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Enhanced dielectric loss of Mg doped $Ba_{0.7}Sr_{0.3}TiO_3$ ceramics

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ABSTRACT

The effect of MgO doping on the structural, microstructural and dielectric properties of $Ba_{0.7}Sr_{0.3}TiO_3$ (BST) ceramic from the point of view of its application in microwave tunable devices has been studied. All the samples crystallize into perovskite structure. There is significant reduction in the value of loss factor with the increase in Mg-level, the dielectric constant and tunability are also reduced with the increase in Mg-level. Interestingly, the Fig. of merit of the material is found to be enhanced with increase of Mg-doping. The observed dielectric properties are explained on the basis of defect chemistry involved when Mg is doped in $Ba_{0.7}Sr_{0.3}TiO_3$ ceramics. The effect of dc field on the dielectric constant and the dielectric breakdown strength of the paraelectric phase Mg doped BST ceramic samples are also studied.

1. Introduction

$Ba_xSr_{1-x}TiO_3$ (BST) is a solid solution of barium titanate ($BaTiO_3$) and strontium titanate ($SrTiO_3$). The Curie point of BST can be controlled by varying the amount of Sr substitution and the material can be brought in the paraelectric phase at room temperature. In the paraelectric phase, there is no spontaneous polarization and hence no fatigue problem, and dielectric properties can be tuned by an applied dc electric field. Paraelectric BST finds extensive applications in tunable microwave devices such as filters, varactors, delay lines and phase shifters because of the strong dependence of the dielectric properties on the electric field [1,2]. The favorable properties for its application in microwave tunable devices are (i) large variation of the dielectric constant with applied field (ii) high dielectric constant (iii) lower value of tangent loss [3]. The dielectric constant (permittivity) of this material can be varied by varying the value of the applied dc field, this change in turn can produce a change in the propagation constant for the high frequency signal passing through the material. The tangent loss of a dielectric material is another important parameter for any dielectric material to find application in microwave devices as the loss factor dissipates or absorbs the incident microwave energy. The insertion loss is lower when the loss tangent is lower and so reducing the tangent loss of BST is required to find its application in microwave tunable devices. By using small concentrations of acceptor ions such as Fe^{2+}, Fe^{3+}, Co^{2+}, Co^{3+}, Mn^{2+}, Mn^{3+}, Ni^{2+}, Mg^{2+}, Ga^{3+}, In^{3+}, Cr^{3+} and Sc^{3+} which can occupy the B sites of the ($A_{2+}B_{4+}O_3^{2-}$) structure the loss of the BST material can be lowered [3–8]. Few authors have studied Mg doped BST thin films [9–11], very little work has been reported on the bulk Mg doped BST ceramics. This paper reports the effect of Mg doping on the material and electrical properties of BST bulk ceramics.

2. Materials and methods

The polycrystalline system $Ba_{0.7}Sr_{0.3}TiO_3$ doped with MgO in the range of 0, 2.5, 5, 7.5 and 10 mol% were prepared by the conventional ceramic processing method. AR grade (99.9% purity of CDH chemicals) chemicals $BaCO_3$, $SrCO_3$, TiO_2 and MgO were taken up for processing. Appropriate amounts of the chemicals were thoroughly mixed in water medium by ball milling with zirconia balls for 24 h. The mixture was then dried, powdered and calcined twice at 1050 °C for 4 h by maintaining the heating rate at 5 °/min. The calcined powder is then compacted in the form of pellets by using a hydraulic press (at a pressure of 30 Ton). The samples were then sintered at 1450 °C for 4 h by heating them at the rate of 2 °/min. The crystal structure of these ceramics was studied using X-ray Diffractometer (Philips Diffractometer PW 3020) with monochromatic CuK_α radiation ($\lambda = 1.54178$ Å) over a 2θ angle from 20° to 70 °C at a scanning rate of 2 °/min. The microstructural properties of the sample were studied from FESEM micrographs recorded by FESEM System (ZEISS, Supra TM 55). For studying the dielectric properties, the thickness of the sintered pellets was reduced to approximately 0.5 mm by grinding. These thin pellets were polished and then electroded with gold by sputtering technique. The dielectric properties were studied using an impedance analyzer (Wayne Kerr 6505B) and a temperature chamber. The

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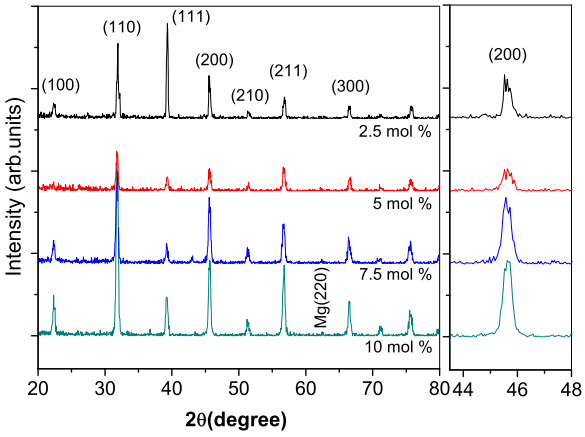

Fig. 1. XRD patterns for the Mg doped $Ba_{0.7}Sr_{0.3}TiO_3$ ceramic samples.

data for dielectric tunability were recorded as cycle sweeps (0 to +ve voltage and from −ve voltage back to 0) to check for any possible hysteresis behavior. Hysteresis behavior of the ceramic samples was recorded by using a Ferroelectric Loop Tracer (Marine India).

3. Results and discussion

The perovskite structure of the Mg doped BST system is evidenced from the XRD patterns shown in Fig. 1. It indicates that the ceramic samples crystallize into cubic structure, the lattice parameters are tabulated in Table 1. As seen in Table 1, the lattice parameter and lattice volume are found to increase with the increase of Mg content. It indicates the replacement of Ti^{4+} by Mg^{2+} (ionic radii of Mg^{2+} and Ti^{4+} are 0.72 A° and 0.61 A° respectively) in the lattice to form a solid solution. It is also seen in the XRD patterns that the ceramic samples with Mg doping level higher than 5 mol% are associated with extra diffraction lines of magnesium oxide indicating the solubility limit of MgO in the present system to be 5 mol%. This is slightly different from the observation of Su et al in $Ba_{0.8}Sr_{0.2}TiO_3$ system in which the solubility limit for MgO was 2 mol% [9]. This difference might be due to difference in the purity level of the chemicals used.

Fig. 2 shows the FESEM Micrographs of the Mg doped BST ceramic samples recorded on fractured ceramic surface. The FESEM micrographs reveal densely packed grains which are distributed uniformly for all the ceramic samples. The FESEM micrograph of BST doped with 2.5 mol% Mg consists of smaller grains (~300 nm) as well as bigger size grains (~1000 nm). As Mg content increases in the ceramics, the grain size distribution becomes more or less uniform with the average grain size of about 600 nm. It is observed (Table 1) that the bulk density of the ceramic samples decreases with the increase of Mg^{2+} concentration. This is due to the increase of lattice volume of the samples with the increase of dopant concentration.

The average grain sizes were determined from the SEM micrographs of Fig. 2 using the linear intercept method and their distribution for each of the sample is plotted in Fig. 3. As seen in this figure, the grain size distribution becomes narrower around the average grain size of ~600 nm as Mg content increases in the ceramics.

Fig. 4 shows the variation of dielectric constant (ε′) and dielectric loss (tan δ) with temperature for different Mg contents, measured at 10 kHz. It is observed that dielectric constant decreases with the increase of temperature for all the ceramic samples. The dielectric constant variation in Fig. 4(a) confirms that all the samples are in paraelectric state at room temperature and the Curie temperature for all the samples are below 20 °C (due to experimental limitations the dielectric measurement could not be performed below 20 °C). As seen in Fig. 4(a), there is a decrease in the value of the dielectric constant with the increase of Mg level; the observed variation is due to the replacement of Ti^{4+} with Mg^{2+} ions which acts as an acceptor dopant and its hardening effect causes a reduction in the value of dielectric constant [6]. The value of tangent loss also decreases with the increase of Mg doping level. The acceptor dopants such as Mn^{2+}, Fe^{3+}, Ni^{2+}, Mg^{2+} are reported to be dopants which can reduce the dielectric loss of the BST ceramics [3–8]. The dielectric loss of ceramic material is affected by the intrinsic as well as extrinsic factors. The origin of the intrinsic losses is due to the interaction of the applied ac field with the phonons of the material. The intrinsic dielectric losses depend on the crystal symmetry and are observed in single crystals [12]. In ceramic samples, dielectric loss is dominated by the extrinsic factors as ceramics are far away from perfect single crystal symmetry. Extrinsic losses are due to the imperfection in the crystal structure such as dopant or impurity atoms, dislocations, grain boundaries, vacancies, microcracks, microstructural defects, order-disorder behavior, secondary phases etc [12–15]. Most of the extrinsic factors are process dependent and can be minimized. In the present case the Mg doped BST samples are sintered at 1450 °C for 4 h. When the BST are sintered at such temperatures there is partial reduction of Ti^{4+} to Ti^{3+} [15] and this causes an increase in dielectric loss. When Mg^{2+} is doped in BST ceramics, large numbers of ionized oxygen vacancies and conduction electrons are created during sintering according to the equation:

$$O_o \rightleftharpoons ½O_2 + V_o + 2e$$

To maintain the equilibrium state of the electron concentration, the produced electrons are almost fully delocalized by hopping motion from one titanate site to another. Mg^{2+} ions are more reducible than the Ti^{4+} ions and so electrons are trapped at these sites. The hopping motion of the trapped electrons from one Mg site to another is almost prohibited. The conduction electrons are localized on these Mg sites; this results in a drop of carrier concentration and leads to decrease of conductivity [4]. Due to the decrease in conductivity, dielectric loss is decreased when Mg is doped in BST [15].

The dc field dependences of the dielectric constant for different ceramic samples are shown in Fig. 5. The dielectric constant decreases with the increase of dc bias field. The dc field effect on the dielectric properties of BST in the paraelectric state originates from

Table 1
Dielectric properties of the samples recorded at 10 kHz.

Mg content (%)	Density (gm/cm^3)	Lattice parameter (Å)	Lattice volume (Å3)	Porosity (%)	ε′	tan δ	Tunability (%) at 20 kV/cm	Figure of merit (FOM)	Dielectric breakdown strength (kV/cm)
2.5	5.68	4.0775	7.7881	0.05	2520	0.013	34	26	15
5	5.54	4.0794	7.8873	2.51	2286	0.012	32	27	20
7.5	5.44	4.0815	7.9921	4.28	2199	0.009	26	29	37.5
10	5.35	4.0836	8.1014	5.86	2037	0.007	22	31	30