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A physical property study of Sr Bi_{5-x} La $_x$ Fe Ti_4 O_{18} prepared through the oxalate precursor method

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ABSTRACT

Ceramic samples of Sr Bi_{5-x} La_x Fe Ti_4 O_{18} (SBLFT) where x=0.65,0.75 and 0.85 were prepared using the oxalate precursor technique. Single-phase formation was confirmed through the XRD. Dielectric measurements such as dielectric constant and dielectric loss have been carried out on all the samples in the temperature range 30°C – 750°C at fixed frequencies. Dielectric constant as well as transition temperature(T_C) were decreased with the increase of La content. Magnetoelectric measurements have been carried out in dynamic ME method and the obtained ME output for SBLFT (x=0.65) is 212mV/cm at an AC field of 3Oe at 1kHz and at 1kOe bias magnetic field.

Keywords: Precursor, Ferroelectromagnetics, Dielectric constant, Magnetoelectric

1. INTRODUCTION

Multiferroics, also termed as ferroelectromagnetics or magnetoelectrics, belongs to the class of materials in which two or three formalisms such as ferroelectricity, ferromagnetism and ferroelasticity can coexist in the same phase [1,2]. As a result, these materials exhibit spontaneous polarization by the application of magnetic field, spontaneous magnetization on the application of electric field and often some coupling between the two giving rise to an effect called magnetoelectric (ME) effect. Thus, these materials have two or more switchable states such as polarization, magnetization or strain [3]. Eventhough there are a number of materials that can have both electric and magnetic ordering, a pronounced interplay between the two has rarely been reported. The non-trivial spin-lattice coupling in these materials has been manifested through various forms such as linear and bilinear ME effects [4,5] , polarization change through field induced phase transitions [6,7], magnetodielectric effects and dielectric anomalies at magnetic transition temperatures. ME effect have been studied the most in multiferroics such as perovskite type $BiFeO_3$ [7], $BiMnO_3$ [8] , $BaMF_4$ (M-divalent transition metal ion), hexagonal $RMnO_3$ (R-rare-earths) such as $YMnO_3$ [9], $TbMn_2O_5$ [10] and in Bismuth layer structured ferroelectric (BLSF) [11,12] $Bi_4Ti_3O_{12}$ + n $BiFeO_3$ system which results in $Bi_5FeTi_3O_{15}$, $Bi_6Fe_2Ti_3O_{18}$, $Bi_7Fe_3Ti_3O_{21}$ etc.. Wood & Austin [13] suggested various applications of magnetoelectric materials in as a) multiple state memory elements b) electric-field-controlled ferromagnetic resonance c) transducers with magnetically modulated piezoelectricity etc.

In the present study, a new ferroelectromagnetic system Sr Bi_{5-x} La $_x$ Fe Ti_4 O_{18} (SBLFT), has been prepared by the oxalate precursor technique. The material belongs to the group of Bi_4 Ti_3 O_{12}+ n Bi Fe O_3, which is a BLSF and are described by the general formula: $\mathbf{(Bi_2\ O_2)^{2+}\ (A_{m-1}\ B_m\ O_{3m+3})^{2-}}$ where A=Sr^{2+}, Ba^{2+}, Pb^{2+} etc., B=Ti^{4+},Ta^{5+} etc. and n is the number of perovskite-like layers between Bi_2O_2 layers. Materials of this group exhibits both electrical and magnetic ordering, and hence magnetoelectric effect. Present work describes the synthesis, dielectric and magnetoelectric properties of Sr Bi_{5-x} Lax Fe Ti_4 O_{18} ceramics with x=0.65,0.75,0.85 (SBLFT65, SBLFT75 and SBLFT85 respectively)

2. EXPERIMENTAL

SBLFT ceramics were synthesized using the oxalate precursor technique. All the starting materials of Sr, Bi, Ti, Fe were first converted to oxalates. The powders thus obtained were ground in alcohol for 1hour for proper mixing and then burned in the temperature range 600-900^{o}C for 3hours. The powder was again ground to obtain fine powders and pressed in to cylindrical discs of varying thickness. These discs were final sintered in the temperature range 1050-1250^{o}C in air. Formation of single phase was confirmed by the X-ray diffraction [Panalytic (X'pert)].

Dielectric properties namely dielectric constant and dielectric loss were carried out on the electrically poled samples of SBLFT using HP4192 Impedance analyzer. Electrical poling was done on the samples at 25kV/cm at 200^{o}C. Poling above 200^{0}C is not possible because of increased conductivity. Variation of dielectric constant and dielectric loss with temperature were studied at fixed frequencies from 1kHz-4MHz.

Magnetoelectric measurements were carried out using the dynamic ME set-up [14]. All the samples were poled electrically and magnetically prior to the ME measurements. An AC magnetic field at a frequency of 1kHz was superimposed on the varying DC bias field. The importance of this dynamic method of ME measurements is that one can avoid the space charges that will be accumulated at the electrodes of the specimen.

3. RESULTS AND DISCUSSIONS

From the XRD (Fig.1) , single-phase formation was confirmed and no second phase was observed. DC conductivity of the samples was performed using the conventional two-probe method. Room temperature resistivity of the samples is of the order of 10^{11} Ω-cm and the value increases slightly with the increase of lanthanum content in the ceramic.

Fig.2 shows the variation of dielectric constant and dielectric loss with temperature at fixed frequencies. From the figure, dielectric loss of all the compositions is in the range $2X10^{-3}$ - $3X10^{-3}$ at room temperature and is frequency dependent. The room temperature dielectric constant for the samples increases slightly with the increase of La content in the samples. Whereas the maximum dielectric constant and transition temperature (T_C), decreases with the increase of La. From the plots, the hump like behaviour around 400^{o}C and a peak at high temperatures is observed. Deverin [15], in 5-layered $Bi_6Fe_2Ti_3O_{18}$, observed the similar kind of behaviour, which they attributed to the change in the magnetic ordering. It is known that even and odd layered compounds exhibit two transitions and one transition respectively [16] . It was reported earlier that the substitution of trivalent ions for bismuth site significantly affects the Curie temperature of the layer material. The broad peak observed in the present study is attributed to the random arrangement of cations in the structure, leading to the microscopic heterogeneity in the composition due to the presence of 5 types of cations occupying A and B sites randomly in the crystal, leading to the multiple relaxation behaviour. 5-layered SBLFT can be described with the molecular formula Bi_2O_3 .5 [$(Sr_{1/5}\ Bi_{3-x/5}La_{x/5})$ $(Ti_{4/5}Fe_{1/5})\ O_3$]. In the formula, the terms inside the bracket [] represents the ABO_3 where cations Sr2+/Bi3+/La3+ and Fe3+/Ti4+ occupy A and B sites respectively.

The decrease in the values of T_C and $\varepsilon_r^{'}$ with La are in good agreement with the results obtained in La-doped $Bi_4Ti_3O_{12}$ [17]. La modification introduces a large quantity of oxygen vacancies at the surfaces of ceramic grains as well as at the domain walls by formation of defect dipoles, such as $V_{\bar{O}} - V'''_{La,Bi}$ and $V_{\bar{O}}$-$O''_{ad,}$ where O''_{ad} represents the absorbed oxygen ions. The polarization of defect dipoles as well as polar clusters thermally fluctuates between the equivalent directions of crystal variants around the phase transition, which contribute considerably to the dielectric response. The frozen-in defect dipole polarization at room temperature leads to a reduced permittivity.

Magnetoelectric nature of the samples was tested by the measurement of voltage output by varying the AC magnetic field at fixed bias magnetic field and vice versa. Fig.3 shows the variation of ME output with varying bias magnetic field at fixed AC fields at 1kHz frequency. Obtained ME output for the SBLFT65, SBLFT75 and SBLFT 85 are tabulated. From the graph, SBLFT65 showed a maximum ME output of 212mV/cm at an AC field of 3Oe at 1kHz frequency and 1kOe bias magnetic field.

The material SBLFT can be thought of the combination of ferroelectric $SrBi_4Ti_4O_{15}$ and magnetoelectric $Bi_{1-x}La_xFeO_3$. It is known that $BiFeO_3$ is a ferroelectric and a weak ferromagnet having G-type antiferromagnetic ordering [18]. It has a cycloidal magnetic spin and incommensurate structure, gives rise to the non-linear effects with a spin-flop[19]. Antiferromagnetic nature of the material should give rise to the linear ME effects, where as a quadratic signal may be arising due to slight canting of the Fe-O-Fe chains of spins in the regular octahedral, which is slightly tilted. Magnetization studies at room temperature and at low temperatures, are under process to study the magnetic nature of the samples better.

4. CONCLUSION

A new polycrystalline material system SBLFT is prepared by the oxalate precursor technique. X-ray diffractograms reveals the formation of single-phase. Dielectric properties such as dielectric constant and dielectric loss have been measured. A decrease in the value of dielectric constant and Tc with the increase of La content in the samples is observed. The material system also exhibits magnetoelectric behaviour.

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FIGURES

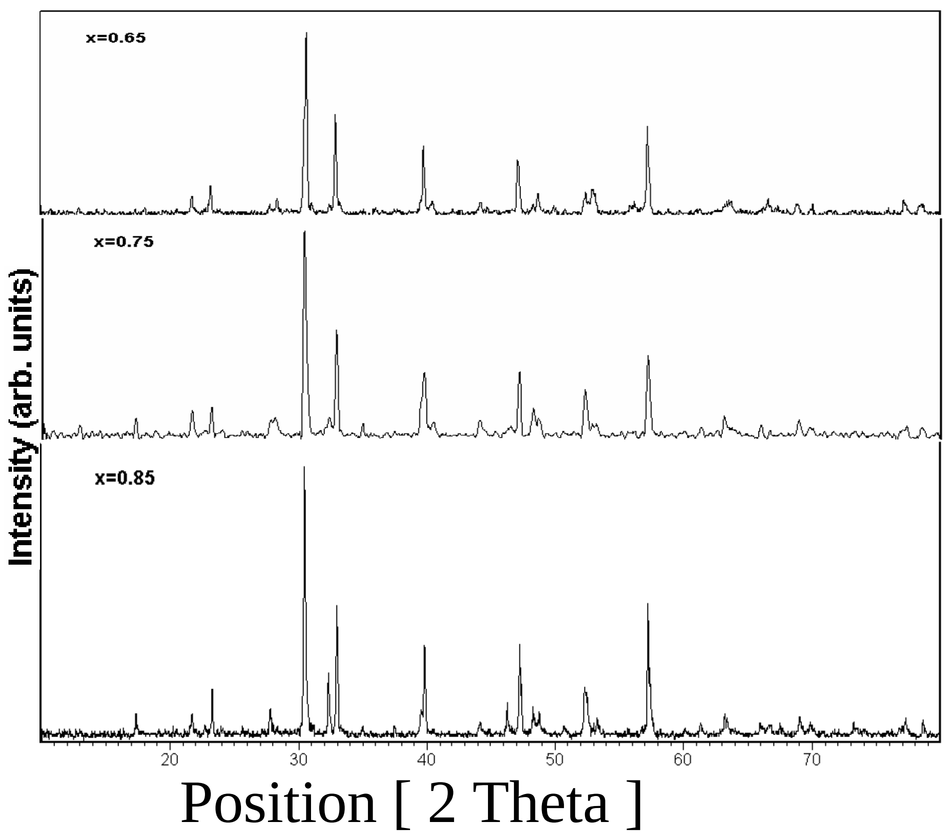

Fig.1 X-ray diffractograms of the SBLFT system

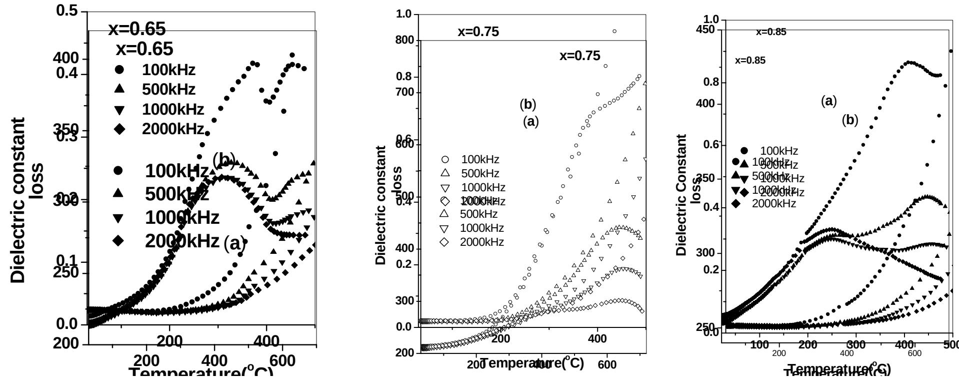

Fig2. Variation of a) dielectric constant b) dielectric loss with temperature for x=0.65,0.75 and 0.85

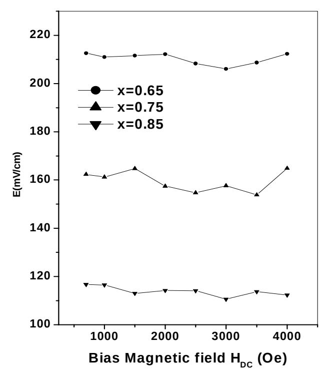

Fig3. Variation of ME output with bias magnetic field at fixed AC magnetic field.