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Non-destructive characterisation of Ni doped $La_{0.7}Sr_{0.3}MnO_3$Perovskite manganites

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Abstract: In-situ ultrasonic measurements on $La_{0.7}Sr_{0.3}Mn_{1-x}Ni_xO_3$ perovskite manganite material (x = 0.0 and 0.02) have been carried out on the samples synthesized by solid state reaction technique. The X–ray diffraction patterns show that the samples have single phase rhombohedral structure. The temperature dependent ultrasonic longitudinal and shear velocity measurement on the samples was used to reveal the phase transition temperature i.e., Ferro to Para magnetic phase transition temperature (T_C).The ultrasonic measurementsalso confirm that the Ni doping in $La_{0.7}Sr_{0.3}Mn_{1-x}Ni_xO_3$ perovskites lead to a decrease in T_C. The replacement of Mn^{4+} ions by Ni^{2+} ions caused the change in the structural parameters, the constitution of Mn^{3+} and Mn^{4+} ions and makes the AFM phase stronger in the samples.
Keywords :–Perovskite manganite; Ultrasonic velocity; Phase transition.

Introduction and Experimental:

The studies on ABO_3 perovskite manganite materials give vital results through the doping of rare earth ions or alkaline earth ions at A site [1-2]. The change in A site ions leads to the distorted lattice structure and destroy the uniformity of the distance in Mn-O plane and the angle between Mn^{3+}-O-Mn^{4+}. It is observed that the metal-semiconductor transition and FM coupling are very sensitive to these changes [3-4].$LaMnO_3$ is an antiferromagnetic (AFM) insulator. When doping with divalent elements it gives rise to rich electric and magnetic properties like AFM insulating, FM insulating, PM insulating and FM metallic [3]. Doping of Sr in the place of La leads to a change from AFM insulating ground state to FM metallic state due to the increase in number of holes due to the conversion of trivalent Mn^{3+} into tetravalent Mn^{4+} [3]. The double exchange (DE) interaction gives rise to the ferromagnetism and metallic behavior in this compound [4].

Much attention has been given to the replacement of Mn siteby magnetic and non-magnetic ions to explore the information about the structural, magnetic and electric properties. The doping of Ni on $La_{0.7}Sr_{0.3}MnO_3$magneticmaterials show a change in the Mn^{3+}-O-Mn^{4+} bond and destroy the DE interaction causing an increase in the resistivity [5]. The ultrasonic measurements of longitudinal and shear velocity are used to study the phase transition, structure/ lattice then to correlatewith the perovskite magnetic properties. The ultrasonic measurements are used to obtain the phase transitions and correlate the differences between AFM, FM and PM phase physical properties of these perovskite manganites [6].

In the present study, the magnetic ion Ni of composition x =0 and 0.02 are substituted in the Mn site of the perovskite sample $La_{0.7}Sr_{0.3}MnO_3$. The samples Ni0 and Ni2 have been prepared using solid state reaction route. In order to confirm the crystalline nature, the XRD patterns of the prepared samples were obtained using powder X-Ray diffractometer (X'PERT PRO PANalytical, the Netherland). A fundamental frequency of 5 MHz is used to measure the longitudinal ultrasonic velocity (U_L) and shear ultrasonic velocity (U_S). The measurements have been carried out in the temperature range from 300 to 400 K at an accuracy of $\pm$ 1 K [7].

Result and Discussion:

The XRD patterns (shown in Fig.1) of the samples Ni0 and Ni2 confirm the crystalline nature of the samples and show that the samples have rhombohedral structure with R3C space groupand have no secondary phases. The observed sharp peaks in the XRD patterns indicate that they are in close agreement with the samples of JCPDS file No. 51-0409.The temperature dependence of U_L and $U_S$is shown in Fig. 2. The graphs shown in these figures have three different regions which were represented in Table 1.

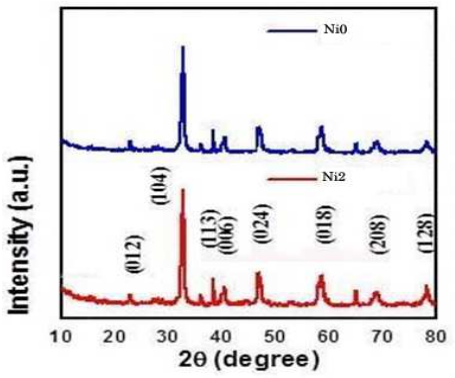

Fig.1. X-Ray diffraction pattern of Ni0 and Ni2 samples

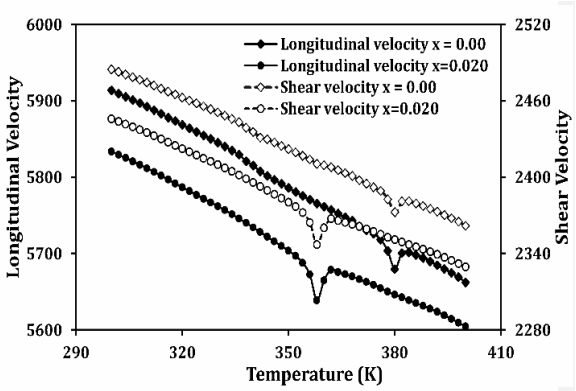

Fig.2. Temperature dependence of longitudinal (U_L) and shear (U_S) velocities of Ni0 and Ni2 samples

Table 1 Different temperature regions of Ni0 and Ni2 samples

Sample		Ni0	Ni2
Region	I	300 -376	300-354
	II	376-384	354-362
	Anomaly	380	358
	III	384-400	362-400
Transition Width (ΔT)		8	8
Width (ΔU_L) (m/sec)		31	44.5
Width (ΔU_S) (m/sec)		12	23

From Fig.2; it is observed thatU_L and U_S for the sample Ni0 region I and III occur from 300 to 376 and from 384 to 400 respectively. As in any other solid material, the values of U_L and U_S decrease monotonically with an increase in temperature in the regions I and III. However, an anomalous behaviour is observed in the region II that occurs between 376 and 384 for the sample Ni0.In this region, there is sharp decline in velocities that reach the temperature380 K followed by a sharp rise up to 384 K. Hence region II in the Fig.2 is of considerable importance as it reveals an anomalous behaviour in the variation in velocities with the

temperature. The temperatures at which the velocity is minimum in the anomalous region are 380 and 358 K for the samples Ni0 and Ni2 respectively. From the earlier phase transition studies [7], it is confirmed that the minimum temperature at which the anomaly in velocity takes place is the Curie temperature (T_C) of the perovskitesample.

The decrease in $T_C$shown in Table 1 from 380 to 358 K due to the doping Ni is attributed to the weakening of DE interaction and the ferromagnetism is suppressed and destroys the ratio of Mn^{3+}-O-Mn^{4+} bonds. This is ascribed to the increase inAFM interaction pairs Mn^{4+}- Mn^{4+}, Ni^{2+}- Mn^{4+}, Ni^{2+}-Mn^{3+}, Ni^{2+}-Ni^{2+}due to the increase in Mn^{4+} caused by the substitution of Ni^{2+}[8-9].The increase in acoustical energy $E_P$due to the doping of Ni content in the perovskite samples is confirmed by the observed decrease in ultrasonic velocity and an increase in attenuation according to Arrhenius relation as reported elsewhere [10]. The increase in transition height due to the doping of Ni content in the perovskite samples indicates that the linear magnetostriction effect increases. As a result, the spin-phonon interaction increases with the linear magnetostrictioneffectwhich in turn reduces the phase transition temperature T_C.The increase in width of transition in velocity with an increase in Ni content confirms that an AFM phase is stronger than FM phase which is due to super exchange interactionpairs [8].

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