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, yLSMO+(1-y)xBCT-(1-x)BZT particulate composites are prepared for y = 0.1 & 0.175 and for x = 0.50. Ferrite La0.65Sr0.35MnO3 (LSMO) is synthesized via hydroxide co-precipitation route while ferroelectric composition [xBa0.7Ca0.3TiO3-(1-x) (BaZr0.2Ti0.8O3)] (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 yLSMO+(1-y)xBCT-(1-x)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 δ 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 (A,BiBa,Ca,MnO3) which have shown interesting colossal magneto resistance (CMR) behavior at their respective transition temperature (Tc) [8]. Amongst the perovskite manganite LSMO is known to possess its Tc just above room temperature [9]. Further, LSMO is expected to show Tc at room temperature [10]. The dielectric constant (ε) in the composites yLSMO + (1-y) [xBCT-(1-x)BZT] is due parent [xBCT-(1-x)BZT] ferroelectric and the interfacial polarization occurring at the interfaces between ferrite (LSMO) and ferroelectric [xBCT-(1-x)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 εr 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 La(CaH2O4)3, H2O, SrNO3, KMnO4, MnCl2.4H2O are used as precursors, while a mixture of NH4OH 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 BaCO3, CaO, ZrO2, and TiO2 with high purity (>99.9%) are used [4]. The powders were pre-sintered at 1100 °C for 12 hours. Composition of xBCT-(1-x)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 Bi2O3 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/cm2 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>
<thead>
<tr>
<th>y</th>
<th>Weight of LSMO (gm)</th>
<th>x</th>
<th>Weight of (BCT-BZT) (gm)</th>
<th>weight of Bi2O3 (gm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.1</td>
<td>1.006</td>
<td>0.50</td>
<td>8.994</td>
<td>0.15</td>
</tr>
<tr>
<td>0.175</td>
<td>1.762</td>
<td>0.50</td>
<td>8.238</td>
<td>0.15</td>
</tr>
</tbody>
</table>

3. Results and Discussion

3.1 Structural Analysis

Fig.1 shows the XRD spectrum of La0.65Sr0.35MnO3 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 La$_{0.7}$Sr$_{0.3}$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].

3.2 Micro-Structural Analysis

Fig. 3 shows the SEM image for La$_{0.67}$Sr$_{0.33}$MnO$_3$. The 
La$_{0.67}$Sr$_{0.33}$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.

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.

Fig.4 shows the SEM photographs of 0.1LSMO– 
0.9(0.50BCT-0.50BZT) 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$_2$O$_3$ 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$_2$O$_3$). 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$_2$O$_3$, the liquid phase, formation of 
denser aggregates would be favored. This may cause 
ocurrence 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.
3.3 Dielectric Properties

The HP4284A LCR-Q meter is used for the measurements of dielectric constant. The dielectric constant in case of yLSMO+(1-y)(xBCT-(1-x)BZT) composites is expected to have two contributions, one due to parent [xBCT-(1-x)BZT] ferroelectric and other due to the interfacial polarization occurring at the interfaces between ferrite (LSMO) and ferroelectric [xBCT-(1-x)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 yLSMO+(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 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 at high temperatures 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 δ. 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 δ 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 δ as a function of frequency are determined in the frequency range 100 Hz to 1 MHz and are shown in Fig. 6 for yLSMO+(1-y)(0.50BCT-0.50BZT) for y = 0.1 and 0.175 composites sintered at 1150 °C. From this figure it is observed that tan δ 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 yLSMO+(1-y) [xBCT-(1-x)BZT] composites possess a large contribution of interfacial polarization for y=0.175.
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 $y_{LSMO} + (1-y)[0.50BCT-0.50BZT]$ 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.

5. Acknowledgement

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References


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