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Effect of Rare Earth Ions on Transition Temperature in Perovskite Materials by On-Line Ultrasonic Studies

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On-line measurements of ultrasonic longitudinal velocity, shear velocity and longitudinal attenuation were carried out on $R_{1-x}Sr_xMnO_3$ perovskites (R = La, Pr, Nd and Sm) for different compositions of Sr, at a fundamental frequency of 5 MHz over wide range of temperatures using the through-transmission method. The observed maxima/minima in velocities and attenuation have been discussed with decrease in ionic radii and composition. As a decrease in the ionic radii of rare earth elements leads to a decrease in transition temperature (T_c), the results that are observed show that measurement is one of the best tools to explore the structural/phase transition on-line velocity in perovskite manganese materials as a function of the ionic radii of rare earth elements.

Keywords: *perovskite, magnetic materials*

1. Introduction

$R_{1-x}Sr_xMnO_3$ (where R is a rare earth element such as La, Nd, Sm, Pd) perovskite manganites have been a subject of interest due to their exotic properties and phenomena like colossal magnetoresistance (CMR)[1-3]. It exhibits a very rich phase diagram due to the subtle competition among the interactions involving the spin, lattice and charge degrees of freedom[1]. The modest variation in the dopant concentration, preparation methods, cation deficiency etc., can cause profound changes in their magnetic states i.e., ferromagnetic (FM) and antiferromagnetic (AFM)[4]. The transport properties like dirty metal, insulator, semiconductor, polaron hopping and the structural characteristics such as Jahn-Teller induced strains and orthorhombic to rhombohedral transformation depends on dopant and its concentrations[5-6].

The phase transition temperature (T_C) which separates FM metallic state from paramagnetic (PM)/AFM insulating states depends on the concentration of rare earth and alkaline elements[6]. Further, the substitution on dopant results in the CMR effect several times larger than pristine manganite. It is evident that the absence of unpaired electrons on the doped Mn sites which break the hole propagation in the manganese oxygen lattice as the doping content increases, and consequently leads to a decrease in T_C[7-8]. The small difference between the different substitutions may be due to the combined effects of size and valence of the dopant. The substitution of trivalent by divalent element leads to the replacement of Mn^{3+} ions by Mn^{4+} sites[9]. The doping of rare earth ions on Mn sites with unchangeable tetravalent element inevitably weakens the double exchange (DE) interactions in Mn^{3+}-O-Mn^{4+} co-valent structures. Hence, it is expected that the electrical/magnetic properties and the CMR effect of the perovskite manganite material are more sensitive due to the substitution of the dopant element[10]. The interactions between Mn^{3+} and Mn^{4+} ions play a vital role in the determination of the phase transition of manganite perovskites. The DE interactions between Mn^{3+} and Mn^{4+} ions are also affected by the influence of ionic radius of trivalent elements (rare earth elements) and tetravalent elements (Mn sites)[11].

Rare earth oxides such as La, Sm, Pr and Nd are one of the most important additives in $SrMnO_3$ based perovskites for sensor applications[12-13]. The various attempts[14-17] have been focused on perovskites doped with various rare earth elements. Even though, it is necessary to investigate the correlation between the phase transition temperature and with ionic radius of the rare earth elements. The structural changes in the substitution of rare earth element in $SrMnO_3$ perovskite manganite materials are well reflected in the density/modulus and hence, these changes are well reflected in the measured ultrasonic velocities. The excellent property of the ultrasonic waves makes it to gain knowledge about the origin of the metal-insulator transition, structural changes, phase transitions and magnetostriction effects. The importance of ionic radii in addition to the change in composition of Sr has been studied extensively employing resistivity[17], conductivity[18], Mossbauer[19] and magnetic[20] studies.

Even though, different techniques are known in exist to explore structural/phase transition temperatures in perovskites manganite materials, on-line ultrasonic measurement is important tool due to their precise on-line evaluation of structural/phase transitions, non-destructive method of measurement, accurate and reproducibility of results than any other experimental methods[21]. It is inferred from the literature that no attempts have been made to

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compare the T_c using ultrasonic studies by changing the R and x values.

In the present investigation, a systematic study has been made on ultrasonic longitudinal velocity (U_L), shear velocity (U_s) and longitudinal attenuation (α_L) in $R_{1-x}Sr_xMnO_3$ perovskites manganite materials for different Sr contents over wide range of temperatures. The observed anomalous behaviour in ultrasonic velocities and attenuation are discussed with the phenomenon such as phase transition, CMR and GMR effects with the change in ionic radius of rare earth elements and Sr content.

2. Experimental

2.1. *Sample preparation*

$La_{1-x}Sr_xMnO_3$ (LSMO; x = 0.28, 0.31 and 0.36), $Pr_{1-x}Sr_xMnO_3$ (PSMO; x = 0.28, 0.33, 0.35, 0.38 and 0.41), $Nd_{1-x}Sr_xMnO_3$ (NSMO; x = 0.31, 0.35, 0.37, 0.39 and 0.41) and $Sm_{1-x}Sr_xMnO_3$ (SSMO; x = 0.25, 0.30, 0.37, 0.40 and 0.44) perovskite samples were prepared using a solid-state reaction technique22-25]. The measurement of U_L, U_s and α_L was made over a wide range of temperatures as described elsewhere[22-25].

2.2. *Ultrasonic velocity measurements*

Ultrasonic velocities were measured using a high-power ultrasonic process control system (FUI1050; Fallon Ultrasonics Inc., Canada), a 100 MHz DSO (54600B; HP, USA) and a PC as discussed in our earlier studies[22].

2.3. *Attenuation measurements*

The attenuation coefficient was calculated by measuring the amplitude of received pulses with waveguides ($A_w(f)$) and waveguides with sample ($A_s(f)$), using the following relation[22]:

$$\alpha(f)=\frac{1}{d}\left[InT+In\left(\frac{A_w(f)}{A_s(f)}\right)\right] \qquad (1)$$

3. Results and Discussion

The T_c values of each composition in all the perovskites were obtained from the observed maxima/minima in U_L, U_s and α_L. The composition- and ionic radii-dependent T_c values are shown in Figure 1. The observed prominent peaks in U_L and U_s for all perovskites with different compositions have been obtained from the measured velocities[22-25]. The T_c values obtained from the magnitude of U_L and U_s in all perovskites and compositions are shown in Figures 2 and 3 respectively. The maxima/minima values in velocities that are observed are mainly because of the occurrence of lattice softening, that is, the contributed effects of lattice softening above T_c and lattice hardening below T_c[23,26]. Similarly, the attenuation maxima/minima in all perovskites at the respective T_c value that are observed have been identified. The maxima/minima α_L as a function of perovskites and their composition are shown in Figure 4. The T_c in all perovskites that is observed shows the existence of competition among the PM, FM and AFM phases[21,24,26]. The values of ionic radii for rare earth elements, La, Pr, Nd and Sm, are 1.172, 1.13, 1.123 and 1.098 Å respectively.

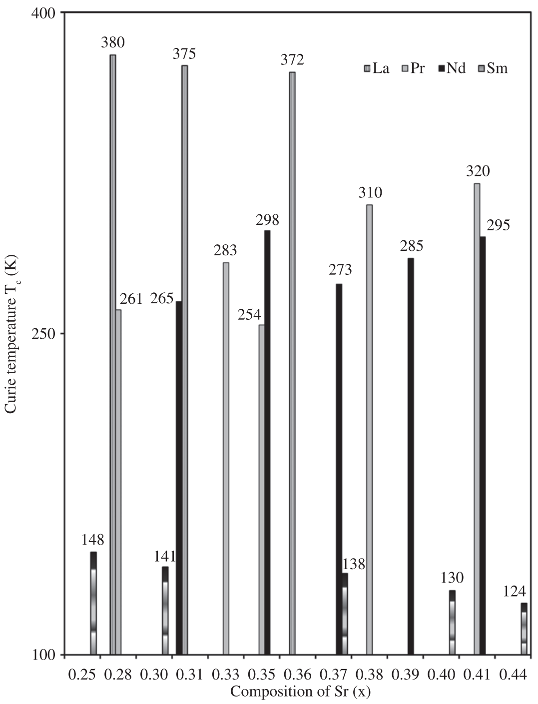

Figure 1. Variation of Curie temperature as a function of composition.

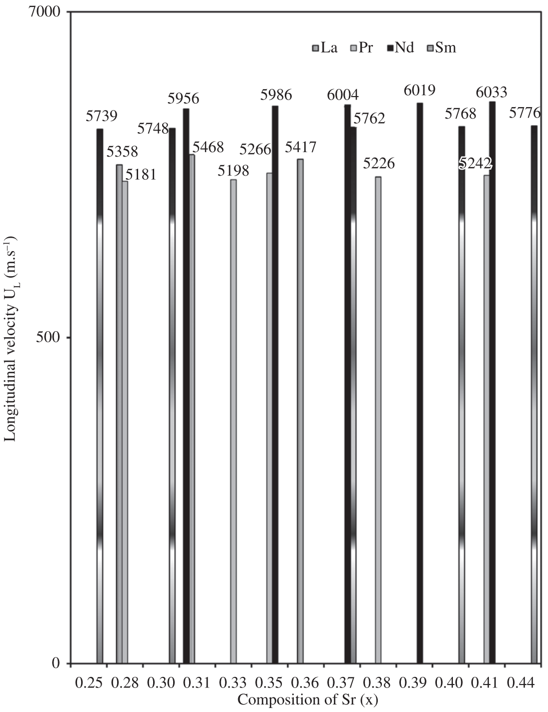

Figure 2. Variation of longitudinal velocity as a function of composition.

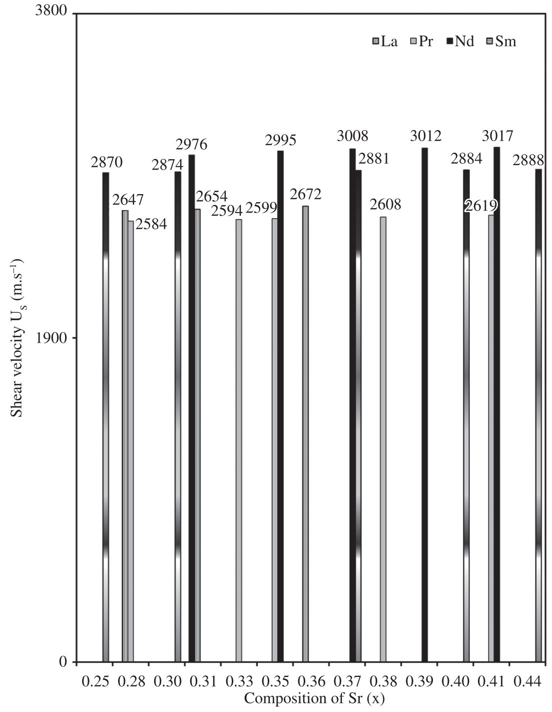

Figure 3. Variation of shear velocity of as a function of composition.

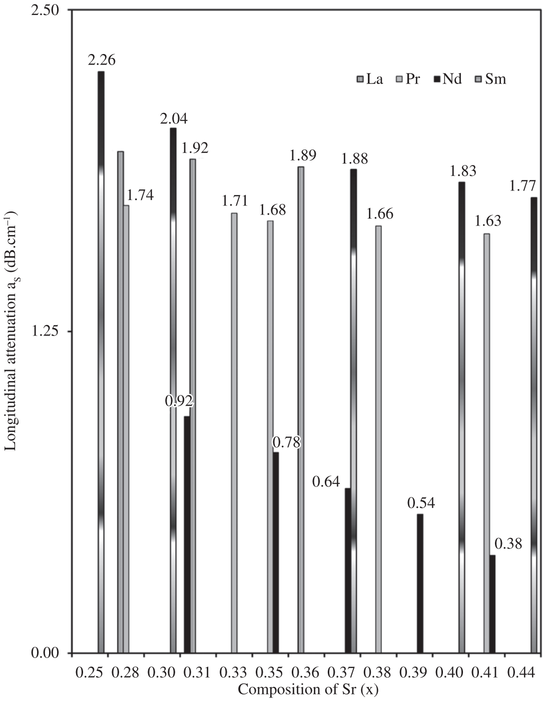

Figure 4. Variation of attenuation of as a function of composition.

Figure 1 shows that T_c values strongly depend on the ionic radii of rare earth elements. For example, at a fixed composition of Sr, say $x = 0.28$ in case of $La_{1-x}Sr_xMnO_3$ and $Pr_{1-x}Sr_xMnO_3$ perovskites, the replacement of the rare earth element, La, by Pr reduces the T_c value from 380 to 261 K. Similarly, for $x = 0.35$, the replacement of Pr by Nd ($Nd_{1-x}Sr_xMnO_3$) leads to a reduction in T_c from 298 to 254 K as discussed above. It is further evident that if one considers the replacement of Nd by Sm ($Sm_{1-x}Sr_xMnO_3$) for the composition, $x = 0.37$, the value of T_c decreases from 273 to 138 K. A detailed discussion of the basic properties of rare earth oxides supports the above observation[27]. It is clear that the basic strength of rare earth oxides is attributed to lanthanide contraction, that is, the strength of the basic sites decreases with a decrease in the ionic radii of rare earth elements. It is inferred from above observations that the transition temperature T_C decreases with decrease in ionic radii of rare earth elements.

The ultrasonic parameters cannot directly correlate with ionic radius of the rare earth element; rather it depends on the structural compactness of sample which is influenced by various factors like preparation method[28], sintering temperature[29] and particle size[30]. However, attempts have been made to reveal the ultrasonic behaviour of rare earth element[31-32] and found that a decrease in ultrasonic velocities with an increase in ionic radii.

It is known that the perovskite structure is distorted with a decrease in the ionic radii of rare earth elements. The distortion of the perovskite-type structure causes a decrease in electrical and thermal conductivities[33]. The variation of T_c as a function of the average size of A-site cations (Ln and Sr) has been observed in $Ln_{0.5}Sr_{0.5}MnO_3$ (Ln = La, Pr, Y, Sm and Gd)[33]. It is interesting to note that a decrease in T_c value from 310 to 85 K corresponds to a decrease in ionic radius from 1.263 to 1.221 Å. Further, the ionic radii of the R ions are used to know the state of perovskites, that is, PM or AFM states[34]. On the basis of the above studies, it is concluded that a decrease in the T_c value, which is obtained from the maxima/minima that are observed in the ultrasonic parameters, strongly supports the results obtained from resistivity, electrical, Mossbauer and magnetic property studies[16,17,19,22-25].

4. Conclusions

On-line ultrasonic velocity measurement as a function of temperature determines the T_c in perovskites. T_c that is observed with a decrease in the ionic radii of the rare earth elements decreases as observed by other studies such as conductivity. Thus, it is concluded that an on-line ultrasonic velocity/attenuation measurement is one of the best tools to explore the structural/phase transition in perovskites as a function of the ionic radii of rare earth elements.

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