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Magnetodielectric Properties of $La_{0.67}Sr_{0.33}MnO_3$ and $Ba_{0.7}Sr_{0.3}TiO_3$ Thin Film Heterostructures

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The paper discuses synthesis and magnetodielectric properties of $La_{0.67}Sr_{0.33}MnO_3$ (LSMO), $Ba_{0.7}Sr_{0.3}TiO_3$ (BST), and BST/LSMO thin film heterostructures. The XRD spectra are determined for confirmation of the crystal structure of LSMO, BST and formation of a pure bi-phase composite. The paper presents variation of Cp and tanδ as a function of frequency between 100 Hz to 1 MHz and applied magnetic field up to 0.6 T. The observed variation of Cp, tanδ, magnetocapacitance and impedance spectra are analyzed in terms of a possible equivalent circuit model. The present analysis shows that the method of impedance spectra could be used to separate out the possible contributions.

Keywords: magnetodielectrics, impedance spectroscopy, LSMO, BST, spin coating technique, thin film heterostructures

1. INTRODUCTION

Investigations of magnetodielectric (MD) systems have gained momentum in recent years, owing to the useful values of magnetocapacitance (Mc) reported for various composites and double perovskite systems.[1-10] Here Mc is defined as (Cp(H)-Cp(0))/Cp(0), where Cp(H) and Cp(0) are the values of parallel capacitance Cp, with and without applied magnetic field, respectively. It is observed that Mc is maximum for the systems where the ferroelectric phase and ferromagnetic/CMR phase possess the transition temperature Tc simultaneously at a particular temperature.[10] Therefore as a basic requirement one opts to select ferroelectric as well as CMR systems possessing Tc in the vicinity of room temperature. $Ba_{1-x}Sr_xTiO_3$, $BaZr_xTi_{(1-x)}O_3$, $Ba_{(1-x)}Ca_xTiO_3$, $BaTi_{(1-x)}Mg_xO_3$ are the ferroelectric phases of interest. Regarding CMR materials like $La_{(1-x)}Ba_xMnO_3$, $La_{(1-x)}Sr_xMnO_3$, $La_{(1-x)}Ca_xMnO_3$ have shown interesting results. It is also observed that the CMR material like $La_{0.67}Sr_{0.33}MnO_3$ (LSMO) possesses CMR as well as large magnetostriction at Tc and therefore it is of immense interest in terms of applications as well as theoretical viewpoints.[2,10] The recent report by Zang *et al.* explores similar systems and it is observed that for BSPT/LSMO composite thin films, the Mc is initially negative for (H < 0.3 T) and then becomes positive for H up to 7 T. The negative Mc is associated to the stress induced change in dielectric constant ε, while the positive Mc occurs because of Catalan type contribution of interfacial polarization to the ε.[2,10] Thus one may select a ferroelectric material with useful values of polarization P, ε and magnetic material with sufficient CMR effect as well as coefficient of magnetostriction λ.

Owing to the discussion above, the present paper reports the synthesis and magnetodielectric properties of LSMO and $Ba_{0.7}Sr_{0.3}TiO_3$ (BST) thin film heterostructures.[7,11] The thin films are spin coated on SiO_2/n-Si(100) substrates. Here the base layer of LSMO itself is used to form the conducting bottom electrode of magnetodielectric systems.[12] Further parallel capacitance Cp and tanδ of heterostructures is measured by the deposition of a top electrode of 1mm diameter, forming a metal ferroelectric metal configuration. The present paper reports interesting results on Mc and the observed impedance spectra are understood in terms of a possible RC resonant circuit model.

2. EXPERIMENTAL

For the present studies, thin film heterostructures of LSMO and BST are deposited by employing citrate gel root (modified Pechini method) followed by spin coating tech-

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nique. Here hydroxide co-precipitates of the respective cations are used as starting materials. For the formation of hydroxide co-precipitates of Ba, Sr, and Ti, stoichiometric amounts of $Ba(NO_3)_2$, $Sr(NO_3)_2$ and $K_2TiO(C_2O_2)_4{\cdot}2H_2O$ of purity > 99.9% are used as starting materials, while KOH is used as a precipitating agent. Further details of the synthesis of BST are already reported earlier.[12] Similarly LSMO is also synthesized using the modified Pechini method as discussed above. For the deposition of thin films of BST and LSMO, the concentration of citrate gel is selected to be 0.2 M/L. To determine the thickness of a single layer of spin coated thin film, a cross sectional image of two layers of LSMO + BST was obtained. It was observed that the thickness of single layers of LSMO and BST were nearly 160 nm. In the present studies LSMO and BST heterostructures were formed by depositing consecutive layers of LSMO and BST. Each heterostructure possesses two alternations of LSMO and BST. After deposition of each layer, films are pyrolized at 400°C, and after the deposition of each layer of LSMO or BST the heterostructure is sintered as two different batches at a temperature Ts equal to 800°C and 900°C. Two different sintering temperatures are used to understand the effect of sintering temperature on the magnetodielectric properties of the heterostructures.

3. RESULTS AND DISCUSSIONS

Figure 1(a), (b) and (c) show x-ray diffraction (XRD) spectra of thin films of LSMO, BST and BST/LSMO heterostructures respectively. From the Fig. 1, it could be seen that the films grown are polycrystalline in nature and all the peaks in the spectra could be accurately indexed using standard JCPDS data on the respective compositions. The LSMO is observed to exhibit the rhombohedral crystal structure with hexagonal axis of symmetry. Here the values of lattice parameters a, c are observed to be 5.52 Å and 13.36 Å respectively, as reported earlier.[12] The BST is observed to exhibit a nearly cubic crystal structure with a signature of mild tetragonal character and lattice parameter a (BST) = 3.97 A^0.[12] The peaks in Fig. 1 are indexed with corresponding miller indices (h k l). From the Fig. 1(c) it could be seen that in the case of BST/LSMO, the majority of the peaks of LSMO and BST overlap with each other. From the XRD spectra, it is seen that the compositions under investigation are polycrystalline and phase pure.

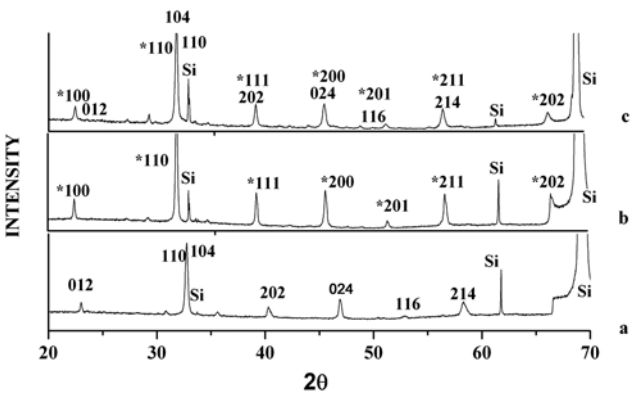

Fig. 1. XRD spectra of a) LSMO, b) BST, c) BST/LSMO thin film heterostructures deposited on SiO_2/n-Si(100) substrate.

Figure 2(a), (b) show FESEM images of LSMO, BST0.3 thin films grown on SiO_2/n-Si(100) substrate. It is observed that the particles of LSMO and BST0.3 possess average grain size of nearly 50 nm. It is reported that the BST0.3, or similar thin films prepared via soft chemical route and sintered for temperature above 700°C, exhibit formation of grain growth and therefore films appear a little porous. The microstructure in Fig. 2(a) and (b) is fairly uniform and concurrent to the earlier reports.[13,14]

Figure 3(a) shows the variation of parallel capacitance Cp as a function of frequency f for applied magnetic field H equal to 0, 0.2 and 0.6 T, for BST/LSMO heterostructure sintered at 900°C. From Fig. 3(a), it is observed that for the increase in magnetic field up to 0.2 T, Cp increases with H, while for further increase in H up to 0.6 T the Cp decreases with the increase in H. This is more clear from Fig. 3(b), which shows the variation of the Cp with magnetic field at f = 10 kHz. The variation of Cp with f, with varying H for the heterostructures sintered at 800°C is similar to the observations in Fig. 3. This is a typical magnetodielectric (MD) behavior. It is also known that variation of Cp as a function of H could be associated with strain induced variation of dielectric constant or variation of interfacial polarization due to the CMR effect of LSMO.[2,5,10] In fact both the contributions, one due to the CMR effect and other due to the strain induced by the giant magnetostriction of LSMO, are expected to occur simultaneously. To separate out these two contributions, one may determine impedance spectra and associate the observed variation of Z'' versus Z' with possible equivalent circuit models.[15]

In addition to the variation of Cp it is also interesting to record variation of loss tangent tan δ as a function of frequency f and H from 0 to 0.6 T. This variation is as shown in Fig. 4 for the heterostructures sintered at 800°C. The varia-

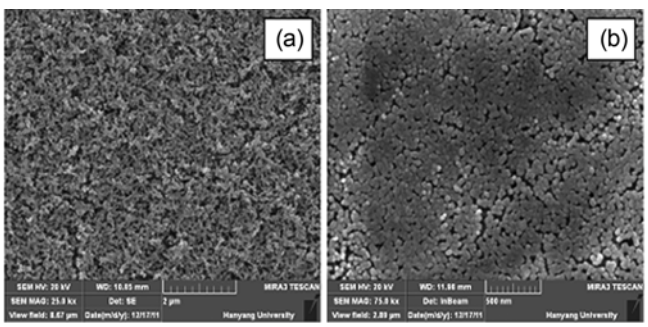

Fig. 2. FESEM images of a) LSMO and b) BST thin films.

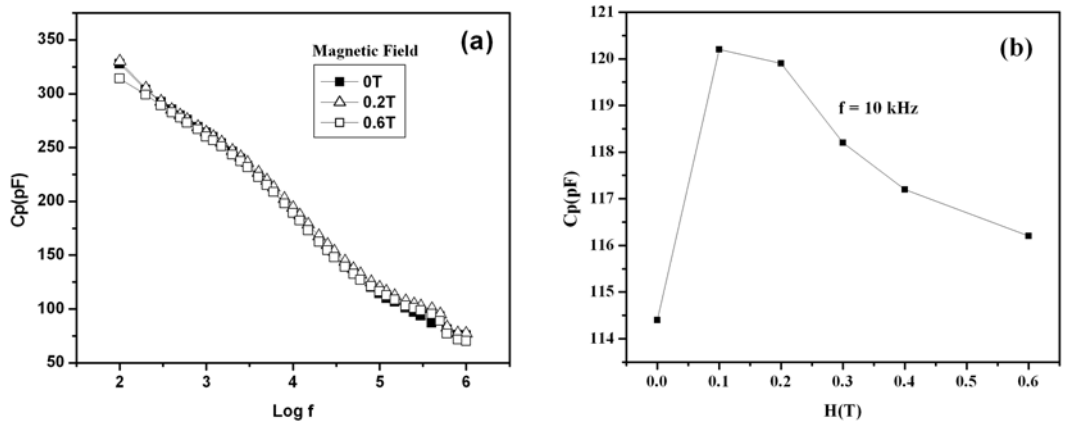

Fig. 3. a) Variation of capacitance Cp versus log f for various applied magnetic fields, b) Variation of capacitance Cp versus applied magnetic field H for BST/LSMO thin film heterostructure at f = 10 kHz (Ts = 900°C).

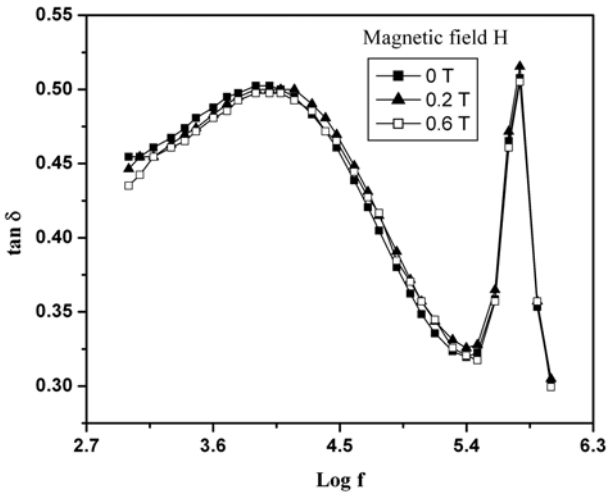

Fig. 4. Variation of tanδ versus log f for various applied magnetic fields for BST/LSMO thin film heterostructures (Ts = 800°C).

tion of tanδ as a function of f for the heterostructures sintered at 900°C is similar in nature with variation shown in Fig. 4. It is observed that the tanδ passes through a resonance peak in the vicinity of 50 kHz, which is typical of BST or similar compositions.[2,11] It is also observed that the tanδ passes through a sharp peak in the vicinity of 500 kHz, which may correspond to the electromechanical resonance frequency for the radial mode of the oscillations. Further, the application of the magnetic field causes the resonance peak in tanδ to shift slightly towards the lower frequency side. Nevertheless, instead of analyzing the variation of tanδ and Cp separately, it is convenient to understand the variation of Z" verses Z'.

Before we analyze impedance spectra let us look at the variation of Mc with f and H. Table 1 shows values of Mc at various frequencies for the heterostructures sintered at 800°C and 900°C. It is observed for H up to 0.2 T the Mc is positive, while for the magnetic field between 0.2 to 0.6 T

Table 1. Variation of positive magnetocapacitance (Mc-1) and negative magnetocapacitance (Mc-2) for BST/LSMO heterostructures and sintering temperature Ts = 800°C and Ts = 900°C.

Freq. f (kHz)	Mc-1 (Ts = 800°C)	Mc-2 (Ts = 800°C)	Mc-1 (Ts = 900°C)	Mc-2 (Ts = 900°C)
0.1	-	-	0.7	–4.9
1	1.2	–2.8	0.1	–1.5
10	2.5	–3.0	2.4	–2.5
100	1.6	–2.6	4.9	–3.2
500	1.2	–2.0	2.2	–6.5
1000	1.0	–3.9	2.1	–9.0

the Mc is negative for all the frequencies. The positive and negative values of Mc are being represented as Mc-1 and Mc-2 respectively. It is observed that the Mc shows an increasing trend as the frequency increases. The positive value of Mc is associated with the Catalan type contribution, while the negative value of Mc is expected to occur because of induced stress.[1,2,5,6] For the heterostructure sintered at 900°C, the maximum value of magnetic tunability, Mc, is observed to be –9%, while for that sintered at 800°C, it is –3.9%. It would be interesting to associate these variations with a particular effect only after impedance spectra is analyzed.

Figure 5 shows the observed impedance spectra for the heterostructure sintered at 900°C with varying H. The spectrum for the heterostructure sintered at 800°C is similar to Fig. 5. From inspection of Fig. 5 and the impedance spectra as discussed in an earlier report on simulation, it appears that the dielectric properties of the heterostructures could be represented as two parallel RC circuits connected in series with a capacitance Ci.[4,15] Figure 6 shows the required equivalent circuit for MD heterostructures, comprised of $R_1||C_1$, $R_2||C_2$ and Ci all connected in series. Here the R_1, C_1, represent low frequency semicircle at ω_{01}, while R_2, C_2 represents a

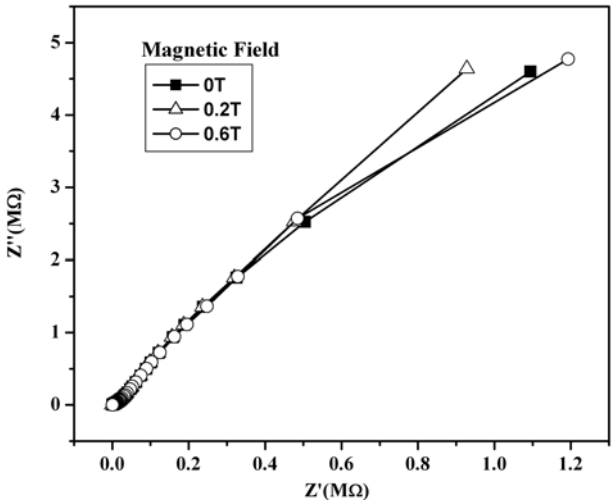

Fig. 5. Observed variation of complex impedance Z'' versus Z' for various applied magnetic fields for BST/LSMO thin film heterostructures (Ts = 900°C).

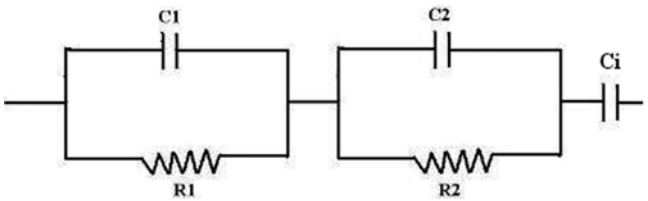

Fig. 6. Equivalent circuit model for MD thin film heterostructures.

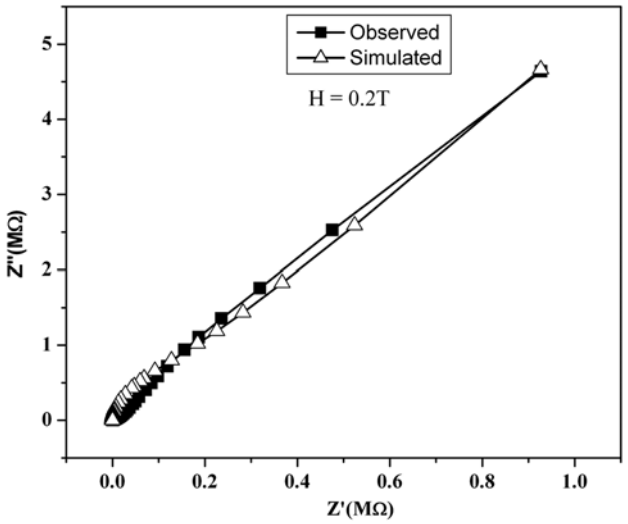

Fig. 7. Observed and simulated variation of complex impedance Z versus Z for BST/LSMO thin film at the applied magnetic field equal to 0.2T.

high frequency resonant circuit at ω_{02} and Ci represents capacitance due to interfacial polarization. High and low frequency semicircles occur because of heterogeneity of acceptor states in the bulk and grain boundaries of BST grains or other similar titanate compositions.[16,17] The Ci is interfacial capacitance due to the difference in the resistivity and dielectric constant of the LSMO and BST layers. A similar contribution is already modeled by Catalan.[1] For the purpose of simulation of the impedance spectra Ci is determined by making use of the data at low frequencies, while the values of R_1, C_1, ω_{01} and R_2, C_2, ω_{02} are determined after subtracting this contribution from the observed impedance spectra. Table 2 shows the values of R_1,C_1, ω_{01}, R_2, C_2, ω_{02} and Ci for the heterostructures investigated in the present case. The magnitudes of R_1, C_1, R_2, C_2 and Ci are calculated so that the observed and simulated curves closely match with each other with maximum possible accuracy. Both the observed as well as simulated impedance spectra for heterostructures sintered at 900°C with 0.2T applied magnetic field are shown in Fig. 7.

From Table 2 it is seen that for the sintering temperature of 800°C the variation in R_1, C_1, or R_2, C_2 or Ci are comparable but low, and it is expected that both the Catalan type and stress induced effect in polarization are equivalent for these heterostructures. This may lead to very low values of Mc. This feature could be confirmed from the observations in Table 1. For low sintering temperature the tetragonality of BST could be low and may lead to lower values of ε per unit cell. Further for the annealing temperature of 900°C the R_1, C_1 vary significantly as compared to the variation in Ci. Therefore the strain induced contribution to Mc would be significant. From the magnitude of Ci for the samples annealed at 800°C and 900°C, it is observed that the Ci reduces with increasing annealing temperature. From Table

Table 2. Variation of the impedance parameters for BST/LSMO heterostructure sintered at 800°C and 900°C for various applied magnetic field H.

Sintering Temp. (°C)	H (T)	R_1 (MΩ)	C_1 (pF)	ω_{01} (Rad/Sec)	R_2 (MΩ)	C_2 (pF)	ω_{02} (Rad/Sec)	Ci (pF)
800	0	0.084	947	12560	0.04	199	75360	955
800	0.6	0.086	925	12560	0.04	199	75360	780
900	0	1.52	1047	628	0.32	829	3768	420
900	0.2	1.27	1253	628	0.30	884	3768	400
900	0.6	1.61	989	628	0.40	663	3768	400

II it is seen that the Ci decreases with the increase in magnetic field H. This observation suggests that the contribution of interfacial polarization, i.e. $Z'' = 1/(\omega Ci)$, is more for increased sintering temperature. This feature may occur because of the reduction of interfaces between LSMO and BST as the sintering temperature increases. It is also known that for greater Catalan type contribution the Mc would be less negative or positive, while for the greater contribution of stress induced polarization Mc would be more negative. Therefore, as the contribution due to stress induced effect is greater, the comparative magnitude of Mc is expected to be larger and negative. The magnitudes of Mc in Table 1 are concurrent with the qualitative predictions made above. Thus in the case of BST the stress induced effect, i.e. Gridnev type contribution, dominates over the Catalan type contribution.[1,5] Thus it seen that the above contributions could be separated out using the present equivalent circuit model as shown in Fig. 6.

4. CONCLUSIONS

The present studies show that the analysis of impedance spectra could be used to separate out the Catalan type and Gridnev type contributions to the dielectric constant. Further, the analysis may provide guidelines for the design of various heterostructures possessing large positive or negative magnitudes of Mc.

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