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Magnetodielectric properties of $la_{0.67}sr_{0.33}mno_3$ - $ba_{0.95}ca_{0.05}ti_{0.925}zr_{0.075}o_3$ multiferroic composite

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ABSTRACT

The paper reports the synthesis of $Ba_{0.95}Ca_{0.05}Ti_{0.925}Zr_{0.075}O_3$ composition via ceramic route of synthesis to result into the BCZT composite and the synthesis of $La_{0.67}Sr_{0.33}MnO_3$ using hydroxide coprecipitation result into the LSMO composite. Further, the magnetodielectric (MD) composites of BCZT are formed by addition of LSMO at y = 0.10, 0.15 and 0.20. The composites LSMO-BCZT (LBCZT) are investigated for the variation of dielectric constant and impedance spectra as a function of applied magnetic field for the frequency between 20Hz to 1MHz. The observations on MD effect show that the dielectric constant possesses contributions due to magnetic field dependant interfacial polarization and variations due to the induced stress.

KEYWORDS: BCZT- LSMO, Magnetodielectric composites, Magneto-capacitance, CMR.

INTRODUCTION

Recently 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 (Catalan *et al* 2005; Chavan *et al* 2016; Gridnev *et al* 2009). The magnetocapacitance 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. Therefore as a basic requirement is to select ferroelectric as well as CMR systems possessing transition temperature Tc in the vicinity of room temperature.

$Ba_{1-x}Sr_xTiO_3$, $BaZr_xTi_{(1-x)}O_3$, $Ba_{(1-x)}Ca_xTiO_3$ and $BaTi_{(1-x)}Mg_xO_3$ 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. Owing to the discussion above, the present paper reports the synthesis and magnetodielectric properties of $La_{0.67}Sr_{0.33}MnO_3$ (LSMO) and $Ba_{0.95}Ca_{0.05}Ti_{0.925}Zr_{0.075}O_3$ **(**BCZT) multiferroiccomposite. Further parallel capacitance Cp and tan δ of composite are measured. The present paper reports interesting results on MC and the observed impedance spectra.

EXPERIMENTAL

SYNTHESIS OF $Ba_{0.95}Ca_{0.05}Ti_{0.925}Zr_{0.075}O_3$(BCZT):

The BCZT solid solutions have been synthesized using ceramic route of synthesis using the precursors $BaCO_3$, CaO, ZrO_2 and TiO_2 of AR grade. The stoichiometric amounts of the precursors were well mixed together and ground for 2 hours in an agate mortar with pestle. Considering the earlier reports, the calcinations was carried out at 1150^0C.The calcined powder was mixed with a polyvinyl acetate (PVA) binder solution and compacted into disk shaped samples with a diameter of 1.0 cm and a thickness of nearly 1.0 mm. The final sintering process was carried out at 1200^0C for 24 h in two steps. The silverpaint was used for electroding the samples. The temperature dependent dielectric constant was measured to study the curie temperature (Tc) in between temperature range of 30 ^{0}C –150 ^{0}C.

SYNTHESIS OF $La_{0.67}Sr_{0.33}MnO_3$(LSMO)

The $La_{0.67}Sr_{0.33}MnO_3$ (LSMO) has been synthesized by employing hydroxide coprecipitation route followed by ceramic process of synthesis. The AR-grade $La(NO_3)_3.6H_2O$, $Sr(No_3)_2$, $KMnO_4$, and $(CH_3COO)_2.Mn.4H_2O$ are used as precursors, while a mixture of NH_4OH and KOH is used as precipitating agent. The details of the co-precipitation route are similar as reported earlier (Sutar *et al* 2012; Kim *et al* 2008;Veer *et al* 2008). The precipitate formed is washed thoroughly and calcinated at 1000^0C for 12 h to achieve complete ferromagnetic phase formation. The LSMO powder is pelletized in the form of disc of 1.2 cm diameter using pressure of nearly 2 ton per cm^2. Further, the pellets are sintered at 1100 ^{0}C for 12 h to achieve a dense ferromagnetic composition.

FORMATION OF COMPOSITE

The resulting powders of LSMO and BCZT are ground thoroughly to form uniform and submicron level particle size. The powder of LSMO and BCZT thus formed are used to form the required MD composites using the following formula

$$yLSMO + (1- y)\ BCZT = yLBCZT$$

with y = 0.10, 0.15 and 0.20.

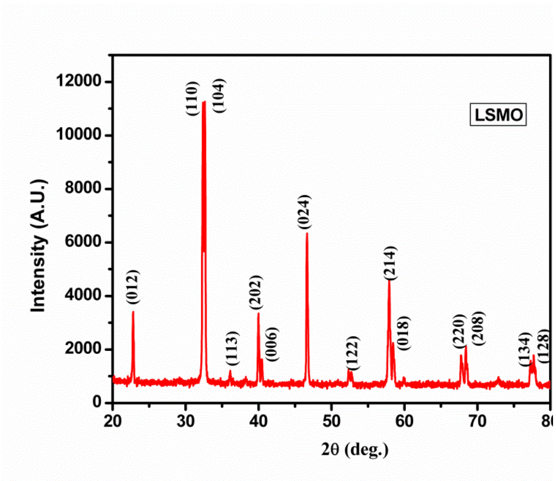
The composites above are termed as 0.10LBCZT, 0.15LBCZT, 0.20LBCZT respectively during the course of further discussions.

The sintered powder of LSMO and BCZT was grounded together thoroughly using agot mortor and pestol. The pellets of diameter 1.2 cm are formed. The pellets are sintered at 1100^0C for 6 h to form desired MD composites. The parent compositions LSMO and BCZT as well as their composites are investigated for the structural properties using Bruker D8 advance X-ray powder diffractometer. For dielectric measurements, LCR-Q meter (HP4284A) is used in the frequency range from 100 Hz to

1MHz for temperature between RT and 150^{0}C for measurement of Cp, tan δ as a function of frequency (F), temperature (T) for dielectric characterization of BCZT and magnetic field (H) up to 0.6T applied for MD characterization of the composites.

RESULT AND DISCUSSION

STRUCTURAL ANYLISIS: Figure 1(a), 1(b) and 1(c) show X-ray diffraction (XRD) pattern of LSMO, BCZT and LSMO-BCZT (LBCZT) compositions respectively. From Fig.1 (a), it could be seen that LSMO composition grown are polycrystalline in nature and all the peaks in the pattern could be accurately indexed using standard JCPDS data (JCPDS card no.89-8098) (Sutar *et al.*, 2012). Thus from the XRD pattern, it is revealed that the ferromagnetic compositions were synthesized in the desired rhombohedral structure with hexagonal axes of symmetry without any detectable impurity phase. Here the values of lattice parameters a, c are observed to be 5.52 A^o and 13.36A^o respectively, as reported earlier (Tarale *et al.*, 2012; Sutar *et al.*, 2012). Using the Scherrer's formula, the particle size is calculated and is of the order 23.55 nm.



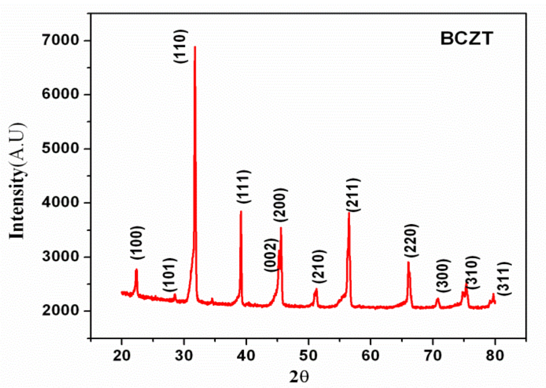


Fig 1(a): XRD pattern of LSMO composition Fig.1(b) XRD pattern of BCZT composition

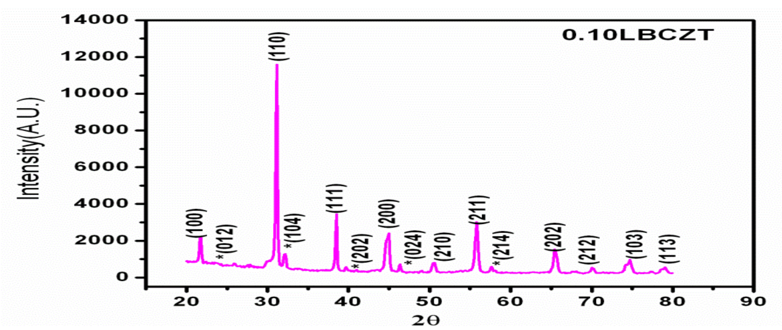


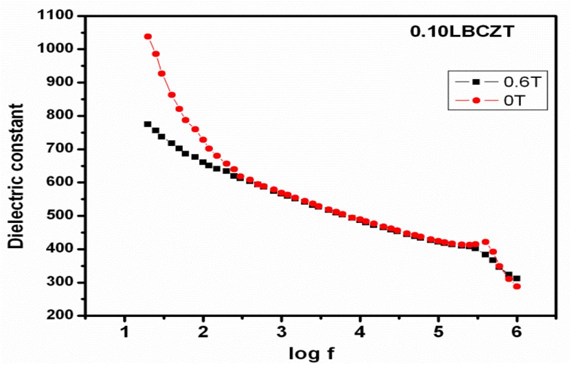
Fig 1: (c) XRD pattern of 0.10LBCZT composite

From Fig 1 (b), it could be seen that the BCZTcomposition is observed to exhibit a nearly cubic crystal structure with a signature of tetragonal character. The lattice parameter 'a' and 'c' corresponding to tetragonal crystal structure and degree of tetragonality (c/a) of BCZT composition are a = 3.789A^{o}, c = 4.001 A^{o}, c/a =1.055 and particle size is 55.40 nm.

Fig 1(c) shows the XRD pattern 0.10LBCZT composite. The peaks corresponding to the reflections of BCZT and LSMO could be indexed separately. From the XRD pattern, it could be seen that the composites formed are phase pure and possess two separate phases viz. LSMO and BCZT.

MAGNETODIELECTRIC PROPERTIES

Fig 2(a), (b), (c) show the variation of dielectric constant ε as a function of log f for yLBCZT, y = 0.1, 0.15 and 0.2 respectively, in the absence as well as in the presence of applied magnetic field (H). The dielectric constant ε is observed to decrease as a function of log f, where the dispersion is faster at lower frequencies as compared to the higher one. The faster decrease of dielectric constant ε at lower frequencies is attributed to the presence of interfacial polarization. The interfacial polarization is known to occur for BCZT compositions because of grain–grain boundary interaction. Further, the additional component of the interfacial polarization is expected to occur in the present case because of the difference of the resistivities of the LSMO and the BCZT phases. The LSMO is known to possess a CMR at room temperature and, therefore, the resistivity of LSMO phase is expected to decrease with increase in the value of applied magnetic field (H) (Urushibara *et al., 1995*; Tang *et al., 2006*). As the resistivity decreases with H, the interfacial polarization should increase with applied magnetic field. This phenomenon is known to cause the Catalon type contribution to MC as reported earlier (Catalan *et al.,* 2006).



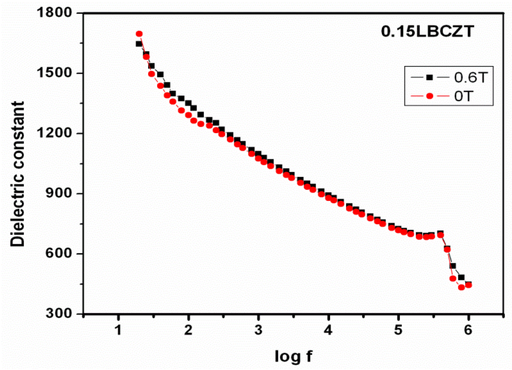


Fig 2(a): ε verses log f for 0.10LBCZT composite. **Fig 2(b): ε verses log f for 0.15LBCZT composite.**

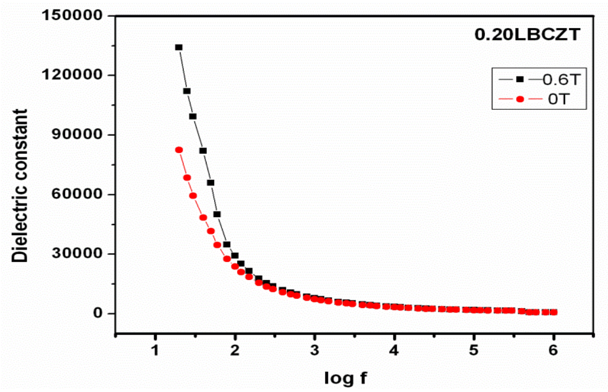


Fig 2(c): ε verses log f for 0.20LBCZT composite

As reported recently, the another competitive phenomenon which causes the magneto-capacitance(MC) is the magnetostriction-induced variation in the dielectric constant ε. Due to the stress induced by the magnetostriction, it is known that the polarization of the ferroelectric phase increases, while the ε decreases with the applied stress, i.e. with increase in H. This phenomenon was reported earlier in the case of PZT-MZF bilayer ME composites. The Gridnev explained this phenomenon on the basis of

Landau thermodynamic theory (Gridnev *et al.*, 2009). If the contribution of CMR induced dielectric constant (ε) is large as compared to the stress-induced effect, the MC would be positive. On the other hand, MC would be negative for substantial contribution of stress-induced effect.

Let us look at the variation of MC with f and H. Table 1 show the values of Mc at various frequencies for the multiferroic composite, when the field applied parallel and perpendicular to composite. It is observed the magnetocapacitance MC is positive also it is negative for all frequencies. The positive value of magnetocapacitance MC is associated with the Catalan type contribution, while the negative value of magnetocapacitance MC is expected to occur because of induced stress (Catalan *et al.*, 2006; Gridnev *et al.*, 2009). The maximum value of magnetocapacitance MC is observed to be -6.940 %.

Table 1: Values of Mc at various frequencies for the multiferroic composite, when the field applied parallel and perpendicular to the composite

Frequency Hz	MC For 0.1LSMO in %		MC For 0.15LSMO in%		MC For 0.20LSMO in %	
	Parallel	Perpendicular	Parallel	Perpendicular	Parallel	Perpendicular
1K	0.4347	0.438	0.4640	-2.262	0.5181	-6.940
10K	0.3553	0.6741	0.6790	-1.3292	1.495	-5.0
100K	0.4678	0.7941	0.3460	-0.8904	1.094	-2.684
500K	0.1587	0.80470	0.4261	-0.8712	0.6748	-0.9566
1M	0.3145	0.8254	0.4097	-0.5546	0.6326	0

Fig 3 shows variation of dielectric constant (ε) versus applied magnetic field H for BCZT/LSMO composite at f = 10 kHz sintered at1100°C. From Fig. 3, it is observed that the dielectric constant ε decreases with increase in magnetic field. The variation of dielectric constant ε with frequency f, with varying applied magnetic field H for the composite sintered at 1100°C is similar to the observations in fig. 3. This is a typical magneto dielectric (MD) behavior. It is also known that variation of dielectric constant ε as a function of magnetic field H could be associated with strain induced variation of dielectric constant or variation of interfacial polarization due to the CMR effect of LSMO (Gridnev *et al.*, 2009).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'.

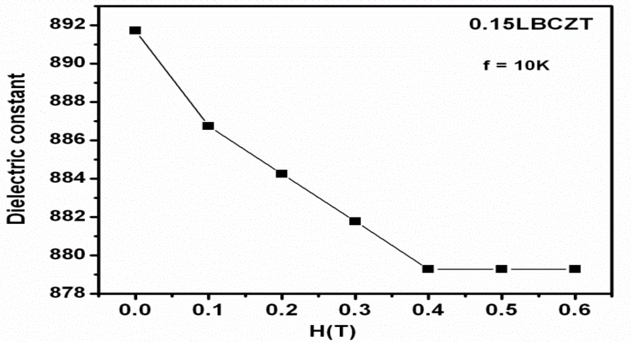


Fig.3: Variation of dielectric constant (ε) versus applied magnetic field H for 0.15LBCZT composite at f = 10 kHz.

As a part of discussion on MC, it is interesting to note the following behavior. As discussed earlier, the MC occurs due to variation of dielectric constant because of the applied stress occurring due to the piezomagnetic effect in the ferrite phase (Gridnev *et al.*, 2009). Further, the MC should be proportional to $\lambda \times k_m \times (d\varepsilon/ds)$, where λ is magnetostrictive coefficient, k_m the magnetomechanical coupling coefficient, $d\varepsilon/ds$ the rate of change of dielectric constant as a function of applied stress. For λ being positive, the stress would increase with increase in H_{dc}, while for λ negative stress would decrease with increase in H_{dc}, and, therefore, ε increases with H_{dc}.

CONCLUSION

It is observed that the ceramic route successfully used to formBCZT composition and hydroxide co-precipitation route could be successfully used to form the LSMO compositions. The particle size of BCZT compositions is observed to be 55.40 nm.The particle size of the LSMO is observed to be 23.55 nm. It was observed that the BCZT composition correctly reproduce the dielectric properties. The MD properties of these systems are observed to be interesting and the Catalan and Gridnev type contribution are observed. The observed magnitude of the magnetocapacitance MC is fairly large with a maximum value equal to -6.940 %.for 0.20LBCZTcomposite. Further, the analysis may provide guidelines for the design of various multiferroic composites possessing large positive or negative magnitudes of magnetocapacitance MC.

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