Bismuth Doped Double Perovskite La_2CoMnO_6: Analysis On Structural, Dielectric And Modulus Character

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Abstract: Influence of volatile bismuth doped double perovskiteLa_2CoMnO_6 with formula $La_{2-x}Bi_xCoMnO_6$ [x =0, 0.1] has been reported. The samples after preparation via solid state route were examined for the structure and type of phase acquired using reliable XRD technique. The data recorded in the angular range of $10^o < 2\theta < 80^o$ was analyzed and it was confirmed that the samples under investigation have crystalized in the monoclinic structure and have acquire a space group $P2_1/n$. The dielectric studies carried out revealed the high dielectric constant and slow rate of decrease in this character as the applied field increases predicting their usability in the electronic devices. The electric modulus studies confirmed the relaxation in the samples.

Keywords: Double perovskites; Structure; Dielectrics; Dielectric relaxation**.**

INTRODUCTION

Double perovskite oxides of the type $A_2B'B''O_6$ (where A = rare earth, B' and B'' = transition metals) exhibit intriguing physical properties La_2CoMnO_6 and have been studied extensively in recent years to explore their multiferroic behavior. Double perovskite based on La_2CoMnO_6 are attractive due to their impressive properties and potential on industrial applications [1-3]. In these perovskites,a FM transition about~220 K has been displayed[4] for an ordered sub-lattice with high spin Co^{2+} and Mn^{4+} pair and FM transition below 150 K [5] for a disordered sub-lattice with low spin Co^{3+} and high spin Mn^{3+}. For low temperature sintered samples-and for the samples prepared at high temperature, reports suggest that the transition temperatures are around T_c(~ 220 K) and T_c(~150K) [4, 6] respectively.

The multiferroic materials have attracted much attention of the researchers. The coupling between ferromagnetic and ferroelectric parameters results in novel effects, such as magnetoelectric and magneto-dielectric effects. Since Charge ordering process provides a hope in a direction toward novel multiferroic materials, double perovskites based on $La_2CoMnO_6$with the ordering of Co^{2+} and Mn^{4+} at B site is also believed to exhibit a local polar behavior suggesting to look for the possible ferroelectricity in La_2CoMnO_6[4].

Despite its application from magneto-dielectric material point of view, it finds hope as insulating barriers in spin filters[1-3]. It is confirmed that the ferromagnetic semiconductor La_2CoMnO_6 with high T_c is $P2_1/n$ is monoclinic structured, in which octahedra with Co and Mn centers are alternately stacking along (111). La_2CoMnO_6 has potential magnetodielectric character at room temperature making it useful in advancement of electronic device [7, 8].

The physical properties are believed to be largely dependent on the synthesis procedures and the conditions associated. We synthesized $La_{2-x}Bi_xCoMnO_6$ [x =0, 0.1] double perovskites with solid state reaction route to get compact and single phase solid state solutions with improved dielectric properties. The samples have been discussed interms of structure, dielectric and electric modulus nature.

EXPERIMENTAL DETAILS

We synthesized double perovskite polycrystalline samples of the type $La_{2-x}Bi_xCoMnO_6$ [x =0, 0.1] via high temperature solid state reaction route. The stoichiometric weighed amounts of oxides of Lanthanum (La_2O_3), Bismuth (Bi_2O_3), Cobalt (Co_3O_4) and Manganese (MnO_2) were mixed in an agate-mortor without further processing. The oxides were ground for 6h until a fine powder of the mixture was obtained. The fine powder was calcined at 1200 ^oC for 10h. The duration of grinding and calcination was repeated to complete the reaction between the precursors. Finally fine powder was added with poly Vinyl Alcohol (binder) matrix to hold the particles for sintering to obtain the compact and dense material. The binder-powder combination was transformed into the pellets of 10mm diameter using hydraulic press under the pressure of 6 tonnes/inch and sintered at 1300^oC. The pellets were then silver polished to make better electrical contact for dielectric measurement.

The double perovskites of the type $La_{2-x}Bi_xCoMnO_6$ [x =0, 0.1] were subjected to x-ray diffraction measurements with $CuK\alpha_1$ (1.5406Å) radiation using Bruker D8 Advance X-ray diffractometer over the angular range 2θ (10°-80°) generating X-ray by 40kV and 40mA power settings. Dielectric measurements were performed as a function of frequency in the range of $2*10^4$Hz–$6*10^6$MHz on Novocontrol alpha-A high performance frequency analyzer at room temperature.

RESULTS AND DISCUSSIONS

The polycrystalline double perovskites $La_{2-x}Bi_xCoMnO_6$ [x =0, 0.1] were successfully synthesized via solid state reaction route. To conform the crystallization of the as prepared samples and their phase, x-ray diffraction technique was employed. We recorded the XRD data in the range of 10^o-80^o and plotted it and has been displayed in the Figure1. The XRD spectra analysis revealed the crystallization of the synthesized samples into the monoclinic structure with the assigned space group of $P2_1/n$. The intensity of the characteristic peaks in both the samples and their narrower FWHM witnesses that the samples are highly crystalline in nature with higher average crystallite size. Also the close observation of the spectra reveals that the intensity decreases with Bi doping in the matrix of the pristineLa_2CoMnO_6 indicative of the introduction of porosity in the stable parent material. The Lattice parameters calculated for La_2CoMnO_6 were a=5.5285□,b=5.4899 □,c = 7.7780 □ and for Bi doped La_2CoMnO_6, a=5.5265□, b=5.4878 □,c= 7.7770□ consistent with the reports[8, 9].The slight decrease in lattice parameters on dopingare attributed to the

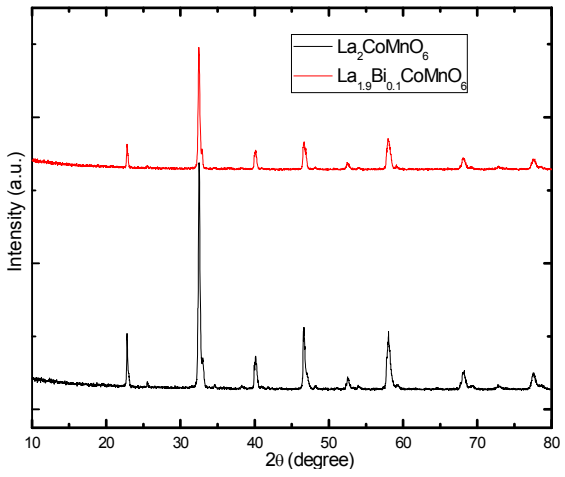

FIGURE 1.XRD of $La_{2-x}Bi_xCoMnO_6$ [x =0, 0.1]..

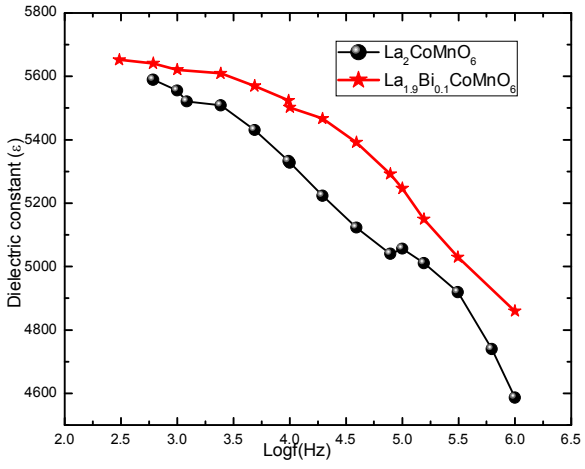

FIGURE 2. Dielectric constantof $La_{2-x}Bi_xCoMnO_6$ [x =0, 0.1] vs Log f(Hz).

lower ionic size of the Bi^{3+} [0.96□] compared to La^{3+} [1.06 □].The average crystalize size calculated for the $La_{2-x}Bi_xCoMnO_6$ [x =0, 0.1] using Scherer's formula, t = kλ/ □cosθ, where 't' is the crystallite size, k = 0.9 and is called the shape factor, □is FWHM while as the θ is Bragg angle were 36nm and 41nm.La_2CoMnO_6 based double

perovskites are usually known as collosal dielectric materials. When it is the case of solid state synthesis of these materials, the dielectric studies are indispensable. We did dielectric characterization of $La_{2-x}Bi_xCoMnO_6$ [x =0, 0.1] double perovskites as a function of frequency. The data has been collected in the frequency range of $2x10^4$- $6x10^6$ Hz, plotted and displayed in the Figure 2.

The plot reveals usual trend of decrease in the dielectric constant with the increase of the field. The charge accumulation at lower frequencies display larger dielectric constant while the character at higher value of applied frequency is the result from the release of trapped charges which results in the decrease of the dielectric constant. At low frequency, the plots indicates strong frequency dispersion. The observed frequency dispersion is associated with Maxwell-Wagner type interfacial polarization and is in agreement with Koop's phenomenological theory. Also the higher dielectric constant in the low region offrequencies may be due to the interfacial dislocations, oxygen vacancies, charged defects, grain boundaries effect and interfacial/space charge polarization due to heterogeneous dielectric structure[10,11]. From the plots, the Bi doped La_2CoMNO_6 shows higher dielectric constant and slower rate of decrease of dielectric constant with the field.

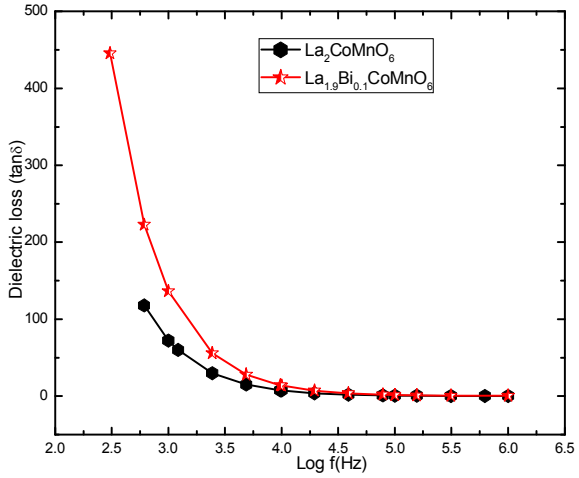

FIGURE 3. Dielectric lossof $La_{2-x}Bi_xCoMnO_6$ [x =0, 0.1] vs Log f(Hz)

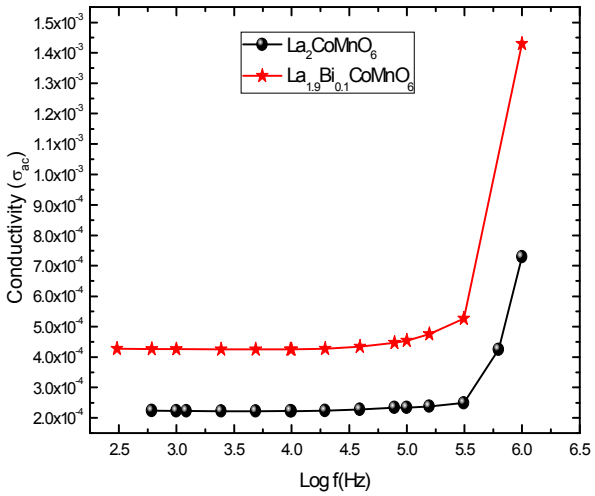

FIGURE 4. *ac* conductivityof $La_{2-x}Bi_xCoMnO_6$ [x =0, 0.1] vs Log f(Hz).

The dielectric loss as a function of frequency depicted in Figure 3, displays a usual trend of decrease in with the increase in the applied field. The gradual decrease in the dielectric constant with the increase in the applied field is mainly the cause of suppression of domain wall motion. Among the other reasons the dielectric loss arises due to the presence of impurities and structural inhomogeneities which lead to the polarization lagging behind the applied alternating field. At lower frequency region where hopping frequency between different ionic sites and the frequency of the applied field is nearly same, the observed loss is usually higher which decrease with increase in applied field and beyond a certain limit, becomes independent of the field[11-13]. Meanwhile, it is worth to mention that though doping of Bi in the matrix of pristine compounds increases its dielectric constant as well as loss value as is clear from the Figure 3..

From Figure 4, it is observed that initially the value of *ac* conductivity remains constant and a limit reaches after which the conductivity starts increasing abruptly with further increase in the applied field. The physics behind this character is that after a certain value of applied field i.e. threshold frequency, the trapped charge gets released and increase in the field increases the kinetic energy of the de-trapped charge carriers resulting in the abrupt increase in *ac* conductivity. Further, the conductivity of doped La_2CoMnO_6 is higher attributed to the creation of charge trap centers upon Bi doping in the stable matrix of La_2CoMnO_6[11,12].

The variation of the electric modulus (M′) of $La_{2-x}Bi_xCoMnO_6$ [x =0, 0.1] as a function vs Log f(Hz) has been studied and displayed in the Figure 5. The graph reveals a constant and very small value for M′ at low frequency region confirms the contribution from electrode polarization is out of context, a continuous dispersion with frequency is scarcity of restoring force that guides the movement of charge carriers, and an asymptotic saturation value at very high frequency due to the mobility of charge carriers over short-range.

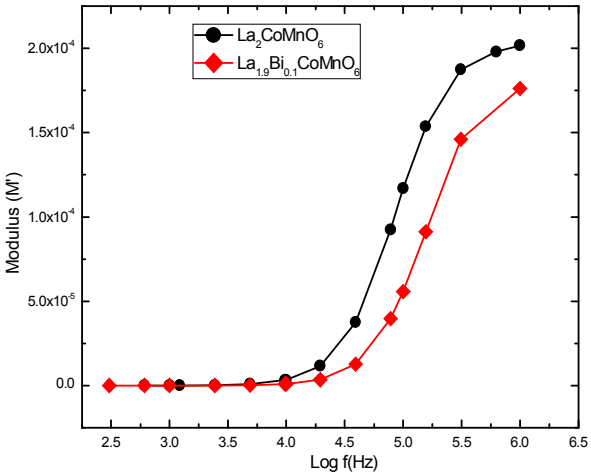

FIGURE 5. Electric modulus (M′)of $La_{2-x}Bi_xCoMnO_6$ [x =0, 0.1] vs Log f(Hz) double perovskites

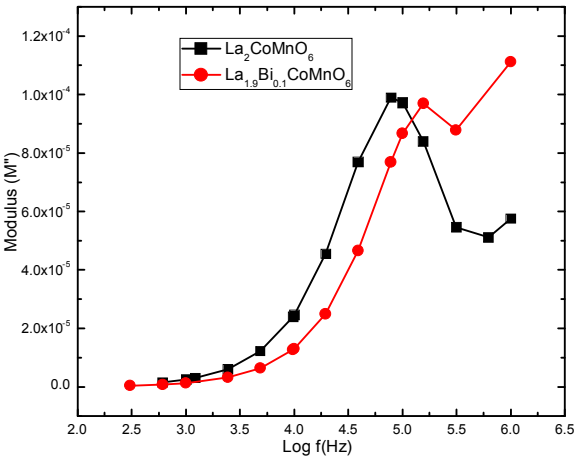

FIGURE 6. Electric modulus (M″)of $La_{2-x}Bi_xCoMnO_6$ [x =0, 0.1] vs Log f(Hz)

The imaginary part of electric modulus (M″) vs Log f(Hz) has been shown in Figure 6. The plots reveal appearance of the peak at higher frequency region which indicates that the material exhibits relaxation character. In the Figure 6, side to the low frequency region of peak shows the ion hopping over long ranges whereas frequency region to the higher frequency side of the peak reveals that the ions within the potential wells have localized motion only [9,12-14].

Conclusively, we synthesized,$La_{2-x}Bi_xCoMnO_6$ [x =0, 0.1] double perovskite in single phase. The crystallization of the synthesized samples in monoclinic ($P2_1/n$) structurewas conformed from XRD spectra analysis. The dielectric properties studies carried our conveyed their good dielectric nature though the loss values seem to be addressed. The modulus studies revealed the as prepared samples possess relaxation character.

ACKNOWLEDGEMENTS

UGC-DAE-CSR, as an institute is acknowledged for providing characterization facilities. Authors are thankful to Dr. V. Ganeshan, Dr. M. Gupta for XRD characterization, Dr. A. M. Awasthifor dielectric measurements. Mr S. Bharadwaj is highly acknowledged for his guidance and fruitful discussions.

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