Temperature Dependent Elastic and Ultrasonic Properties of $La_{0.8}Na_{0.2}MnO_3$perovskite Manganite Material

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Abstract – Ultrasonicvelocity and attenuation measurement is a versatile tool to explore the mechanical properties as well as the phase transition in the perovskite solids. $La_{0.8}Na_{0.2}MnO_3$perovskite manganite sample was prepared employing solid state reaction technique. The rhombohedral structure with R3c space group existing in the prepared samples was confirmed from the obtained X-ray diffractionspectra. In-situ ultrasonic velocity and attenuation measurements were carried out in the range of temperature from 300 to 400K. The observed anomalous behaviour in the ultrasonic parameters and elastic constants were used to explore ferromagnetic (FM) to paramagnetic (PM) phase transition temperature.

Keywords – Manganite, Ultrasonic velocity, phase transition

I. INTRODUCTION

Perovskite manganites, with a general formula $R_{1-x}A_xMnO_3$ where R and Aare trivalent rare earth and alkaline elements respectively, have been recently become a subject of intense investigation in view of their unusual electrical, mechanical and magnetic properties. They show rich phase illustrationdue to the competition among interactions involving the spin, lattice and charge degrees of freedom [1-2]. Because of their special properties such as colossal magneto resistance (CMR), metal-insulator (MI) transition, paramagnetic (PM) to ferromagnetic (FM), antiferromagnetic (AFM) phase transition, they find a wide range of applications in frequency switching devices, magneto storage devices, sensor technology etc which are useful in bio-medical and electronic industries [1]. Measurement of elastic constants using ultrasonic waves is a very sensitive tool to study different types of phase transition like ferromagnetic and structural ones, as they are lattice related properties. These techniques are found to be successful in studying electron-phonon coupling and spin-phonon coupling in manganites [2-3]. The transition temperature (T_C)that separates FM metallic state and paramagnetic PM/AFM insulating state depends on the concentration of rare earth and alkaline earth elements [4].

Survey of the literature reveals that most of the studies carried out in divalent alkaline elements such as calcium and strontium as doping material [5]. In fact the donor property is much pronounced in monovalent alkali elements than divalent alkaline elements like calcium, strontium etc. So one can expect perovskite manganite materials doped with monovalent elements to show distinguishing feature in their structural, electronic and magnetic properties from the ones doped with divalent alkaline elements like sodium, potassium etc [6]. But only a small quantum ofwork has been done with monovalent alkaline earth elements like sodium, lithium, potassium etc [6]. Substitution of lanthanum ions by monovalent potassium ions increases the ionic radius of the La site which produces crystallographic distortion and an increase in the Mn-O-Mn bond angle. As this increase in bond angle is associated with the shortening of Mn-O distance it leads to a stronger double exchange (DE) interaction and an increase the Curie temperature T_C[6].As no work has been reported employing ultrasonic measurements on sodium doped perovskite manganites an attempt has been made to investigate the temperature variation of elastic behavior of $La_{0.8}Na_{0.2}MnO_3$perovskite manganite samples by means of ultrasonic studies employing through transmission technique.

II. MATERIALS AND METHODS

A. Sample preparation

$La_{0.8}Na_{0.2}MnO_3$perovskitemanganite material sample was prepared employing solid state reaction technique. Pure grade manganese carbonate (99.99%; Sigma Aldrich), lanthanum nitrate (99.99%; Sigma Aldrich) and sodium nitrate (99.0%; Himedia GR, India) powders were taken in stoichiometric quantity and weighed in a digital balance. Then, the powders mixed in an agate mortar. The mixture was calcinated two times at 873K in air for 2h and further ground to obtain a homogeneous mixture. Once again the mixture was calcinated at 873K in air for 2h and then the obtained powder was pressed into pellets of diameter 12 mm and thickness 4 mm with a stainless steel dye. The pellets were sintered at 1373K for 12h in the atmospheric air. Thus the sample was prepared in the form of pellets. These pellets were used for further characterization.

B. X–Ray Diffractometry

The X-Ray diffraction (XRD) patterns of the prepared $La_{0.8}Na_{0.2}MnO_3$sample was obtained using powder X- Ray diffractometer (X'PertPro, Analytical, Netherland) at a scan range of 10 – 80^o with an increment

of 0.02^0 using Cu K_α as the radiation source with an operating voltage of 45 kV and a current rating of 35 mA. The crystalline size (D) of the sample was determined from full width at half maximum (β) and angle of diffraction (2θ) of the XRD peaks using Scherrer equation:

$$D = \frac{0.94\lambda}{\beta \text{Cos } \theta} \quad (1)$$

Where λ is the wavelength of the source used in x ray radiation.

C. Density measurement

The density of the sample was measured employing Archimedes principle using CCl_4 as a buoyant. The weight of the sample in air and buoyant, $W_a$and W_b respectively were measured using a digital balance (Sartorius, Germany). The density of the sample was obtained using the formula,

$$\rho = \frac{W_a}{W_a - W_b}\rho_b \quad (2)$$

where ρ_b is the density of the buoyant.The experiment was repeated for five times and then the average value was taken as the density of the sample. The percentage error in the measurement of density was $\pm$ 0.05.

D. Microscopy

A scanning electron microscope (SEM) integrated with the energy dispersive analysis of X- rays (EDAX; JEOL, JED5300, Japan) spectrometer was used to obtain the images of the $La_{0.8}Na_{0.2}MnO_3$sample to explore the morphology, microstructure and the composition of the perovskite sample. The spectrometer was operated at an accelerating voltage of 30kV.

E. Ultrasonic measurement

A high-power ultrasonic pulse receiver (Olympus NDT, 5900PR, USA) was used for the transmission and reception of the ultrasonic signals. For recording the digital RF ultrasonic signals, a computer-in-built 1GHz digital storage oscilloscope (Lecroy, Wave Runner 104Mxi, USA) was used. To produce longitudinal and shear ultrasonic waves X and Y cut transducers operating at a fundamental frequency of 5MHz were used respectively. An indigenously designed experimental setup was used to measure the ultrasonic velocity andattenuation over a wide range of temperature starting from 300 to 400K with the help of a programmable temperature controller (Eurotherm, 2604, USA).The temperature required has been kept under the dynamic mode of operation. The error in temperature measurement was $\pm$ 1K. The ultrasonic velocities (U_L and U_S) of the perovskite samples were obtained using the equation

$$U = \frac{d}{\Delta t} \quad (3)$$

where d is the thickness of the sample in micron resolution and transit time $\Delta t = (t_2 - t_1)$ in of the time taken for the propagation of ultrasonic waves into the specimen which innano second resolution. It was obtained by measuring transit time $t_1$just with the buffer rods (without the sample) and transit time t_2 by placing the sample between the two buffer rods (with the sample). The overall accuracy in the measurement of velocity was $\pm$ 2 m s^{-1}. The amplitudes of the first and second back wall echoes in the time domain trace were measured to obtain attenuation coefficient as follows

$$\alpha(f) = \frac{1}{d}\left(1nT + 1n\left(\frac{A_w(f)}{A_s(f)}\right)\right) \quad (4)$$

where As(f) is the amplitude of the received signal with sample andA_w(f) the amplitude of the received signal without sample.

$$T = \frac{4Z_w Z_s}{(Z_w + Z_s)^2} \quad (5)$$

where Tis the transmission coefficients of the sample-wave guide interface, Z_w and $Z_s$are the acoustic impedance of the wave guide and the sample respectively. The percentage error in the attenuation measurement is ±2.Elastic constants such as bulk (K) and Young's (E) modulus were obtained using following relations.

$$K = L - (4/3)\,G \quad (6)$$

Poisson's ratio

$$\sigma = \frac{L - 2G}{2(L - G)} \quad (7)$$

and

$$E = (1 + \sigma)\,2G \quad (8)$$

III Result and discussion

The XRD pattern (shown in Fig. 1) of the $La_{0.8}Na_{0.2}MnO_3$ perovskite manganite sample confirms the crystalline nature of the sample. The observed sharp peaks in the XRD pattern indicate that they are in close agreement with the samples of similar composition with JCPDS files 89-8122 and 89-8028. From this it is observed that the samples have rhombohedralstructure with R3c space group.

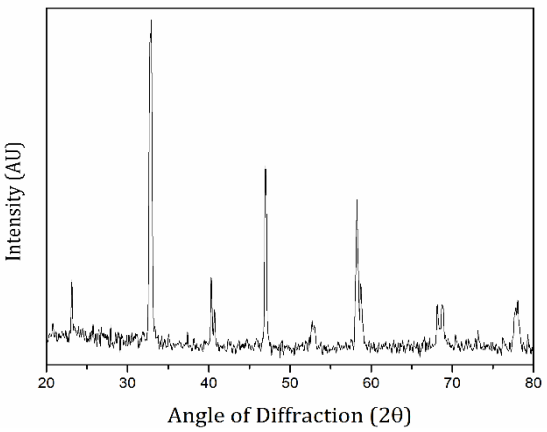

Fig. 1 XRD spectrum of $La_{0.8}Na_{0.2}MnO_3$ sample

The crystallite size of the sample is obtained usingScherrer formula from the obtained diffraction angle (2θ) and full width half maximum(FWHM) of the peaks. The crystallite size of the sample is 29.85 nm.The elemental composition of the constituents of the prepared perovskite manganite $La_{0.8}Na_{0.2}MnO_3$sample was confirmed by the obtained energy dispersive X-ray analysis (EDX) pattern.The SEM image of the prepared sample is shown in Fig. 2. It is inferred that the prepared sample has spherical like particle morphology. The particle size from the SEM image of the sample is found to be 120 nm.

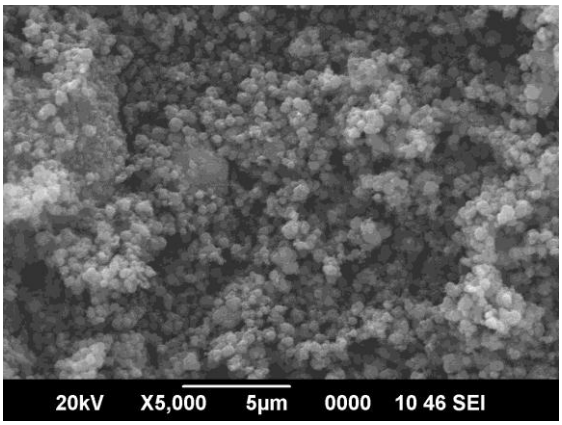

Fig. 2 SEM image of $La_{0.8}Na_{0.2}MnO_3$ sample

The longitudinal velocity (U_L),shear velocity (U_S), longitudinal attenuation (α_L) and shear attenuation (α_S)of the ultrasonic waves were measured over the range of temperature from 300 to 400 K. These measurements were used as an effective tool to obtain the temperature dependent mechanical property of the solids.Using the measured density (ρ = 5457 kgm^{-3}) and ultrasonic velocities(both U_L and U_S), the bulk modulus (K) the Young's modulus (E) were obtained. The bulk modulus and Young's modulus for the sample are 107.15 and 117.99GPa respectively at the room temperature (300 K).

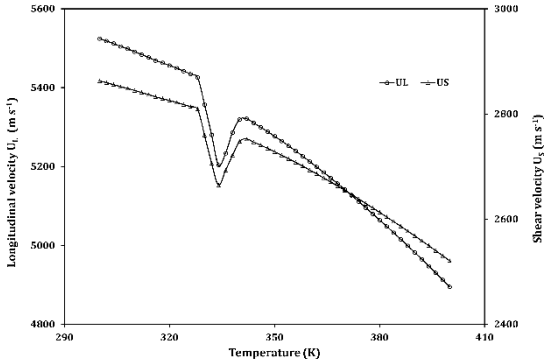

Fig. 3 Variation of longitudinal (U_L) and shear (U_S) velocities with temperature in $La_{0.8}Na_{0.2}MnO_3$ sample

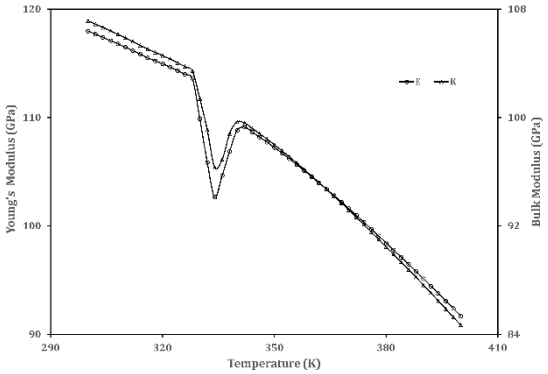

Fig. 4Variation of Bulk (K) and Young's (E) moduli with temperature in $La_{0.8}Na_{0.2}MnO_3$ sample

The temperature dependence of U_L and U_S are shown in Fig. 3 and that of elastic constants are depicted in Fig.4.From Fig. 3and 4, it is observed in the temperature range 300 to 328 K (region I) and from 342 to 400 K (region III) that the ultrasonic velocity and the elastic constants of the sample are monotonically decreases with an increase in temperature. As like in any other solid material,these parameters (U_L, U_S,K and E) decreasemonotonically with an increase in temperature. However, an anomalous behaviourin ultrasonic parameters is observed over atemperature region from 328 to 342 K (region II).There is a sharp decline in both velocity (U_L andU_S)andelastic constants(K and E) that reaches a minimum at the temperature 334 K followed by a sharp rise up to 342 K. Hence, in this regionof the Figs 2-3 areconsiderable importance and it reveals the physical significance of the prepared perovskite manganite sample.

As observed in the measurements using super conducting quantum interference device magnetometer in the study carried out by Xuebin, Yuping Sun et.al, Curie temperature (T_c), the temperature at which a transition takes place from FM to PM state is 333 K for the perovskite material $La_{0.8}Na_{0.2}MnO_3$[7]. Similar observations were also made for the perovskite materials doped with monovalent element potassium [8]. Correlating the above results with the ones observed in this investigation, it is confirmed that the temperature at which U_L, U_S, K and Eare minimum in the anomalous region (334 K)is the Curie temperature (T_C) of the prepared perovskites sample. Thus, the anomalous temperature (334 K) of the ultrasonic parameter is identified as a T_C of the prepared $La_{0.8}Na_{0.2}MnO_3$ perovskite manganite.

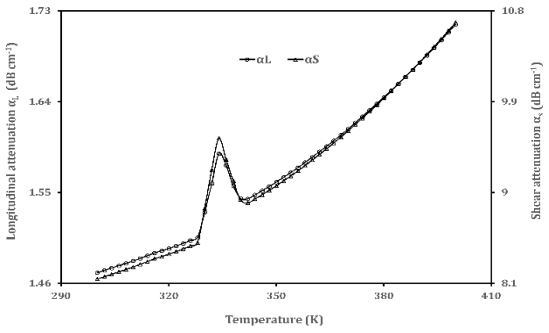

Fig. 5Variation of longitudinal (α_L) and shear (α_S) attenuations with temperature in $La_{0.8}Na_{0.2}MnO_3$ sample

The longitudinal and shear attenuation of ultrasonic waves as a function of temperature is shown in Fig. 5. The attenuation increases as the temperature increases in region I and region III. As like in Fig. 3 and 4, the sample shows an anomalous behavior in region II. At the temperature 328 K the value of α_L and α_S increase steeply and reach a maximum of 1.589and 9.537 $dBcm^{-1}$respectively at 334 K then falls sharply up to 342 K. The occurrence of magneton, electron and lattice ordering features implies strong spin-phonon coupling and electron-phonon coupling known to exist for the rhombohedral coordinated d^4 ion originating in the Jahn-Teller (JT) effect is the reason for such a peak [9]. The Curie temperature of the undoped $LaMnO_3$ material is only 130 K [10] whereas the doping of 20% of sodium makes it as large as 334 K. This fact is attributed to the increase in DE interaction caused by the reduction in Mn-O distance that takes place. This is due to the increase in average ionic radius of La^{3+} (r_{ion}= 1.36A° for CN=12) site produced by the doping of monovalent Na^{1+} (r_{ion}= 1.39A° for CN=12) in the perovskite manganite [11]. Further the coexistence of anomalous behavior in both longitudinal and shear mode in velocity and attenuation confirms the existed electron-phonon interaction in the sample. Also the increase in velocity and the decrease in attenuation of the ultrasonic waves in the sample below $T_C$reveal the occurrence of lattice hardening below the Curie temperature

IV. Conclusion

Perovskite manganite $La_{0.8}Na_{0.2}MnO_3$sample was prepared employing solid state technique. Crystalline nature of the sample was confirmed by the obtained XRD. In- situ ultrasonic measurements of velocity and attenuation were carried out on the prepared sample in the temperature range from 300 to 400 K. Bulk and Young's modulus of the sample were determined using the standard formula. The temperature dependence of the ultrasonic parameters as well as the elastic constantswas used to explore the phase transition in the sample. The results of the investigation show that the doping of sodium causes the increase in the phase transition temperature T_C.The electron-phonon interaction in the sample is ascertained by the anomalous behavior obtained in both longitudinal and shear modes. Further the lattice hardening below T_C is confirmed by the increase in velocity and the decrease in attenuation.As the phase transition temperature T_C is neighboring the room temperature $La_{0.8}Na_{0.2}MnO_3$samples may be used for potential applications.

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