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Structural and dielectric properties of $Ba_6M_{0.67}Nb_{9.33}O_{30}$ ($M =$ Zn and Ni) ceramics

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Recently, some ferroelectric niobates in tungsten-bronze (TB) family 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 [1–5]. Some paraelectric niobates and tantalates with high dielectric constant and low loss are also very important due to the rapid progress in microwave telecommunications, satellite broadcasting and other related devices [6–8] . 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 above-mentioned sites can play an important role in tailoring their physical properties. Some compounds such as $Ba_5RTi_3M_7O_{30}$, $Ba_4R_2Ti_4M_6O_{30}$, $Ba_3R_3Ti_5M_5O_{30}$, have been studied in $BaO\text{-}R_2O_3\text{-}TiO_2\text{-}M_2O_5$ ($R =$ Dy, La, Nd, Sm; $M =$ Nb, Ta) system in order to find some new filled TB niobate ceramics [4–14]. Extensive literature survey on TB compounds reveals that, even though a lot of work has been done on the compounds of this family, not much has been reported on the compounds with TB structure in $BaO\text{-}MO\text{-}Nb_2O_5$ ($M =$ Zn, Ni) system, and as there is no report on these compounds, we have systematically studied the structural and dielectric properties of the compounds $Ba_6M_{0.67}Nb_{9.33}O_{30}$ [$M =$ Zn, Ni] and report the result here.

Polycrystalline samples of $Ba_6Zn_{0.67}Nb_{9.33}O_{30}$ and $Ba_6Ni_{0.67}Nb_{9.33}O_{30}$ [referred to as BZN and BNN respectively] were prepared by a high temperature solid-state reaction technique. The stoichiometric mixtures of the high purity powders of $BaCO_3$ (>99.9%), MO [$M =$ Zn, Ni] (>99.9%), and Nb_2O_5 (>99.9%) were weighed and thoroughly grounded in agate mortar to obtain a homogeneous mixture and calcined at 1300 °C for 48 h. The calcined powders were regrounded into very fine powders and palletized into disks of 11 mm diameter and about 2–4 mm thickness using cold isostatic press at a pressure of 200 Mpa using polyvinyl alcohol as a binder. The pellets were sintered in air at temperature 1330 °C for 4 h 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 ranges from 10 to 70 ° and a Jeol JSM-5610LV scanning electron microscope (SEM). To study dielectric properties, silver paste was applied to the circular surfaces of the samples, then dried at 600 °C for 1 h 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 (10 °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. Those compositions were found to exhibit a single phase tetragonal TB structure in agreement with JCPDS file No. 38-1329 of $Ba_6Ti_2Nb_8O_{30}$. The unit cell parameters of those ceramics refined by least method are as the following: $a = 1.25940(3)$ nm, $c = 0.40008(2)$ nm for BZN; and $a = 1.25926(5)$ nm, $c = 0.39962(5)$ nm, for BNN. The BZN and BNN ceramics show a bulk density of 5.567 g cm^{-3} (96.2%) and 5.595 g cm^{-3} (96.6%) respectively. Fig. 2a and b show the SEM photographs of the fracture sections of the BZN and BNN ceramics. The microstructure indicates a monophase constitution with uniformly packed granular grains in the range 1–7 μm size for BZN and BNN.

Temperature-dependence of the dielectric constant for BZN and BNN is 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. BZN and BNN compounds shows room temperature dielectric constant of around

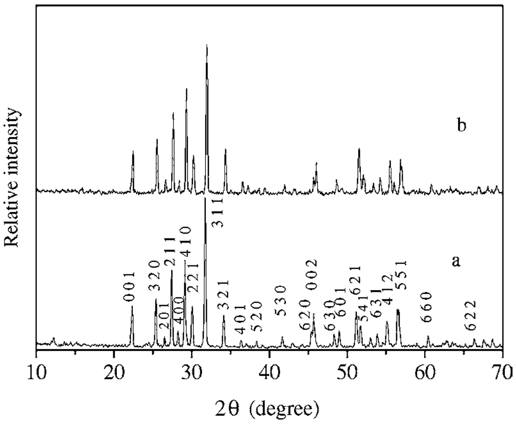

Figure 1 X-ray powder diffraction patterns of (a) BZN and (b) BNN.

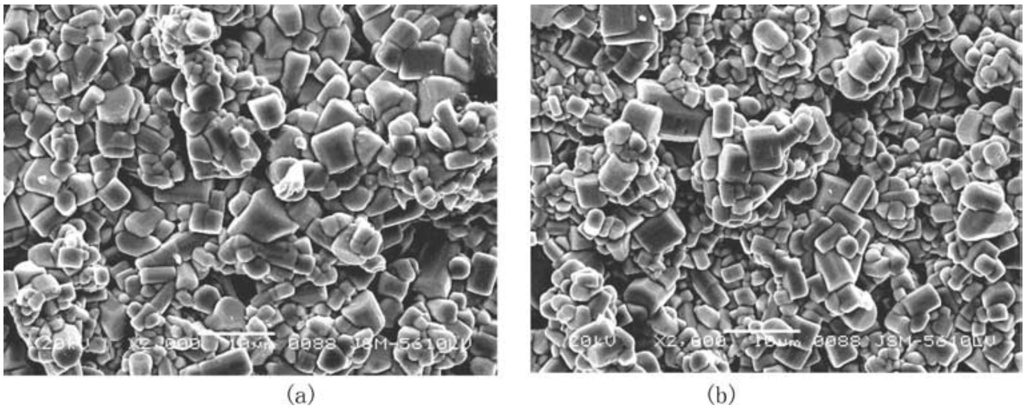
(a) (b)

Figure 2 SEM micrographs of (a) BZN and (b) BNN.

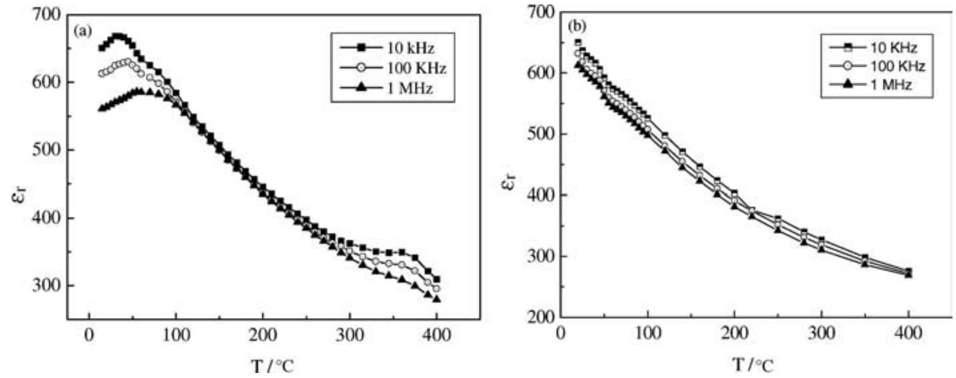

Figure 3 Temperature dependence of dielectric constant of (a) BZN and (b) BNN.

560 and 612 at 1 MHz respectively. As the temperature increases, there was a broad peak of dielectric constant corresponding to ferroelectric-paraelectric phase transition from tetragonal 4 mm symmetry to 4/mmm symmetry for BZN, which confirmed BZN belongs to ferroelectric TB phase with space group P4bm at room temperature [11, 13]. The Curie temperatures (T_C) at frequency of 10 KHz, 100 KHz and 1 MHz are around 30, 45 and 55 °C for BZN ceramic. T_c is found to shift towards higher temperature side at higher frequencies, and this is characteristic of relaxor ferroelectrics with TB structure [5, 10–12]. 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 [15] $\ln(1/\varepsilon - 1/\varepsilon_{\max}) = \gamma \ln(T - T_c) +$ constant. The diffusivities γ calculated at 10 KHz for BZN is 1.47. γ is between 1 and 2 for BZN, which confirms the diffused phase transition.

While the relative dielectric constant ε_r of BNN ceramic gradually decreases from 612 to 269 at 1 MHz as temperature increases from 10 to 400 °C and no dielectric peak for the ferroelectric/paraelectric phase transition is observed, indicating the Curie point is below the room temperature, and BNN 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 -2420 ppm °C^{-1} and 0.0021 repectively. In comparison with ε_r in the range 110–170 and τ_ε in the range -1000–2400 ppm °C^{-1} for ceramics such as $Ba_5NdTi_3Ta_7O_{30}$ and $Ba_5SmTi_3Ta_7O_{30}$ with paraelectric TB structure in BaO-R_2O_3-TiO_2-M_2O_5 ($R =$ Nd, Sm; $M =$ Nb, Ta) system [7, 9], ε_r of BNN is much higher but τ_ε is slightly larger.

Thus it can be concluded that $Ba_6Zn_{0.67}Nb_{9.33}O_{30}$ 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 sample indicates that BZN may have attractive benefits in electrooptic and infrared pyroelectric detector applications when grown in buck single crystal or thin-film form [16]. BNN belongs to paraelectric phase of TB structure at room temperature. BNN ceramics have high dielectric constant of 612 together with low dielectric loss 0.0021 at 1 MHz, and might have potential application in temperature-compensating capacitors.

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