Laminated Composites of Dielectric and Magnetic Properties of Multiferroic (BTSO-LCMO) Material

Anil Kumar Anumula¹, Lukka Prashanth²

¹, ²Assistant Professor at “Mallareddy College of Engineering for Women”, Maisammaguda, gundlapocham pally, Medchal, Malkajgiri district, India.

Abstract: The future of lead-free multiferroic complex are desired to use the lead-based ceramics in Multipurpose devices applications. Layer compounds prepared from ferroelectric and ferromagnetic materials. This paper deals with, the laminated ceramics compound by considering the ferromagnetic La₀.₅Ca₀.₅MnO₃ (LCMO) and the ferroelectric BaTi₀.₈Sn₀.₂O₃ (BTSO) in two types of proportions. Compounds (1-x) LCMO-(x) BTSO with x=1 and 0 (pure materials) were synthesized by the sol gel method and x=0.7 and 0.5 (laminated) compounds were elaborated by welding appropriate mass ratios of each pure material by using the silver paste technique. Structural, dielectric, ferroelectric, microstructure and magnetic characterization were conducted on these samples. X-ray scattering results showed pure perovskite phases confirming the successful formation of both LCMO and BTSO. SEM images evidenced the laminated structure and good quality of the interfaces. The laminated composite materials have a multiferroic characterized by the ferroelectric, ferromagnetic hysteresis loops and the laminated composite samples is mainly attributed to the Maxwell-Wagner polarization.

Index Terms: ferroelectric, ferromagnetic, laminated composites, multiferroics.

1. INTRODUCTION

The development of the electronic technology has become increasingly update Day by day. The challenge for researchers is the modify and the multifunctionality involved in many multifunctional devices such as memory devices, transducers, opticals, actuators and sensors [1]. Among these multifunctional materials, we distinguish the multiferroic compounds consisting of two or more ferroic orders those are ferromagnetism, ferroelectricity, ferroelasticity, or ferrorotoroidicity [2]. In some multiferroics, strong interaction between the ferroic orders can generate additional functionalities, such as the coupling effect, namely the magnetoelectric (ME) effect. In composites containing magnetostrictive and piezoelectric materials, the mechanism behind the ME coupling can be explained as follows. When an electrical field is applied to the composite, the piezoelectric material is strained. This induced strain is transferred as stress to the magnetostrictive material which produce a change in the magnetic moment in the material. The converse effect is also possible, in general, the ME effect in composite materials could be achieved either by the application of an electric field inducing the change in magnetic permeability or by the application of a magnetic field which generates an electric field [3]. Up to now, researchers has been done on synthesis of multiferroic materials with high coupling coefficients, composed of single phase multiferroics or composite multiferroics with different connectivity schemes [4]. In contrast to the single phase multiferroics with weak coupling between the ferroic orders which limits their use in multifunctional devices. Heterostructure composites like 2-2 type, called the laminated composites and grown by alternating ferromagnetic and ferroelectric layers possess generally under leakage current. This makes the electric poling possible, thus enhancing the (ME) effect [5]. In view of the concern with environmental pollution and human health, it is necessary to find appropriate alternative materials for lead-free applications. The calcium-doped lanthanum manganite perovskite (La₁₋ₓCaₓMnO₃) has attracted considerable attention to rich phase diagram as a function of the concentration and temperature. It is known by its competition between the super-exchange interactions, which favors antiparallel alignment of neighboring Mn and double exchange interaction, which favors parallel alignment compared with the common ferrites. In particular La₀.₅Ca₀.₅MnO₃ (LCMO) would be an attractive candidate as a ferromagnetic component for multiferroic materials since its transition temperature near the room temperature has a beneficial role in the ferromagnetic layers applications. On the other hand tin doped barium titanate BaTi₀.₈Sn₀.₂O₃ materials have received particular attention due to their important property of tuning the temperature transition with an optimum Doping of Sn at Ti site of BTO. The BaTi₀.₈Sn₀.₂O₃ (BTSO) was chosen to play the role of the ferroelectric layer because of its transition temperature near the room temperature which coincides with the magnetic transition temperature [6],[7]. In this paper, A 2-2 type bi-layer laminated composite was elaborated by welding a ferromagnetic LCMO and a ferroelectric BTSO ceramics together using the silver paste technique. The structural, dielectric and magnetic characteristics of the multiferroic (1-x) LCMO-(x) BTSO laminated composites were investigated.

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II. EXPERIMENTAL

A. Composite Preparation

All chemicals were used as purchased without further purification. Both La$_{0.5}$Ca$_{0.5}$MnO$_3$ (LCMO) and BaTi$_{0.2}$Sn$_{0.8}$O$_3$ (BTSO) ceramic powders with the necessary compositions were synthesized by sol-gel technique. For this paper, initially the ferromagnetic LCMO was synthesized, a stoichiometric amount of highly pure nitrates reagents La(NO$_3$)$_3$·6H$_2$O, Ca(NO$_3$)$_2$·4H$_2$O and Mn(NO$_3$)$_2$·4H$_2$O were weighed in stoichiometric amounts and dissolved in distilled water, a mixture of citric acid (C$_6$H$_8$O$_7$) and tartaric acid (C$_4$H$_6$O$_6$) were used as chelating agents and added to the solution. The whole mixture was stirred at 85 °C for about 6 hours. By removing the solvent the solution turned into yellow golden gel. Finally the as prepared powder was heat-treated at 750°C for 7h in air with a heating rate of 3 °C min$^{-1}$ in order to get LCMO nanopowder. The ferroelectric ceramic (BTSO) was synthesized by dissolving in acetic acid a precisely weighted amounts of barium nitrate (Ba(NO$_3$)$_2$) and tin chloride (SnCl$_4$), after their total dissolution titanium isopropoxide (C$_3$H$_6$O$_3$Ti) was added. A milky solution was obtained in which ammonium hydroxide (NH$_4$OH) was dropwise added while heating at 80°C for about 1h till getting a transparent solution that turned into a gel by removing the solvents. The resulting product was then calcined at 1000 °C for 2 h. Lastly; the obtained LCMO and BTSO powders were uni-axially pressed into pellets and sintered at 1000°C/2h and 1300°C/2h, respectively.

B. Characterization

X-ray diffraction patterns were noted at room temperature on a diffractometer X’Pert PRO operating with geometry 0-0 using Cu-Kα radiation in the range of 10-80°. The Rietveld analysis of the X-ray diffraction patterns was carried out for both LCMO and BTSO samples. Scanning electron microscopy images and EDX spectra were recorded using a scanning electron microscope. For the dielectric measurements the ceramics were coated with silver electrodes on top and bottom surfaces. The temperature And frequency dependent spectra (173 to 353K; 100 Hz to 1 MHz) were obtained by using a Solartron SI 1260 Impedance Analyzer. Magnetic measurements were performed on a Physical Property Measurement System (Quantum Design, PPMS-DynaCool) components operating in temperature range 2-300K and Magnetic field in the range 0 - 9T. Magnetization was measured using VSM (vibrating sample magnetometer) method which is integrated in this system. The P-E measurements were carried out by using a TF Analyzer 3000 designed by AixACCT.

III. RESULTS

A. Chemical Solution

The oxygen stoichiometry of the ferromagnetic LCMO sample was evaluated using the oxidation reduction method as described as [8]. The value of 3.0066 was found almost equal to the theoretical value of 3. Furthermore the Mn$^{3+}$ and Mn$^{4+}$ ions percentage is carried quantitatively. The chemical analysis has been done as follows: LCMO powder was dissolved in a mixture solution of oxalic acid dehydrate H$_2$C$_2$O$_4$ and dilute sulfuric acid H$_2$SO$_4$ with heating at about 70 °C. The compound reacts with H$_2$C$_2$O$_4$ which reduces both Mn$^{3+}$ and Mn$^{4+}$ into Mn$^{2+}$. The excess of H$_2$C$_2$O$_4$ solution was thereafter titrated using KMnO$_4$ solution. The experimental solutions are found to be 48.67% for Mn$^{3+}$ and 51.33% for Mn$^{4+}$. These results accept with theoretical data and confirm the stoichiometry of our sample.

B. X-ray Diffraction

Fig.1 (a) and (b) represent the room temperature X-ray refined results for LCMO and BTSO that were obtained by using FullProf software [9]. The patterns clearly indicate that both calcined LCMO and BTSO crystallized in the perovskite structure with no evidence of any impurity phases.

As shown in the Rietveld refinement, LCMO is crystallized in the orthorhombic structure with space group Pnma (see Fig.1 (a)), while BTSO ceramic crystallized well in the cubic structure with Pm3m space group as suggested in Refs [10] for Sn doped BaTiO3 materials with a tin concentration higher than 10% (see Fig.1 (b)).

We have started the profile refinement with the scale, zero point and background parameters followed by the unit cell parameters. Then a pseudo-Voigt function was used to describe the individual line profiles, the peak asymmetry and preferred orientation corrections are applied. The values of the fit- quality indicator $\chi^2$ demonstrate a successful refinement. All Rietveld refinements parameters are gathered in Table. I.
Fig. 1. Room temperature X-ray diffraction pattern at 300 K for (a) \( \text{La}_{0.5}\text{Ca}_{0.5}\text{MnO}_3 \) and (b) \( \text{BaTi}_{0.8}\text{Sn}_{0.2}\text{O}_3 \) ceramics including the experimental and calculated profiles as well as their differences.

Table I
LCMO and BTSO as obtained From Rietveld Refinement

| Atomic positions | Lattice parameters | Reliability factors (%) |
|------------------|--------------------|-------------------------|
| \( \text{La}/\text{Ca} \) (0.0132, 0.2500, -0.0044) | \( a=5.4220 \text{ Å} \) | Rp=15.6 |
| Mn (0.0000, 0.0000, 0.5000) | \( b=7.6467 \text{ Å} \) | Rwp=16.8 |
| O1 (-0.0137, 0.2500, 0.4434) | \( c=5.4514 \text{ Å} \) | \( \chi^2=0.9 \) |
| O2 (0.7151, -0.0271, 0.2862) | \( V=226.01 \text{ Å}^3 \) | |
| \( \text{Ba} \) (0.5000, 0.5000, 0.5000) | \( a=b=c=4.0264 \text{ Å} \) | Rp=10.4 |
| Ti/Sn (0.0000, 0.0000, 0.0000) | \( V=65.2742 \text{ Å}^3 \) | Rwp=10.1 |
| O (0.5000, 0.0000, 0.0000) | | \( \chi^2=4.97 \) |
C. **SEM and EDX Investigations**

Fig. 2(a) and 2(b) display the SEM micrographs and particles distribution of LCMO and BTSO ceramics while Fig. 2 (c) depicts the cross-section of the laminated LCMO/Ag/BTSO composite taken on the cleavage surface. The sintered LCMO phase (Fig. 2 (a)) is found to be characterized by homogenous and spherical shaped grains with uniformly distributed grains ranging in size from 10 to 100 nm and the pores are distributed randomly throughout the sample while the BTSO phase (Fig. 2 (b)) was found to consist of grains of about 2–5 µm in diameter with the formation of aggregates. In order to assign the two different phases, EDX analysis were carried out near the two interfaces confirming the existence of the characteristic elements of the two phases namely LCMO and BTSO. Besides, no diffusion has been detected as shown in Fig. 2 (d) and (e).

![SEM micrographs of sintered LCMO and BTSO](image)

![Cross-sectional image of laminated LCMO/Ag/BTSO](image)

![EDX results of ceramics near interfaces](image)

**Fig. 2.** SEM micrographs of sintered (a) LCMO and (b) BTSO. (c) The cross-sectional image of the laminated LCMO/Ag/BTSO, (d) and (e) EDX results of the ceramics near the interfaces.
D. Properties of Dielectric

The temperature dependence of the dielectric constant ($\varepsilon_r$) obtained for the laminated (1-x) LCMO-(x)BTSO samples with (wt%) x=1, 0.7 and 0.5 measured in the temperature range from -100°C to 80°C at different representative frequencies, is illustrated in Fig. 3(a), (b) and (c), respectively. The pure BTSO and 50LCMO-BTSO exhibit a broad ferroelectric-paraelectric phase transition at around $T_c=21°C$ and a phase transition at $T_c=24°C$ for 30LCMO-70BTSO sample. The slightly down shifted Curie temperature observed in the laminated 30LCMO-70BTSO composite confirms that the ferromagnetic soldered part doesn’t affect much the ferroelectric transition temperature, in consistence with previously reported results [11]. In addition, the values of $\varepsilon_r$ at 1 kHz are found to be 1663, 4153 and 6127 for compounds with x=1, 0.7 and 0.5, respectively. In contrast, the dielectric losses (tan $\delta$) remain invariable with relatively low value at around tan $\delta=0.002$ for all samples. It is interesting to note that permittivity of the laminated composites has been significantly increased compared to that of the pure BSTO as presented in Fig. 3(e). Similar behavior has been reported previously in laminated composites $La_{0.7}Ba_{0.3}MnO_3$-BaTiO$_3$ [12] which could be explained by the Maxwell-Wagner polarization mechanism.

Fig. 3(d) shows the hysteresis loops of the laminated composites and the pure ferroelectric sample at T=$-30°C$. All the laminated composites reveal a clear ferroelectric behavior. Table II summarizes the remnant polarization (Pr) and coercive electric fields (Ec) obtained in the vicinity of the transition temperature at T=$-30°C$. We note that the values of Pr and Ec decrease while the amount of the ferromagnetic part increases, in agreement with the results. The decrease in Ec value is probably due to the presence of the ferromagnetic LCMO composite. The applied voltage on the ferroelectric part is reduced by passing through the ferromagnetic layer, thus in the laminated composites, the current drop will increase as the thickness of the ferromagnetic layer is increased.

| Sample        | Ferroelectric | Ferromagnetic |
|---------------|---------------|--------------|
|               | Pr(µC/cm²)    | Ec(Kv/cm)    | Ms(emu/g) | Mr(emu/g) | Hc(Oe)   |
| BTSO          | 0.70          | 1.4088       | -         | -         | -        |
| 30LCMO-70BTSO | 0.38          | 0.3326       | 19.33     | 06.70     | 493      |
| 50LCMO-50BTSO | 0.27          | 0.2995       | 31.13     | 10.02     | 438      |
| LCMO          | -             | -            | 91.35     | 47.12     | 839      |
Fig. 3. Temperature dependence of dielectric constants ($\varepsilon_r$) and dielectric losses for the laminated composites (a) $x=1$, (b) $x=0.7$, (c) $x=0.5$, (d) Hysteresis loops of the pure and laminated samples and (e) Temperature dependence of the real part of the permittivity and the corresponding loss tangents for all the samples.

E. Magnetic Properties

Magnetization temperature profiles $M(T)$ for the pure and the laminated composites were measured under an applied field of 2T. The $M(T)$ measurements for the laminated composite with $x=0.5$ in Fig. 4(a). All the compounds exhibit a paramagnetic, ferromagnetic transition at the Curie temperature $T_c=268$K defined as the inflection point of the $M(T)$ curves and determined from the peak position of the $dM/dT$ curve as in Fig. 4(a). By using the sol gel method, the $T_c$ value is higher than $La_{0.5}Ca_{0.5}MnO_3$ (230 K) using the conventional solid state reaction. The effect of grain size reduction by using the sol gel technique, which induces a strong ferromagnetic interaction in nanoparticle sample. The field dependent magnetization curves of all the laminated $(1-x)L_{CMO-(x)}$BTSO composites at the maximum applied field of 6 kOe at the temperature of 2K in Fig. 4(b). All samples clear hysteresis in
Accordance with the pure LCMO, thus indicating their ferromagnetic properties. The saturation magnetization values were determined by a linear extrapolation of the magnetization in the high field ranges at 2K. The magnetic properties for various samples are determined and listed in Table II. It is evident that the saturation magnetization (Ms) in the laminated composites increases with increasing LCMO content, as expected, because this parameter depends on the total mass of the magnetic material. In the same way remnant magnetization (Mr) increases with the LCMO quantity while no significant variation in coercive field (Hc) is observed. Such behavior was previously reported in other systems [13]. The evolution of ac magnetic susceptibility in the two samples was very different (Fig. 4(c)). Specifically, in the composite material, the ac magnetic susceptibility appears more smeared and suppressed compared to that of pure LCMO and when approaching the phase transition temperature, it gradually decreases. It appears that the ferroelectric layer has an effect on the magnetic spins reducing their susceptibility and slightly shifting the transition to lower temperatures 4(d) represents the M(T) curves measured under different values of the applied electric voltage (0-300 V) across the 50LCMO-50BTSO composite and confirms the absence of an induced shift by the electric field on the M (T) curves or exchange bias effect in a laminated sample. This result underlines the absence of a marked (ME) coupling which can be due to the high conductivity of our samples or to the weak applied electric field [3].

![Graph](image1)

![Graph](image2)

![Graph](image3)
In order to enhance the (ME) coupling in our 3+ ferromagnetic LCMO composite dielectric polarization reversal and memory in a multiferroic material induced by effects of the ferr-omagnetic LCMO composite dielectric 

samples, other method of soldering will be tried in the future. The ferromagnetic performances of the laminated composites were achieved and greatly dependent on the thickness of the ferromagnetic LCMO composite. In order to enhance the (ME) coupling in our samples, other method of soldering will be tried in the future.

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ANIL KUMAR ANUMULA. I received M.TECH degree from NITT, India, in 2010 and currently working as an Assistant Professor at “MALLAREDDY COLLEGE OF ENGINEERING FOR WOMEN”, Maisammaguda, gundlapocham pally, Medchal Malkajgiri district, India. Email id: aumula86@gmail.com.

LUKKA PRASHANTH. I Received M.Sc degree from SATHAVAHANA UNIVERSITY, karimnagar, India, in 2017 and currently working as an Assistant Professor at “MALLAREDDY COLLEGE OF ENGINEERING FOR WOMEN”, Maisammaguda, gundlapocham pally, Medchal Malkajgiri district, India. Email id: prashanthlukkalpr@gmail.com.