

Synthesis and Characterization of LSMO-(BCT-BZT) Composites

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Abstract: The present paper reports synthesis and characterization of LSMO-(BCT-BZT) composites. $y\text{LSMO}+(1-y)[x\text{BCT}-(1-x)\text{BZT}]$ particulate composites are prepared for $y = 0.1$ & 0.175 and for $x = 0.50$. Ferrite $\text{La}_{0.67}\text{Sr}_{0.33}\text{MnO}_3$ (LSMO) is synthesized via hydroxide co-precipitation route while ferroelectric composition $[x(\text{Ba}_{0.7}\text{Ca}_{0.3}\text{TiO}_3)-(1-x)(\text{BaZr}_{0.2}\text{Ti}_{0.8}\text{O}_3)]$ (BCT-BZT) is synthesized via ceramic route. The crystal structures of LSMO, 0.50BCT- 0.50 BZT and LSMO-(0.50BCT-0.50BZT) are proved using X-ray diffractograms, while microstructures are proved using scanning electron microscope. The dielectric properties of composites are determined as a function of frequency in the range 100 Hz to 1 MHz. The dielectric constant (ϵ) in case of $y\text{LSMO}+(1-y)[x\text{BCT}-(1-x)\text{BZT}]$ composites is expected to have two contributions, one due to parent (BCT-BZT) ferroelectric and other due to the interfacial polarization occurring at the interfaces between ferrite (LSMO) and ferroelectric (BCT-BZT) phases. To understand the observed behavior of ϵ in perspective of these models, the variation of loss tangent $\tan \delta$ as a function of frequency are also determined in the same frequency range.

Keywords: Composites, Crystal structure, Surface Morphology, Dielectric properties

1. Introduction

Recent study on (0.50BCT- 0.50BZT) exhibits a morphotropic phase boundary (MPB) near room temperature and it shows an interesting ferroelectric, piezoelectric and elastic properties in vicinity of 25°C [1-7]. A great deal of work is already carried out on perovskite manganite ($\text{A}_x\text{B}_{1-x}\text{MnO}_3$) which have shown interesting colossal magneto resistance (CMR) behavior at their respective transition temperature (T_c) [8]. Amongst the perovskite manganite LSMO is known to possess its T_c just above room temperature [9]. Further, LSMO is expected to show T_c at room temperature [10]. The dielectric constant (ϵ) in the composites $y\text{LSMO} + (1-y)[x\text{BCT}-(1-x)\text{BZT}]$ is due parent $[x\text{BCT}-(1-x)\text{BZT}]$ ferroelectric and the interfacial polarization occurring at the interfaces between ferrite (LSMO) and ferroelectric $[x\text{BCT}-(1-x)\text{BZT}]$ phases. The interfacial polarization occurs because of the difference in the resistivity and dielectric constant of these two distinct phases. As y increases contribution due to ferroelectric phase may decrease, while the contribution due to interfacial polarization may increase as y (1- y). The y (1- y) type of variation becomes maximum for $y=0.175$.

One of the important works as far as the interfacial aspects of magnetoelectric composite is due to Y.H. Tang et al [11]. The observed magnitude and frequency dispersion of ϵ_r is attributed to the interfaces with very large difference in the resistivity. Since the interfacial polarization is a slow process, this effect will be observable primarily at low frequencies or and at high temperatures. From the discussion above it could be seen that at low frequencies the dominant mode of polarization is the interfacial polarization [12, 13].

2. Experimental

The LSMO has been synthesized by employing the hydroxide co-precipitation route. The AR-grade $\text{La}(\text{C}_2\text{H}_3\text{O}_2)_3 \cdot \text{H}_2\text{O}$, SrNO_3 , KMnO_4 , $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$, are used as precursors, while

a mixture of NH_4OH and KOH is used as precipitating agents. The details of the co-precipitation route are similar as reported earlier [14]. The precipitate formed is washed thoroughly and calcined at 1100°C for 12 hours. The individual phases of BCT and BZT were prepared by the conventional ceramic method. The AR grade precursors BaCO_3 , CaO , ZrO_2 , and TiO_2 with high purity ($>99.9\%$) are used [4]. The powders were pre-sintered at 1100°C for 12 hours. Composition of $x\text{BCT}-(1-x)\text{BZT}$ with $x=0.50$ was prepared by same ceramic method. The powders of LSMO and (BCT-BZT) with respective weights are mixed thoroughly using acetone as a medium and process of manual mixing/grinding in an agate mortar for four hours each. 1.5% wt. of Bi_2O_3 is added as a sintering aid to facilitate formation of large grained composites at fairly low sintering temperature. The dried powder is compacted in the form of pellet shaped samples of diameter 1.2 cm and thickness between 1 to 2 mm for further process of investigations. For the purpose of compaction 10 tons/ cm^2 pressure is employed on the powder. A saturated solution of polyvinyl acetate (PVA) in distilled water is used as a binder. The pellets are sintered at 1150°C for 12 hours for further characterisation. Table 1 shows the respective weights of LSMO and (BCT-BZT) for the total weight of 10 gm. of the composites

Table 1: Weights of LSMO, (BCT-BZT) and Bi_2O_3 for formation of composites

y	Weight of LSMO (gm)	x	Weight of (BCT-BZT) (gm)	weight of Bi_2O_3 (gm)
0.1	1.006	0.50	8.994	0.15
0.175	1.762	0.50	8.238	0.15

3. Results and Discussion

3.1 Structural Analysis

Fig.1 shows the XRD spectrum of $\text{La}_{0.67}\text{Sr}_{0.33}\text{MnO}_3$. XRD spectrum of the LSMO powder is carried by X-ray powder diffractometer (Rigaku Miniflex). The lattice parameters 'a'

and 'c' are observed to be equal to 5.40 Å and 13.50 Å and c/a ratio is 2.5. Here crystallite size is calculated by using Debye Scherrer's formula and is 67nm. This is expected because of moderate sintering temperature of 1100 °C [9]. The crystal structure of $\text{La}_{0.7}\text{Sr}_{0.3}\text{MnO}_3$ is rhombohedral with hexagonal axes of symmetry. The space group is R-3c with the hexagonal axes of symmetry, is transformable to standard rhombohedral form [9].

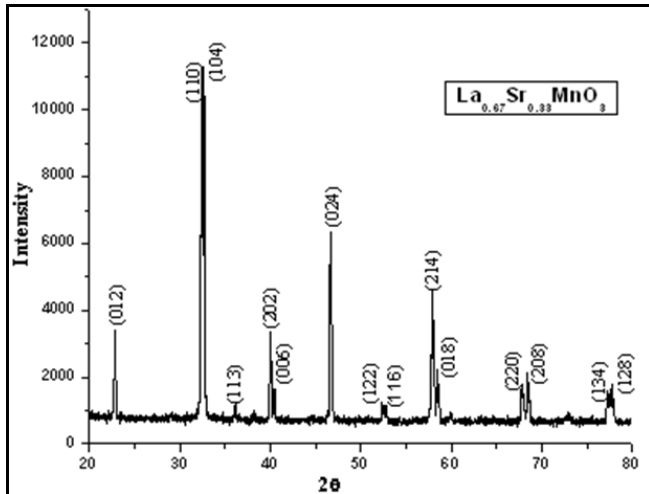


Figure1: XRD spectrum of $\text{La}_{0.67}\text{Sr}_{0.33}\text{MnO}_3$

Fig.2 shows the XRD spectrum of 0.1LSMO + 0.9 (0.5BCT-0.5BZT) composite. The observed peaks could be associated with the reflections corresponding to (0.5BCT-0.5BZT) or LSMO. Further no additional peaks of any impurity phase are observed in the spectrum. Thus, from the XRD spectra it could be seen that the composites formed are phase pure and possess two separate phases of LSMO and (0.5BCT-0.5BZT). The observed peaks could be indexed to individual peaks of LSMO and (BCT-BZT) phases separately. The peaks corresponding to the reflections (110) of LSMO and (110) and (101) of (BCT-BZT) phase appear to overlap and the corresponding peak shows a characteristic broadening. The peaks characteristics of tetragonal (BCT-BZT) i.e. (111) and (200) are observed well separated in the XRD spectra's of the composites.

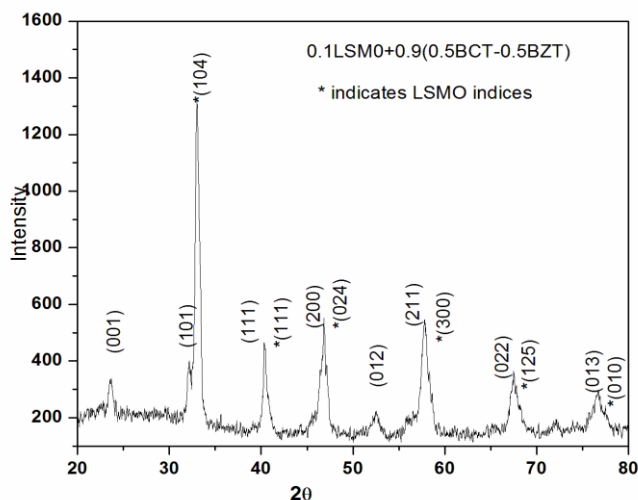


Figure 2: XRD of 0.1LSMO+0.9(0.5BCT-0.5BZT)

3.2 Micro-Structural Analysis

Fig. 3 shows the SEM image for $\text{La}_{0.67}\text{Sr}_{0.33}\text{MnO}_3$. The $\text{La}_{0.67}\text{Sr}_{0.33}\text{MnO}_3$ is successfully synthesized using hydroxide co-precipitate route. The sintering schedule of the precipitate could be tailored to produce nano particles of LSMO in the range 50 nano meters. Fig.3 shows the SEM photograph for the LSMO sintered at 1100 °C. SEM picture is obtained using JEOL-JSM 6360 SEM. From SEM images it is seen that the sample is compact microstructure and with some voids are seen in the SEM images. The observed average grain size from SEM image is nearly 2µm.

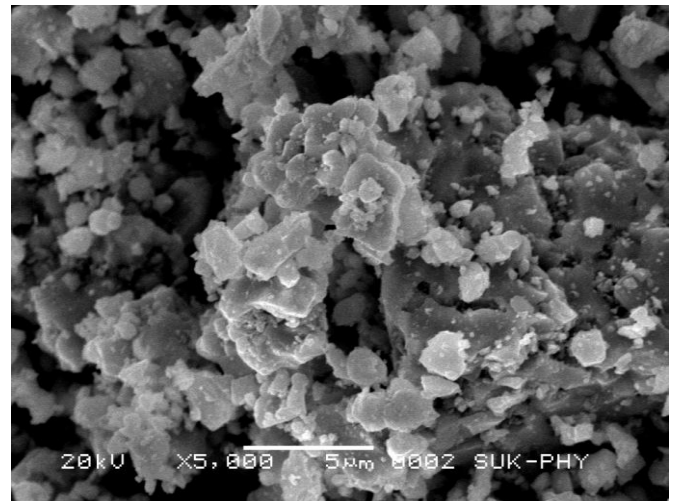


Figure 3: SEM for $\text{La}_{0.67}\text{Sr}_{0.33}\text{MnO}_3$

Fig.4 shows the SEM photographs of 0.1LSMO–0.9(0.5BCT-0.5BZT) composite. The SEM picture clearly shows existence of the individual nanoparticles. Further the SEM pictures indicates occurrence of densification for the composite. From SEM image it is seen that the composite is compact microstructure and with some voids are seen in the SEM images. The observed average grain size from SEM image is nearly 2µm. It is also seen that the effect of addition of the ferrite phase is towards acceleration in the formation of the grain compacts. The ferrites are known to be softer for sintering as compared to the hard sintering phases like BCT-BZT. Therefore increase in the quantity of ferrite may cause the acceleration in the formation of grain compacts. It has been observed that the presence of Bi_2O_3 forms a liquid phase, which favours aggregation of the particles of LSMO and (BCT-BZT) during the sintering above 856°C (Melting point of Bi_2O_3). Particles aggregates of average 2 to 3 µm appear for all the composites. Despite of the aggregation, the SEM pictures clearly show existence of the individual nanoparticles. Due to Bi_2O_3 , the liquid phase, formation of denser aggregates would be favored. This may cause occurrence of the pores at the boundaries between these compacts. Such behavior occurs commonly for ceramics sintered using sintering aids or for sintering at higher temperatures.

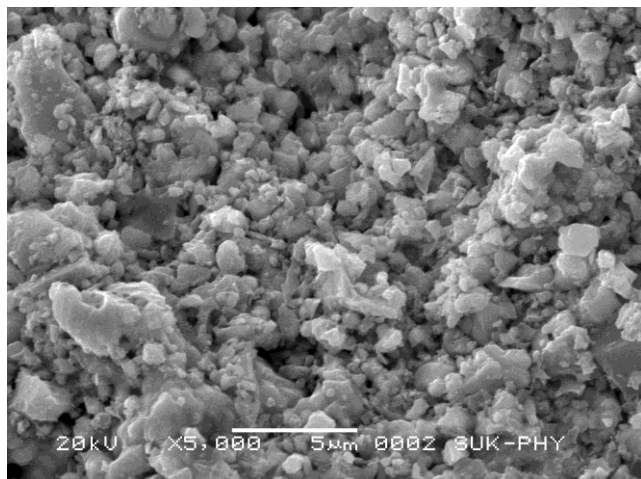


Figure 4: SEM for 0.1LSMO-0.9(0.50BCT-0.50BZT)

3.3 Dielectric Properties

The HP4284A LCR-Q meter is used for the measurements of dielectric constant. The dielectric constant in case of $y\text{LSMO}+(1-y)[x\text{BCT}-(1-x)\text{BZT}]$ composites is expected to have two contributions, one due to parent $[x\text{BCT}-(1-x)\text{BZT}]$ ferroelectric and other due to the interfacial polarization occurring at the interfaces between ferrite (LSMO) and ferroelectric $[x\text{BCT}-(1-x)\text{BZT}]$ phases. The interfacial polarization occurs because of the difference in the resistivity and dielectric constant of these two distinct phases. As y increases contribution due to ferroelectric phase may decrease, while the contribution due to interfacial polarization may increase as y (1- y). Fig. 5 shows the variations of ϵ as a function of frequency for $y\text{LSMO}+1-y$ (0.50BCT-0.50BZT) composites for $y = 0.1$ & 0.175. Interesting observation of ϵ versus frequency behavior is that the ϵ increases with y . Here the increase in the ϵ is steeper for increasing y . This feature is known to occur because of interfacial polarization, occurring at boundaries between the (BCT-BZT) and LSMO phases due to difference in the resistivity of these two phases. Interfacial polarization is known to be prominent at low frequencies [9, 15, 16]. Here the Table 2 shows variation of ϵ and Q at room temperature (at $f = 1$ kHz) for the composites. It has been observed that as y increases the ϵ also increases. This feature may occur because of decreasing content of (BCT-BZT) as y increases. The observed magnitude and frequency dispersion of ϵ_r is attributed to the interfaces with very large difference in the resistivity. Since the interfacial polarization is a slow process, this effect will be observable primarily at low frequencies or and at high temperatures

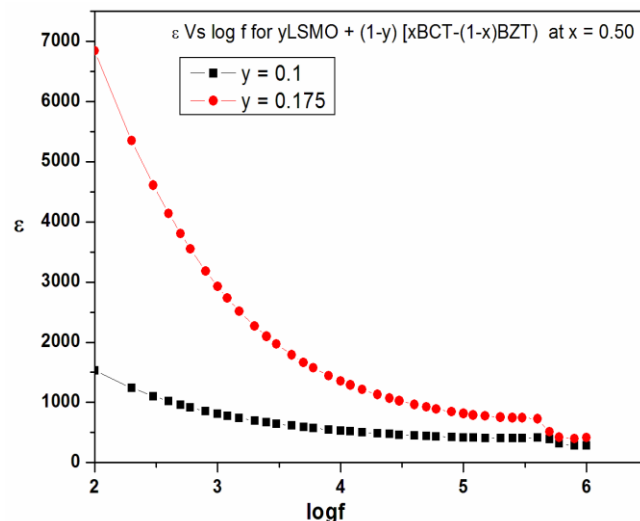


Figure 5: Variation of dielectric constant (ϵ) with frequency for $y\text{LSMO}+(1-y)(0.50\text{BCT}-0.50\text{BZT})$ composites

Table 2: Values of ϵ and Q at room temperature of $y\text{LSMO}+(1-y)(0.50\text{BCT}-0.50\text{BZT})$ composites (at $f = 1$ kHz)

Composite	y	ϵ	Q
LSMO+(0.50BCT-0.50BZT)	0.1	811	1.96
	0.175	2924	0.62

When an electric field acts on any matter the latter dissipates a certain quantity of electrical energy that transforms into heat energy. This phenomenon is commonly known as “the expense” or “loss” of power, meaning an average electric power dissipated in matter during a certain interval of time. The amount of power lost in a dielectric under the action of the voltage applied to it is commonly known as dielectric loss. The power dissipation in an insulator or capacitor is directly proportional to the dielectric loss factor $\tan \delta$. Consequently, this factor is of great concern for many applications of ceramic materials. Indeed, one of the main advantages of ceramics as dielectrics is that this loss factor is small compared to that of other available materials. Sometimes the quality factor of an insulating portion is determined as the value reciprocal of the loss tangent. Quality factor (Q) = $1/\tan \delta$ is used as a figure of merit in high frequency applications.

To understand the observed behavior of ϵ in perspective of these models, the variation of loss tangent $\tan \delta$ as a function of frequency are determined in the frequency range 100 Hz to 1 MHz and are shown in Fig. 6 for $y\text{LSMO}+(1-y)[0.50\text{BCT}-0.50\text{BZT}]$ for $y = 0.1$ and 0.175 composites sintered at 1150 °C. From this figure it is observed that $\tan \delta$ passes through a resonance peak. The resonance occurs at the frequency where the time required for the charge to transfer across the interface matches with reciprocal of applied frequency. Similar observations are reported for the other titanate systems [17]. From the above discussion and figures it could be said that the dielectric properties of $y\text{LSMO} + (1-y)[x\text{BCT}-(1-x)\text{BZT}]$ composites possess a large contribution of interfacial polarization for $y=0.175$.

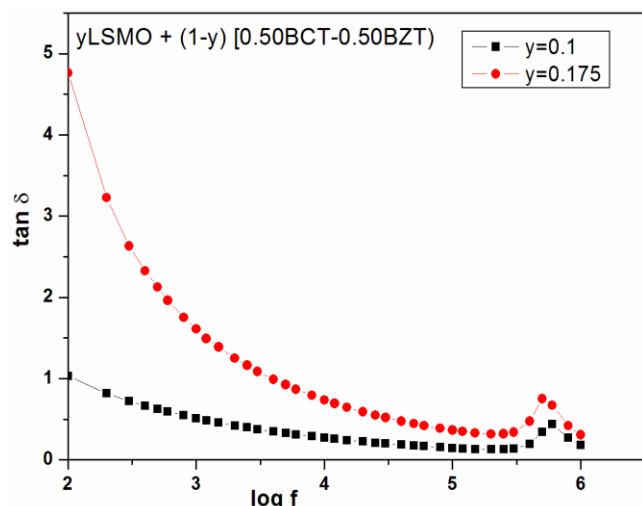


Figure 6: Variation of $\tan \delta$ as a function of $\log f$ For $y\text{LSMO} + (1-y) [0.50\text{BCT}-0.50\text{BZT}]$ composites

4. Conclusion

It is observed that the hydroxide co-precipitation and ceramic routes could be successfully used to form nano particles of the LSMO and (BCT-BZT). The $y\text{LSMO} + (1-y)[0.50\text{BCT}-0.50\text{BZT}]$ composites synthesized by ceramic route. The XRD spectra of the composites show that it is phase pure and possesses two separate phases. From SEM image it is seen that the composite is compact microstructure. From dielectric properties it is observed that interfacial polarization prominent at low frequencies. From variation of the loss tangent with frequency it is observed that $\tan \delta$ passes through a resonance peak. The resonance occurs at the frequency where the time required for the charge to transfer across the interface matches with reciprocal of applied frequency.

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