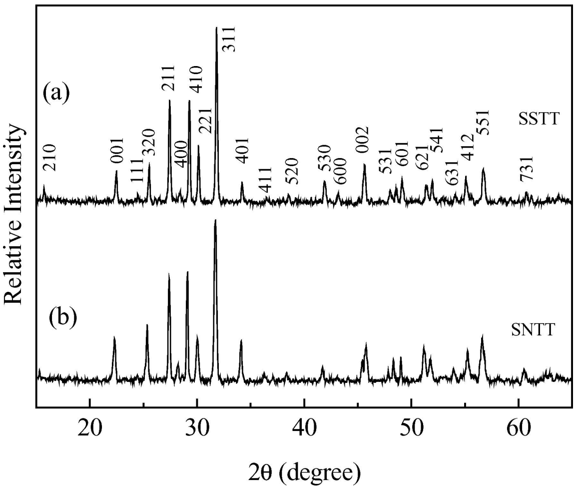

Figure 1 XRD patterns of SSTT and SNTT.

The room temperature XRD patterns obtained using Cu K_α radiation are shown in Fig. 1. The two materials were found to exhibit single phase tetragonal TB structures in agreement with JCPDS file No. 54-109 for $Sr_6Ti_2Ta_8O_{30}$. All peaks were indexed, and there was no evidence for any secondary phase(s) present. The unit cell parameters of the ceramics refined by the least-square method are as follows: $a = 1.22755(3)$ nm, $c = 0.38661(1)$ nm for SNTT; and $a = 1.22482(3)$ nm, $c = 0.38611(1)$ nm for SSTT. The replacement of Nd with the relatively smaller Sm leads to the smaller unit

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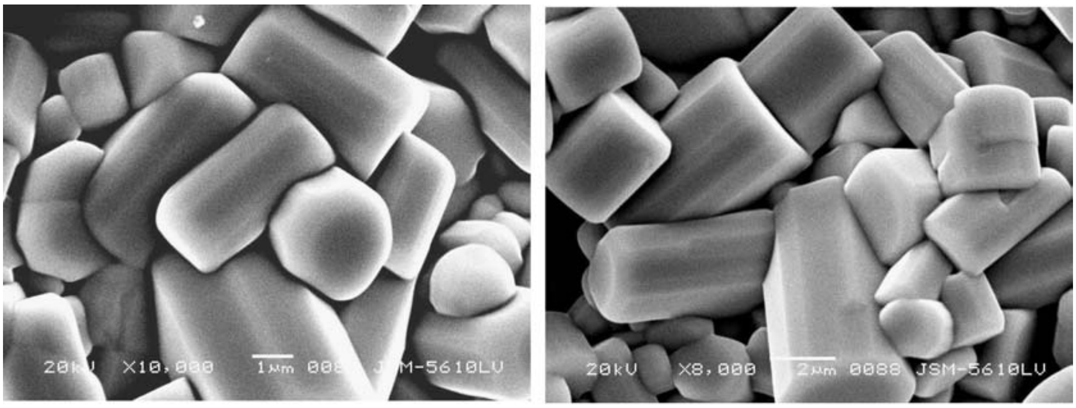

(a) (b)

Figure 2 SEM micrographs of fracture surfaces of (a) SSTT and (b) SNTT.

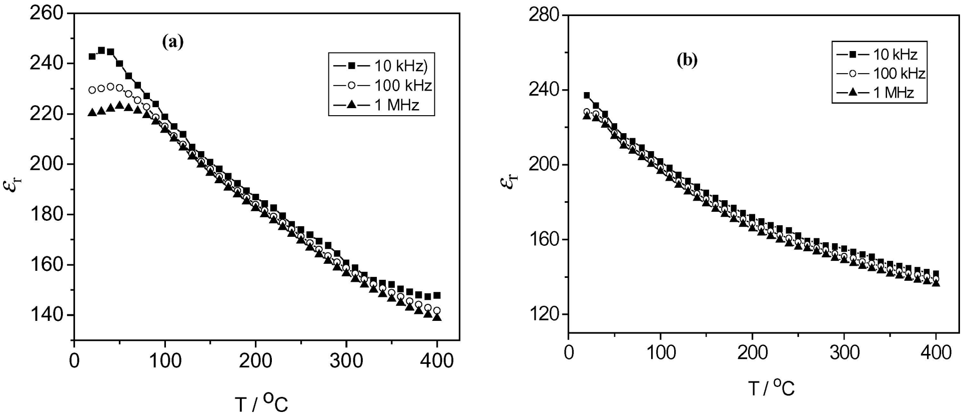

Figure 3 Temperature dependence of dielectric constants of (a) SSTT and (b) SNTT ceramics.

cell parameters of SSTT compared to that of SNTT. The SNTT and SSTT compositions sintered into dense ceramics with relative densities of 94.7 and 95.4%, respectively. Fig. 2 shows the SEM micrographs of the fracture surfaces of the SSTT and SNTT ceramics. The microstructure is monophasic with packed grains in the size range 2–8 μm for SSTT and 2–6 μm for SNTT.

Temperature-dependence of the dielectric constant for SNTT and SSTT are shown in Fig. 3a and b, respectively. Dielectric constant increases with decreasing frequency due to the presence of all different types of polarization (electronic, ionic, dipole and space charge) at low frequency. SNTT and SSTT show room temperature dielectric constant of around 225 and 220 at 1 MHz, respectively. As temperature increased, there was a broad peak of dielectric constant corresponding to ferroelectric-paraelectric phase transition from tetragonal 4 mm symmetry to 4/mm symmetry for SSTT, which confirms that SSTT belongs to ferroelectric TB phase with space group P4bm at room temperature [3, 9]. The Curie temperature (T_c) for SSTT ceramic at frequency of 10 kHz, 100 kHz and 1 MHz are around 30, 40 and 50 °C, respectively. The T_c is found to shift towards higher temperature side at higher frequencies, and this is the characteristic of relaxor ferroelectrics with TB structure [4, 11]. The broadening of the dielectric peaks may be attributed to the disorder distribution of cations at the B sites in TB structure. The degree of disorderness or diffusivity (γ) can be calculated using the equation $\ln(1/\varepsilon - 1/\varepsilon_{\max}) = \gamma \ln(T - T_c) +$ Constant [20]. The diffusivities γ calculated at 10 kHz for SSTT is 1.37. γ is between 1 and 2 for SSTT, which confirms the diffused phase transition.

Although the relative dielectric constant ε_r of SNTT ceramic gradually decreases from 225 to 136 at 1 MHz as temperature increases from 20 to 400 °C and no dielectric peak for the ferroelectric/paraelectric phase transition is observed, indicating T_c is below the room temperature, and SNTT belongs to paraelectric phase of TB structure at room temperature. The temperature coefficients of the dielectric constant (τ_ε) and the dielectric loss at 1 MHz are -1610 ppm °C^{-1} and 0.0011, respectively. In comparison with ε_r in the range of 103–159 for paraelectric TB ceramics such as $Ba_4Nd_2Ti_4Ta_6O_{30}$ and $Ba_5NdTi_3Ta_7O_{30}$ in BaO-Nd_2O_3-TiO_2-Ta_2O_5 system [10], the ε_r of SNTT is much higher and more encouraging, but its negative τ_ε is so large that precludes its practical applications as microwave dielectric resonators. However, through appropriate substitution or introducing secondary phases with positive τ_ε, it may be possible to obtain a near-zero temperature coefficient of the dielectric constant.

The T_c of $Sr_4Ln_2Ti_4Ta_6O_{30}$ (Ln = Sm and Nd) decreases as the ionic radius of the Ln ion increases, and these results agree with the work of Bhanumathi *et al.* [21]. The T_c of $Sr_4Sm_2Ti_4Ta_6O_{30}$ is higher compared to that of $Sr_5SmTi_3Ta_7O_{30}$ (−40 °C) [12], and this is similar to the situation in $Sr_5SmTi_3Nb_7O_{30}$ (250 °C) and

$Sr_4Sm_2Ti_4Nb_6O_{30}$ (370 °C) [8, 19]. To some extent, this can be explained by the ordered–disordered state of A-sites ions in the TB structure. For $Sr_4Sm_2Ti_4Ta_6O_{30}$, the larger Sr^{2+} ions occupy A_2-sites and the smaller Sm^{3+} ions occupy A_1-sites; thus this phase more easily forms ordered state. In contrast in $Sr_5SmTi_3Ta_7O_{30}$ 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 $Sr_4Sm_2Ti_4Ta_6O_{30}$ is higher than that of $Sr_5SmTi_3Ta_7O_{30}$.

Thus, it can be concluded that $Sr_4Sm_2Ti_4Ta_6O_{30}$ belongs to ferroelectric phase of TB structure and undergoes diffuse type of ferroelectric-paraelectric phase transition around 30 °C. The comparatively low room temperature dielectric constant observed in the ceramic sampleindicates that it may have attractive benefits in electrooptic and infrared pyroelectric detector applications when grown in buck single crystal or thin-film form [3]. $Sr_4Nd_2Ti_4Ta_6O_{30}$ belongs to paraelectric phase of TB structure at room temperature. Its ceramic exhibits high dielectric constant of 225 together with low dielectric loss 0.0011 at 1 MHz, and might have potential application in temperature-compensating capacitors.

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