STRUCTURE, MICROSTRUCTURE AND DIELECTRIC STUDY OF $(Ba_{0.6}Sr_{0.4})(Zr_{0.6}Ti_{0.4})O_3$-$Nb_2O_5$-$Fe_2O_3$-RE (RE=$La_2O_3$,$Gd_2O_3$) CERAMICS

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Abstract

The influence of La and Gd doped on the microstructure and dielectric properties, including the phase structure, temperature dependence of permittivity, $(Ba_{0.6}Sr_{0.4})(Zr_{0.6}Ti_{0.4})O_3$–$Nb_2O_5$–$Fe_2O_3$(BSZT40NF) materials have been investigated by X-ray diffraction, SEM, and LCR analyzer, respectively. Experimental results revealed that incorporation of proper content of La and Gd basically soluted in the lattice of BSZT40NF and can control the grain growth, reduce the dielectric loss of the BSZT40NF materials. The development of microstructure promoted by the additives can result in the improvement of the dielectric constant.

Keywords: Perovskite, BT, BSZT, Rare earth ion, SEM, dielectric properties.

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1. INTRODUCTION

Barium titanate (BT) is the most widely used perovskite structured ceramic compound which finds large number of electronics applications among all perovskite structured ceramics [1]. Doping process is undertaken for certain properties of ceramics and dopant plays an important role in modifying the ceramics behavior such as multilayer ceramics capacitor, data storage media, high capacity memory cells and thermistors etc. BT-based ferroelectric exhibiting high dielectric nonlinearity has become one of the promising materials to realize the potential applications for tunable ceramic capacitors and tunable microwave devices [2, 3]. Barium strontium titanate (BST) is another vital material which has significant performance in the microwave frequency range, because of its large dielectric constant (ε_r) and high dielectric tunability at room temperature has been frequently used in the tunable filters [4]. Barium zirconate titanate (BZT), as an important member of the $BaTiO_3$-based ferroelectric materials family, has received extensive attention due to its eminent dielectric performance. BZT ceramics present high voltage resistance characteristics because Zr^{4+} is chemically more stable than Ti^{4+} [5-8]. Barium strontium zirconate titanate (BSZT) has the advantages of both additives Sr and Zr [9].

Dielectric materials with high tunability, low dielectric loss, and moderate dielectric constant are desired for tunable microwave applications. Many researchers [10–12] have reported that better dielectric properties of $BaTiO_3$-based ferroelectric ceramics have been obtained by substitution of some rare earth ions. Among them rare earth and transition elements all most important kind of dopant, the microstructural and dielectric properties of BSZT had been reported [13].The effects of rare earth oxides on the dielectric

properties and reliability have been discussed in several recent papers, [14, 15] whereas little research has been carried out focusing on La_2O_3-doped BSZTNF. The microstructural and dielectric properties of BSZTNF system have not been reported to our knowledge. The Nb_2O_5 is a donor dopant, which resulted in the lattice distortion and increased the tetragonality, and Fe_2O_3 is an acceptor dopant, which led to the high density of oxygen vacancy and promoted crystal grain growth of BSZT ceramics. In this paper, we report the influence of the rare earth elements such as La_2O_3, Gd_2O_3 on the microstructure and dielectric properties of BSZTNF materials.

2. EXPERIMENTAL

Ceramics samples were prepared by conventional solid slate reaction method from the weighed amount of $BaCO_3$, $SrCO_3$, ZrO_2, TiO_2, Nb_2O_5, Fe_2O_3, La_2O_3, and Gd_2O_3 (all hi media, India purity 99.99%. The starting material were ground for 4 hours and calcined at 1000°C for 12 hours, they were further ground for 2hours, and subjected for pre-sintering at 1000°C. This product obtained was again ground for 2hours and pressed into circular shaped disk pellet (diameter 10mm and thickness 1-2mm) using 5% PVA as a binding agent. Pellets were sintered at 1000°C for 8 hours for good electrical contact a silver paste is applied on both the sides of pellets.

The room temperature X-ray diffractograms of synthesized samples were recorded by using X-ray diffractometer. (Phillips, X'perts-PRO, PAN analytical) with Cu-Kα radiation (λ = 1.54056Å) with a step size of 0.02° and scanning rate of 2°/min., micrographs was taken from SEM (JSM / 8048 / SM, JEOL, Japan and the grain size was determined by the linear intercept technique and dielectric properties were measured by LCR meter.

3. RESULTS AND DISCUSSION

The tolerance factor for the modified samples was calculated with the ionic radius of A-site cation Ba^{2+} = 1.35$\overset{\circ}{A}$, Sr^{2+} = 1.13 $\overset{\circ}{A}$, B-site cation Zr^{4+} = 0.79 $\overset{\circ}{A}$, Ti^{4+} = 0.88 $\overset{\circ}{A}$, Fe^{3+} =

0.64 $\overset{\circ}{A}$, Nb^{5+} =0.70 $\overset{\circ}{A}$, La^{3+} = 1.04 $\overset{\circ}{A}$, Gd^{3+} = 0.94 $\overset{\circ}{A}$ and anion O^{2-} = 1.4$\overset{\circ}{A}$, respectively, by Goldschmidt equation [16].
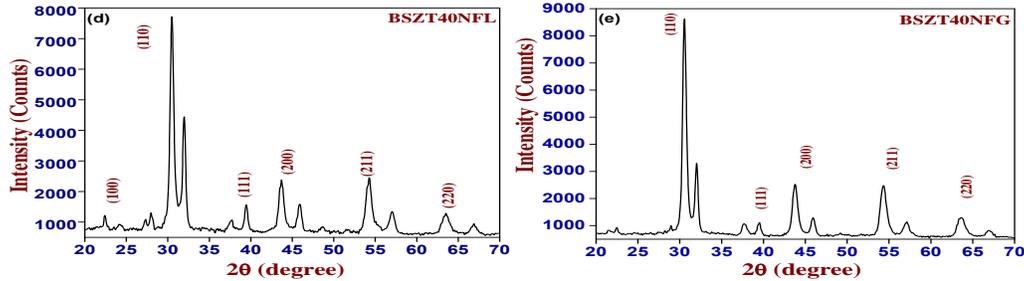
Fig 1: XRD pattern for BSZT40NFL and BSZT40NFG

The XRD patterns shown in figure 1 reveals that, all indexed peaks corresponds to perovskite phase indicating single phase of the compound. By the addition of rare earth ions (La and Gd) shifts the phase transition temperature to lower values and as a consequence, rhombohedral, orthorhombic and tetragonal phases co-exists at room temperature in La and Gd doped BSZT40NF materials. Cell volume, x-ray density and the particle size was calculated and given in the Table 1.

Table-1 Crystallographic data of BSZT40NF-RE ceramics

Sample code	Lattice parameter (Å)			Cell volume(Å)³	Particle size (nm)	X-ray density (ρ) (gm/cm³)
	A	c	c/a			
BSZT40NFL	4.133	4.146	≈1.00	70.84	2.31	22.04
BSZT40NFG	4.129	4.12 5	≈1.00	70.34	2.60	24.24

From table 1, it is observed that the c/a ratio for the BSZT40NFL, BSZT40NFG is almost equal to 1.00 which leads to cubic phase transition [17].
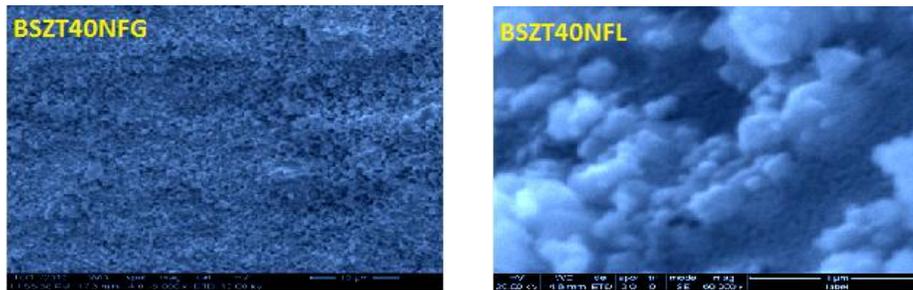
Fig 2: Scanning electron micrographs of BSZT40NFL and BSZT40NFG

Figure 2 depicts the micrographs of the samples. By the addition of La and Gd to BSZT40NF the grain size is of about 0.81nm and shows no appreciable difference in grain size in the synthesized ceramic compounds. From figure 2, it is also observed that BSZT40NFG show a small needle shape phase located on grain boundaries. Such defect would affect the transport phenomenon and thereby modifying the resistivity of the material [18]
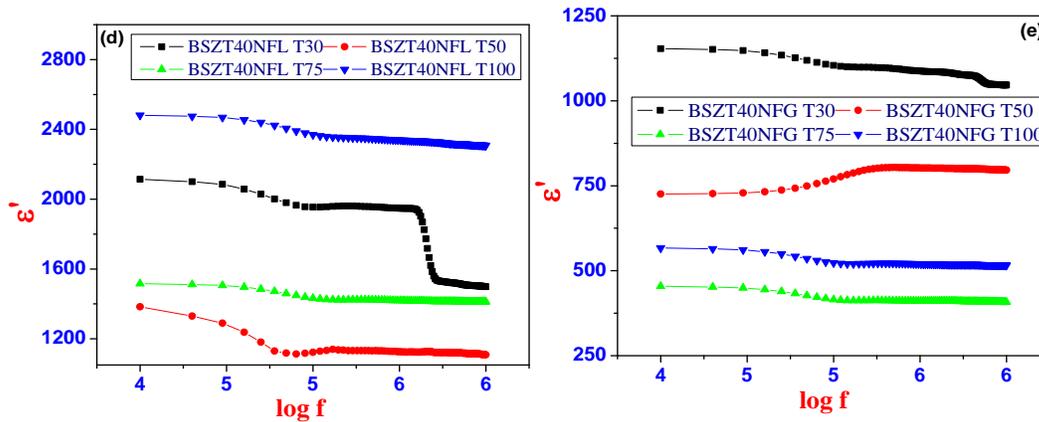
Fig 3: Frequency dependence of dielectric constant for BSZT40NFL and BSZT40NFG

The frequency dependence of dielectric constant behaviour at different temperatures for BSZT40NFL and BSZT40NFG are shown in Fig.3. The dielectric properties are measured at different temperatures (30^0C, 50^0C, 75^0C and 100^0C) respectively. Small frequency dispersion is observed for the temperature 75^0C and 100^0C. A strong dispersion is found at the temperature 30^0C and 50^0C for the BSZT40NFL and BSZT40NFG ceramics, respectively. The temperature T_m, corresponding to the maximum value of the dielectric constant, is shifted to higher temperature and the maximum value of the dielectric constant is decreased with increasing frequencies. This shows that samples have similar regularity in the frequency dispersion. This phenomenon demonstrates typical ferroelectric relaxor behavior.

4. CONCLUSIONS

BSZT40NFL and BSZT40NFG ceramics are fabricated via the conventional solid-state reaction method. Rare-earth ions with various ionic radii enter the unit cell to substitute for *A*-site Ba^{2+} ions maintaining the perovskite structure of solid solution. The rare-earth substituted ions are effective to inhibit the grain growth. The grain size of ceramics is almost same for both the samples and found to be 0.81nm.The typical ferroelectric relaxor behavior is induced for rare-earth ion (La and Gd) substituted BSZT40NF ceramics. The effect of La_2O_3 and Gd_2O_3 content on the microstructure and dielectric properties has been investigated on ceramics in the ternary system $(Ba_{0.6}Sr_{0.4})(Zr_{0.6}Ti_{0.4})O_3–Nb_2O_5–Fe_2O_3$. The addition of La and Gd induced that BSZT40NF ceramics has cubic structures and that the solubility of Nb_2O_5 and Fe_2O_3 in BSZT with 0.99 wt%, 1.465 wt% La and Gd is below 5.66 wt%. The dielectric properties of BSZT ceramics with La and Gd additions are strongly dependent on the densification and the microstructure.

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