Observation of High Dielectric Properties of Mg Substituted BST Ceramic Synthesized by Conventional Solid State Route

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Research Article

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Abstract

Barium Strontium Titanate exhibits ferroelectric or paraelectric behaviour that depends upon the composition and other factors, making it suitable for a number of applications. We have adopted conventional solid state reaction route to synthesize magnesium substituted barium strontium titanate with low concentration of Mg (Mg= 0.005, 0.010 and 0.015). X-ray diffraction has confirmed the perovskite cubic single phase. The dielectric studies were carried out as a function of temperature at different fixed frequencies (1kHz, 10kHz, 50kHz and 100kHz) and as a function of frequency at room temperature. The Curie's temperature of pure BST was 96°C and for Mg substituted BST samples it dropped from 85°C to 63°C. The dielectric permittivity firstly suppressed and then maximum value observed for Mg content 0.015 and dielectric loss is also less than one. The remanance (P_r) and coercivity (E_c) are obtained and analysed for ceramics samples. Improvement in dielectric properties due to substitution of Magnesium is observed.

1. Introduction

Lead free oxide type ceramics with perovskite structure (ABO_3) have attracted researchers towards itself because of its wide applications in piezoelectric, capacitor, pyroelectric, microwave devices, memory storage, solar cells etc [1, 2]. Mostly studied ferroelectric material of this group is $BaTiO_3$ (BT) having excellent properties like high dielectric constant and low dielectric loss. However, high permittivity and high loss have some limitations also but that can be adjusted by the doping of softeners (donors) and hardeners (acceptors) on either A site or B site [3–6]. Addition of donors like La, Sr on Ba or A site enhances the value of dielectric constant, mechanical losses and reduces the strength of coercive field and elastic modulus. Similarly, addition of acceptors like Fe for Ti) enhances conductivity, increases mechanical quality factor and reduces dielectric constant [7]. Barium strontium titanate (BST) showing low dielectric loss and high dielectric permittivity becomes the most optimistic materials for many applications. However, high dielectric permittivity of pure ferroelectric BST ceramic also limit its application in microwave devices which require low dielectric constant with low dielectric loss [8]. The various properties can be modified by substituting various selected ions on either A site or B site [9, 10]. The high tangent loss and permittivity of BST have hindered its application [11]. To meet the requirements, elements of different groups are added or their composites are synthesized to minimize the value of dielectric constant and put down the tangent loss [12]. The dielectric tunability is lessened, by attaining higher sintering temperature. Recently, composites consisting BSTO/MgO are awaited to show good response as tuneable devices because of their low permittivity and low tangent loss [13–15].

It has been reported by various research groups that magnesium oxide is an important non-toxic insulator material and addition of Mg or MgO in BST can put down the dielectric permittivity and losses [16]. Few reports are available on the effect of Mg doped barium strontium titanate on different properties [17]. Recently, improved dielectric properties, good tunability and low leakage current has been revealed in 0 to 10 mol% of magnesium doped BST. Chou et. al revealed from their work that ferroelectricity is diluted, diffused phase transition was shown and Curie temperature of composite ceramics is decreased in comparison to pure $Ba_{0.5}Sr_{0.5}TiO_3$ due to Magnesium (Mg^{2+}) substitution [18].

In the present paper, magnesium substituted barium strontium titanate ($\text{Ba}_{0.95-x}\text{Sr}_{0.05}\text{Mg}_x\text{TiO}_3$) is synthesized using conventional ceramic method. In order to check the impact of Mg substitution we have carried out X-ray Diffraction, dielectric performance as a function of temperature (at fixed frequencies) and frequency (at room temperature) and PE loop measurements at room temperature.

2. Experimental Details

The pure and Mg substituted BST powder samples were prepared using Conventional Solid-State Reaction method. AR (Analytical Reagent) grade BaCO_3 (purity > 99%, Sigma Aldrich, India), SrCO_3 (purity > 99%, Sigma Aldrich, India), MgO (purity > 99%, Qualikems Fine Chem. Pvt. Ltd., China) and TiO_2 (purity > 99%, Sigma Aldrich, India) were used as raw materials for the synthesis process. These powders were taken and weighed according to stoichiometric composition of $\text{Ba}_{0.95-x}\text{Sr}_{0.05}\text{Mg}_x\text{TiO}_3$ with $x = 0, 0.005, 0.010$ and 0.015 . Once the powder was weighed it was ball milled with acetone as medium and zirconia balls as grinder or mixer for 5 h to form slurry. The slurry was poured into beaker, dried in hot air oven for 8 h. The dried powder was then kept in high temperature programmable muffle furnace at 1000°C for 4 h with a heating rate $5^\circ\text{C}/\text{min}$. The process of ball milling and calcination was repeated once again. Finally formed double calcined powder was pressed into pellets of diameter 15mm and thickness about 1-2mm in a uniaxial hydraulic press. The pellets were then sintered in high temperature programmable muffle furnace at 1325°C for 4 h.

The structural and microstructural analysis of sintered pellets were done using X-ray Diffractometer (XPRT-PRO Philips PW 3064) having Cu-K α radiation ($\lambda = 0.15418\text{nm}$) and Scanning Electron Microscope (JSM 6490). Dielectric studies were carried out with the help of HIOKI IM 3536 LCR meter. For carrying out this study the sintered pellet was coated with silver paste and then dried in oven at 400°C to ensure good ohmic contacts. The data was recorded as a function of temperature at four different frequencies (1kHz, 10kHz, 50kHz and 100kHz) and as a function of frequency at room temperature. The ferroelectric analysis of the material was done with PE Loop Tracer (Marine India) at applied electric field 10kV/cm at room temperature.

3. Results & Discussions

3.1 Structural and Microstructural Analysis

Fig. 1 shows the diffraction pattern of Mg substituted barium strontium titanate with magnesium i.e. $\text{Ba}_{0.95-x}\text{Sr}_{0.05}\text{Mg}_x\text{TiO}_3$ with x having values 0.005, 0.010 and 0.015. It is revealed that Mg substituted barium strontium titanate exhibit ABO_3 cubic perovskite structure with high orientation at (110). The substitution of magnesium in BST lattice is confirmed by X-ray diffraction. The peaks 100, 110, 111, 200, 210, 211 and 220 are observed around angles $22^\circ, 32^\circ, 39^\circ, 45^\circ, 51^\circ, 56^\circ$ and 66° . X-ray diffraction patterns revealed the absence of additional peak of other material or phase which indicates that addition of magnesium has not formed any new phase such as MgCO_3 , MgO etc. in the samples. The well-defined crystallinity of material is increasing on increasing the magnesium concentration as indicated by the sharp peaks. On referring to pure

BST it has been observed from Fig.1 that diffraction peak shift towards higher angle on adding Mg. This implies that magnesium has successfully substituted Barium on A site of ABO_3 on surface. Since the atomic radius of Mg ($0.72\text{\AA}$) is smaller than Ba ($1.35\text{\AA}$) and when a smaller element has substituted a larger ion, on whole there is lattice contraction. Wang et al. in 2010 and Gao et al. in 2020 have also reported the lattice contraction and cubic structure of barium strontium titanate on doping magnesium [17,19]. The average crystallite size (t) of magnesium substituted barium strontium titanate powder samples is calculated using Scherrer's formula as mention below:

$$t = \frac{0.94\lambda}{\beta \cos\theta}$$

Where, λ is the wavelength of Cu-K α radiation source ($\lambda=0.15418\text{nm}$), β (in radians) is the full width at half maxima and θ is the Bragg's angle. The calculated values of average crystallite size are shown in Table 1. Crystallite size is in the range of nano scale and pure BST have smaller crystallite size than Mg substituted BST. The lattice constant and density seems to decrease with increasing Mg^{+2} concentrations. This emphasises that Magnesium is successfully substituted on Ba (A) site in barium strontium titanate lattice.

Table 1

Change of lattice constant, volume of unit cell, density crystallite size of $\text{Ba}_{0.95-x}\text{Sr}_{0.05}\text{Mg}_x\text{TiO}_3$ with Mg content:

Mg Content	Lattice constant $a(\text{\AA})$	Volume $v(\text{\AA})^3$	Density $\rho(\text{g/cc})$	Crystallite Size $t(\text{nm})$
x=0	3.9838	63.688	6.014	32.89
x=0.005	3.9926	63.647	6.003	35.24
x=0.010	3.9916	63.599	5.989	40.11
x=0.015	3.9893	63.488	5.988	40.36

3.1.2 Microstructural Analysis

Fig. 2 shows the microstructure of fractured surfaces of pure and Magnesium consisting Barium Strontium Titanate ($\text{Ba}_{0.95-x}\text{Sr}_{0.05}\text{Mg}_x\text{TiO}_3$) with Mg = 0, 0.005, 0.010 and 0.015. The micrographs were analysed using Image J Software and the size of grain was calculated with the help of line intercept method. The average grain size of pure BST samples was measured to be $2.185\text{ }\mu\text{m}$, and the average grain size was observed to decrease with the increasing concentration of Magnesium. The grain size reduced from 2.315 to $1.789\text{ }\mu\text{m}$ in Magnesium substituted samples. The grains are distributed evenly and seem to scatter all around. The

increased scattering of the grains show the increasing porosity in Mg substituted samples. The agglomeration of the grains is reducing with Mg content. All samples have uneven shape and size of the grains as can be seen from the micrographs.

3.2 Dielectric Properties

The modification of dielectric constant (ϵ) as a function of frequency at room temperature for pure and Mg^{+2} substituted barium strontium titanate ($\text{Ba}_{0.95-x}\text{Sr}_{0.05}\text{Mg}_x\text{TiO}_3$; $x=0, 0.005, 0.010$ and 0.015) ceramic system is plotted in Fig. 3a. As we had limited experiment range of frequency so we have taken frequency from 100Hz – 800 kHz. The dielectric permittivity decreases with the increase in frequency confirming general characteristic of ferroelectric materials. The high value of dielectric constant for all samples measured at low frequency and decrease in the dielectric constant with increasing frequency is due to the presence of dipolar & electronic polarization that may be justified by Maxwell-Wagner space charge polarization model [20]. The values of dielectric constant were found to decrease with increase in Mg content and maximum value was observed for Mg concentration $x=0.015$, which refers to better crystallinity and from table 2 it is observed that BST with Mg concentration 0.015 is most crystalline among all the compositions that have also been confirmed by XRD study. It is observed that there is a decrease and then sudden increase in value of dielectric constant at maximum concentration of magnesium. The Curie temperature also shows a non-linear and decreasing behaviour with magnesium concentration. Similarly, the effect of Mg^{+2} substituted BST on dielectric loss (D) as a function of frequency at room temperature was also monitored as shown in Fig. 3b. The value of dielectric loss is very much less than 1 for all the samples which makes the samples applicable for dielectric applications. Moreover, these low values of $\tan\delta$ accounts for the impurity and defect free sample.

Table 2

Dielectric and ferroelectric parameters for Mg substituted BST.

Mg Content	Curie's Temperature (T_C)	Dielectric Constant at T_C	Dielectric Constant at RT	Tangent Loss $\tan\delta$	Remnant Polarization (P_r)	Coercive Field (E_C)	Saturation Polarization (P_s)
x=0	96	5307	2946	0.023	3.69	3.55	18.23
x=0.005	85	8509	2662	0.041	6.71	2.77	20.36
x=0.010	66	2589	2527	0.044	1.87	1.87	13.64
x=0.015	63	3840	3301	0.028	1.05	1.35	12.987

The plot of temperature dependent dielectric constant and tangent loss ($\tan\delta$) at frequencies (1kHz, 10kHz 50kHz and 100kHz) for pure and Mg substituted BST is shown in Fig. 4a and 4b. The dielectric peaks for

Mg⁺² substituted Barium Strontium Titanate (BST) ceramics are not dispersed which encouraged that all prepared ceramic samples behaves like normal ferroelectrics. Sample with x=0 and x=0.005 shows sharp maxima and the other two compositions have broad peaks with increasing Mg content. The broadening of peaks may be due to compositional variation which lead to different transition temperatures and decrease in dielectric constant. There is no shift observed in dielectric maxima with increment in frequency. All the samples show the increase in dielectric constant with increasing temperature up to transition temperature and then decrease with increase in temperature showing typical ferroelectric behaviour. The tangent loss factor also decreases with increasing concentration of Mg and values in every sample are less than 1. A noticeable improvement has been seen in all samples with varying Mg content. The dielectric effects of Mg doped barium strontium titanate are reported in earlier literature also. Liu et al. in 2012 also reported value of dielectric constant of Mg substituted BST thick films around 385 [21] and similar value was reported by Venkata et al. in 2009 [22]. Shujuan from his work reported the value of dielectric constant as a function of frequency in the range of 3.1-3.8 [17]. When the same material is synthesized by sol- gel technique the value of dielectric constant was reported around 14000 [19]. The peaks observed from Fig. 4a help in determining ferroelectric to paraelectric transition at Curie temperature. The Curie temperature for pure BST ceramics system observed in present study is about 20°C to 23°C less than reported earlier in the literature [23] and nearly same as mentioned for samarium substituted BST [24]. This may be attributed to internal stress that has caused reduction in Curie temperature. The shift of T_C toward lower temperature is due to the decrease in grain size that is because of increase in internal stress [25].

3.3 Ferroelectric Properties

The polarization (P) versus electric field (E) behaviour was measured using an electric field at 10kV/cm at 50Hz. The P-E loop characteristics for Mg substituted barium strontium titanate are shown in Fig. 5. The sharpness of the loops indicates the crystallinity and homogeneity. The values of Remanence (P_r), Saturation polarization (P_s) and Coercive field (E_c) of all the samples observed from the graphs are listed in table 2. All samples shows well saturated typical ferroelectric hysteresis loop. The remnant polarization (P_r) and Coercive field (E_c) of pure BST are 3.69 μ C/cm² and 3.55kV/cm respectively at maximum field 21.753kV/cm and with substitution of Mg, x=0.005, coercive field decreases to 2.77kV/cm while remnant polarization increases, in fact has highest value of remanence among all compositions. For other two compositions the values of both remnant polarization and coercive field has decreased. The composition with Mg=0.005 (lowest Mg concentration among all concentration) has maximum value of P_r which shows that in this composition internal energy is more than other compositions referring to greater dipole alignment [7]. The trend observed from table 2 showing decrease in P_r with increasing Mg concentration may be due to presence of pores in addition to the increase in grain size. The reduction in the value of E_c indicates the softening of the material on increasing Mg content. The sample having x= 0.005, P_r/P_s (0.329) ratio have stable value and then it decreases with Mg concentration i.e. for x=0.010, P_r/P_s is 0.137 and for x=0.015, P_r/P_s is 0.081.

4. Conclusions

The ceramic samples were prepared by conventional solid state reaction route. All samples are formed with single crystalline perovskite cubic phase and showed the increase in crystallinity of the samples with increasing Mg content in XRD pattern. The density was found to decrease with magnesium content. The dielectric constant decreases with Mg concentration and maximum value of dielectric constant observed for $\text{Ba}_{0.935}\text{Sr}_{0.05}\text{Mg}_{0.015}\text{TiO}_3$. The T_C peaks of ceramics prepared are suppressed, broadened, and shifted to lower temperature with the increase of Mg content. The value of remnant polarization (P_r) and Coercive field (E_c) decreases as Mg concentration increases. It is concluded from the results that temperature stability of dielectric properties of Mg substituted

BST is of great practical use. The results indicate that the material $\text{Ba}_{0.935}\text{Sr}_{0.05}\text{Mg}_{0.015}\text{TiO}_3$ is the most promising candidate for capacitive and other engineering applications.

Declarations

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Figures

Figure 1

X-ray diffraction pattern of Mg substituted BST ($\text{Ba}_{0.95-x}\text{Sr}_{0.05}\text{Mg}_x\text{TiO}_3$) and inset of angle shifting towards higher.

Figure 2

SEM micrographs of Magnesium substituted BST (Ba_{0.95-x}Sr_{0.05}Mg_xTiO₃) as S1 (x=0), S2 (x=0.005), S3 (x=0.010) and S4 (x=0.015).

Figure 3

Variation of dielectric constant (a) and loss tangent (b) as a function of frequency at room temperature for $\text{Ba}_{0.95-x}\text{Sr}_{0.05}\text{Mg}_x\text{TiO}_3$ ceramic with ($x=0, 0.005, 0.010, 0.015$).

Figure 4

4(a) Variation of dielectric constant for Mg substituted BST ceramics as a function of temperature for $x=0, 0.005, 0.010$ & 0.015 . 4(b) Variation of dielectric loss for Mg substituted BST ceramics as a function of

temperature for $x=0, 0.005, 0.010$ & 0.015 .

Figure 5
Polarization versus Electric field loops for Mg substituted BST.