Preparation, structural, and dielectric properties of $Ba_5YZnM_9O_{30}$ (M = Nb, Ta) ceramics

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Electronic materials of high dielectric constant, low loss, and good stability of temperature coefficient of resonant frequency have been extensively studied because of their applications in discrete and multilayer (MLC) capacitors, microwave telecommunication applications, and low loss substrates for microwave integrated circuits [1–4]. The high dielectric constant materials are also very important in advanced microelectronic technologies such as dynamic random access memories (DRAM) [5]. So far, many dielectric materials have been studied such as $Ba(Zn_{1/3}Ta_{2/3})O_3$, $Ba_2Ti_9O_{20}$, $(Zr,Sn)TiO_4$, and rare earth titanates in $BaO\text{-}Re_2O_3\text{-}TiO_2$ [3]. Among these materials perovskite ceramic $Ba(Zn_{1/3}Ta_{2/3})O_3$ in the $BaO\text{-}ZnO\text{-}Ta_2O_5$ system is extremely important for applications at high frequency (>10 GHz) and at high power due to its high Q-values and near zero temperature coefficient [3]. Considering some ceramics with filled tungsten-bronze (TB) structure such as $Ba_3Ln_3Ti_5Nb_5O_{30}$, and $Ba_5LnTi_3Ta_7O_{30}$ in the $BaO\text{-}Ln_2O_3\text{-}TiO_3\text{-}Ta_2O_5/Nb_2O_5$ system (Ln = La, Sm, Nd) reported by Sebastian *et al.* and Chen *et al*. have high dielectric constant and low loss [6–13], and closed-shell ions like Zn^{2+} would make the materials poor conductors, and hence, TB ceramics in the $BaO\text{-}ZnO\text{-}Nb_2O_5/Ta_2O_5$ system might possess useful dielectric properties. However, very little data are available on TB ceramics in this system, and there is no report on the titled compounds. This paper firstly presents the preparation, characterization, and dielectric properties of two new TB compounds $Ba_5YZnNb_9O_{30}$ and $Ba_5YZnTa_9O_{30}$.

High purity powders of $BaCO_3$ (>99.5%), Y_2O_3 (>99.5%), ZnO (>99.95%), and M_2O_5 (M = Nb, Ta) (>99.9%) were weighed to $Ba_5YZnM_9O_{30}$ (M = Nb, Ta) stoichiometry, respectively. The compounds with M as Nb and Ta will be referred to as BYZN and BYZT respectively in the remaining part of the text. The powders were ground in an agate mortar to obtain a homogeneous mixture and calcined at 1300 and 1420 °C for 24 hrs for BYZN and BYZT, respectively. The calcined powders were reground into very fine powders and pressed into disks of 11 mm diameter and about 2–4 mm thickness using a cold isostatic press with a pressure of 200 MPa. The pellets were sintered in air at 1350 and 1450 °C for 4 hrs for BYZN and BYZT respectively.

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 X-ray diffractometer (XRD) using Cu K_α radiation ($\lambda = 0.15406$ nm) and a JSM-5610LV scanning electron microscope (SEM). To study dielectric properties, silver paste was applied to the circular faces, then dried at 600 °C for 20 mins and cooled naturally to room temperature. Temperature-dependent dielectric measurements were made using an HP4284A LCR meter equipped with a thermostat from room temperature (20 °C) to 400 °C at 1, 10, 100 kHz, and 1 MHz. The temperature coefficient of the dielectric constant (τ_ε) was calculated using the data in the temperature range of 20 to 85 °C at 1 MHz. The capacitance and loss factor were determined at room temperature in the range 1 kHz to 1 MHz.

The XRD patterns are shown in Fig. 1a and b. These compositions were found to exhibit a single phase tetragonal TB structure in agreement with JCPDS file No. 51-1869 of $Ba_6Zn_{0.67}Nb_{9.33}O_{30}$. The unit cell parameters of those ceramics refined by the least squares method are $a = 1.25524(4)$ nm, $c = 0.39705(2)$ nm for BYZN; and $a = 1.25693(4)$ nm, $c = 0.39522(2)$ nm for BYZT. The BYZN and BYZT compositions sintered into dense ceramics without the use of any additive. They showed a bulk density of 5.462 gcm^{-3} (95.4%) and 7.545 gcm^{-3} (96.2%) respectively. Fig. 2a and b show the SEM micrographs of the fracture sections of BYZN and BYZT ceramics. These ceramics have good sinterability with a low porosity. The microstructure indicates a single phase constitution with uniformly packed columnar grains in the range 2–7 μm size for both BYZN and BYZT.

Temperature-dependence of the dielectric constant at 10 k, 100 k, and 1 MHz frequency for both the compounds are shown in Fig. 3a and b. Dielectric constant increases with decreasing frequency due to the presence of different types of polarization (electronic, ionic, dipole, and space charge) at low frequency [6, 7]. The room temperature dielectric constant and dielectric loss of BYZN are 456 and 0.0065, respectively. As temperature increases, there is a broad peak of dielectric constant corresponding to ferroelectric-paraelectric phase transition from tetragonal 4*mm* symmetry to 4 *mmm* symmetry for BYZN [9–12]. The Curie temperature (T_C) at frequencies of 10 kHz,

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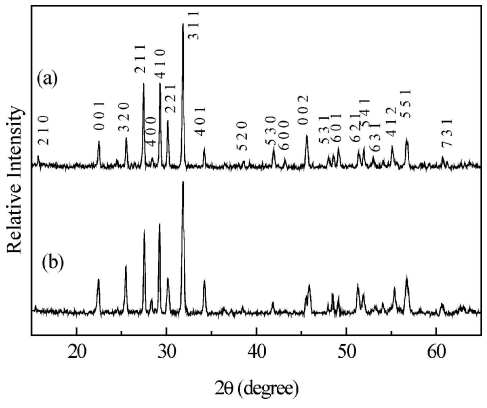
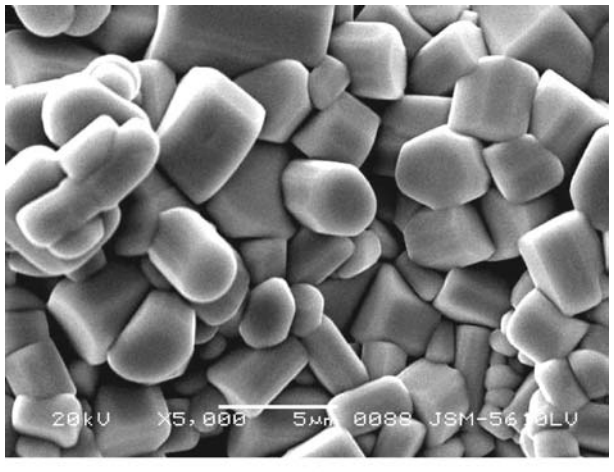
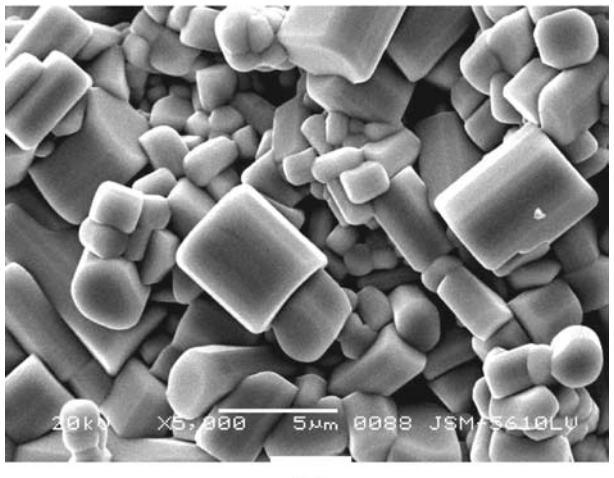


Figure 1 XRD patterns of (a) BYZN and (b) BYZT.



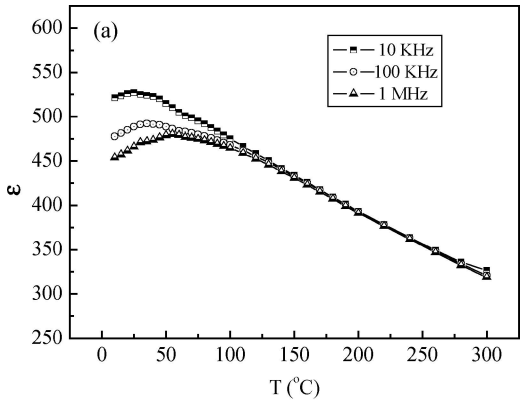
(a)



(b)

Figure 2 SEM micrographs of (a) BYZN and (b) BYZT ceramics.

100 kHz and 1 MHz are around 25, 35, and 50 °C for BYZN ceramics. 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 [6, 8]. The broadening of the dielectric peaks may be attributed to the different types of disorder and defects in the system. The degree of disorder or diffusivity (γ) can be calculated using the equation [14] $\ln(1/\varepsilon - 1/\varepsilon_{max}) = \gamma \ln(T - T_c) + \text{constant}$. The diffusivities γ calculated at 10 kHz for BYZN is 1.51. γ is between 1 and 2 for BYZN, which confirms the diffused phase transition.



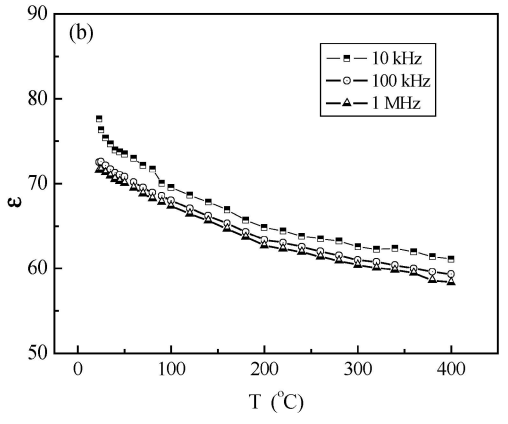


Figure 3 Temperature dependence of dielectric constant of (a) BYZN and (b) BYZT ceramics.

While the relative dielectric constant ε_r of BYZT ceramic gradually decreases 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 BYZT belongs to paraelectric phase of TB structure at room temperature. The room temperature dielectric constant, dielectric loss, and temperature coefficients of the dielectric constant (τ_ε) at 1 MHz are 72, 0.0051, and -798 ppm°C^{-1} respectively. 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-Ln_2O_3-TiO_2-Ta_2O_5 (Ln = La, Nd, Sm) system [7, 9], the τ_ε of BYZT ceramic is much smaller, while its ε_r is slightly smaller than those ceramics too [13].

$Ba_5YZnM_9O_{30}$ (M = Nb, Ta) ceramics have tetragonal TB structure at room temperature. BYZN ceramic undergoes diffuse type of ferroelectric-paraelectric phase transition around 50 °C at 1 MHz. BYZN has a high dielectric constant of 456 and low loss of 0.0065, and is a possible candidate for practical applications in advanced high microelectronic technology. BYZT shows dielectric constant of 72, low dielectric loss 0.0051 as well as relatively small temperature coefficients of the dielectric constant (τ_ε), and might have potential application in temperature-compensating capacitors [6, 7].

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