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Elastic properties of double layered manganite $La_{1.2}Sr_{1.8-x}Ca_xMn_2O_7$ (x = 0.0–0.4)

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Polycrystalline bulk samples of double layered manganite system $La_{1.2}Sr_{1.8-x}Ca_xMn_2O_7$ (x = 0.0–0.4) have been synthesized by the sol-gel method. Based on powder X-ray diffraction, it has been found that their lattice parameters decrease with increasing Ca content. The elastic behaviour of the system has been investigated at ~300 K employing ultrasonic pulse transmission technique at 1 MHz. The values of elastic moduli and acoustic Debye temperatures have been computed from the longitudinal and shear wave velocities. The measured values of elastic moduli have been corrected to zero porosity using various correction methods. The variation of elastic moduli with Ca content is interpreted in terms of the strength of interatomic bonding.

Key words: *manganite; CMR; elastic properties; porosity*

1. Introduction

During the past decade, there has been upsurge in the study of various manganites due to colossal magnetoresistance (CMR) phenomenon exhibited by these compounds. Recently, CMR effect has been observed in the n = 2 member of the Ruddlesden–Popper (RP) series of manganites $La_{1.2}Sr_{1.8-x}Ca_xMn_2O_7$ [1, 2]. From the fundamental research point of view, the elastic constants are important to elucidate the nature of binding forces and to understand thermal properties like the specific heat or Debye temperature of a solid. When one thinks about the application of any polycrystalline material, although much attention is paid to the 'primary' material property for a given application, mechanical properties are of critical importance in the incorporation of the material into a functional device. On the other hand, it is known that elastic modulus is

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a function of temperature, thus room temperature measurements give an idea about the minimum strength of the material.

Until now, the measurements of mechanical properties of manganites have not received much attention. In the past five years, a few reports have been available on some measurements of these properties [3–7]. Of course, these reports deal with La-based cubic perovskites. To our knowledge, no work has been reported on elastic behaviour of double layered manganites.

In this paper, we report on the values of elastic constants and acoustic Debye temperatures of $La_{1.2}Sr_{1.8-x}Ca_xMn_2O_7$ (x = 0.0–0.4) system determined by ultrasonic pulse transmission technique at ~300 K. Obtaining information about the elastic behaviour of such compounds may greatly help in further studies of temperature dependences of the elastic constants of present and other double layered manganites and of their interplay with the magnetoresistance effect.

2. Experimental

$La_{1.2}Sr_{1.8-x}Ca_xMn_2O_7$ (x = 0.0–0.4) powders have been prepared by the sol-gel method [8]. High purity powders of La_2O_3, $MnCO_3$, $Sr(NO_3)_2$ and $Ca(NO_3)_2.4H_2O$, weighted in appropriate proportions, were used to obtain the nominal compositions of $La_{1.2}Sr_{1.8-x}Ca_xMn_2O_7$ (x = 0.0–0.4). La_2O_3 and $MnCO_3$ were converted into nitrates prior to use. All the nitrates were dissolved in citric acid solutions and then the pH was adjusted to ~6 with ammonia solution. After getting the water evaporated, ethylene glycol was added and heated at about 90 ºC until a gel-type solution was formed. The gel was dried at 150 ºC and then decomposed at 250 ºC in air for 2 h to decompose nitrates and all organic materials. The resultant ash was ground to get a fine homogeneous powder. The powder was calcined in air at 1100 ºC for 10 h and then pressed into circular pellets. The pellets were finally sintered in air at 1400 ºC for 6 h.

The structural characterization has been carried out by the powder X-ray diffraction technique employing X-pert pro system, M/S Panalytical, using CuK_α radiation. The X-ray density (ρ_x) values have been calculated from the corresponding lattice constants and the values of bulk densities (ρ) of the samples have been determined by the immersion method. Using the values of ρ_x and ρ, pore fraction (C) has been determined using the formula $C = 1 - \rho/\rho_x$.

The ultrasonic measurements have been carried out by the ultrasonic pulse transmission (UPT) technique at ~ 300 K, with a variation of $\pm$ 2 K [9]. X- and Y-cut quartz transducers, with a fundamental frequency of 1 MHz, have been used to transmit and receive the longitudinal and shear waves, respectively. The r.f. pulses generated by the pulse oscillator have been applied to the transmitting transducer, which converted them into acoustic pulses. The acoustic pulses, after propagating through the test sample, have been converted back into electrical signals by the receiving transducers. The amplified output signal has been displayed on a 100 MHz digital storage oscilloscope

(Tektronix model No.2221). The difference in time (ΔT) between two overlapping received pulse trains has been recorded using a timer. The velocity of sound has been measured using the equation $V = t/\Delta T$, where t is the thickness of the sample. The overall accuracy of these measurements was ± 10 m·s^{-1} which is about 1% in sound velocity and 2% in elastic moduli.

3. Results and discussion

The XRD patterns of $La_{1.2}Sr_{1.8-x}Ca_xMn_2O_7$ (x = 0.0–0.4), shown in Fig. 1, confirm the single phase formation of the samples. The samples have been indexed to the $Sr_3Ti_2O_7$ type structure with a tetragonal unit cell (space group: *I*4/*mmm*). It can be seen that the lattice constants (a and c) and cell volume (V) decrease as Ca content increases, which is due to the substitution of smaller Ca^{2+} ions (1.18 Å for the coordination number 9) for larger Sr^{2+} sites (1.31 Å for the coordination number 9) [10] (see Fig. 2).

Elastic constants and acoustic Debye temperatures (Table 1) have been calculated using the longitudinal (V_L) and shear (V_S) wave velocities (at ~300 K) obtained from UPT technique. For a polycrystalline ceramic sample, a standard isotropic elastic medium approximation applies. In the approximation, shear modulus $G = \rho V_S^2$, where ρ is the bulk density of the sample, bulk modulus $B = \rho V_L^2 - 4G/3$, Poisson's ratio $\sigma = (3B - 2G)/(6B + 2G)$ and Young's modulus $E = (1+\sigma)2G$ [9, 11]. The acoustic Debye temperature (θ_D) has been determined using the Anderson formula [12].

$$\theta_D = \frac{h}{k_B}\left(\frac{3\rho N_A q}{4\pi M}\right)V_m$$

where h is the Planck constant, k_B is the Boltzmann constant, ρ is the bulk density of the sample, N_A is the Avogadro number, q is the number of atoms in the unit formula (in the present case, q = 12), M is the molecular weight and V_m is the mean sound velocity given by

$$V_m = \left[\frac{1}{3}\left(\frac{1}{V_L^3} + \frac{2}{V_S^3}\right)\right]^{-1/3}$$

In general, the perovskite materials are porous and it is well known fact that porosity plays a key role in governing the elastic properties of materials. Hence, the measured elastic moduli have been corrected to zero porosity using the Hasselman –Fulrath (HF) [13] and Ledbetter–Datta (LD) formulae [14] (Table 2). The values of elastic moduli corrected to zero porosity using the two models are in good agreement and increase with increasing Ca concentration.

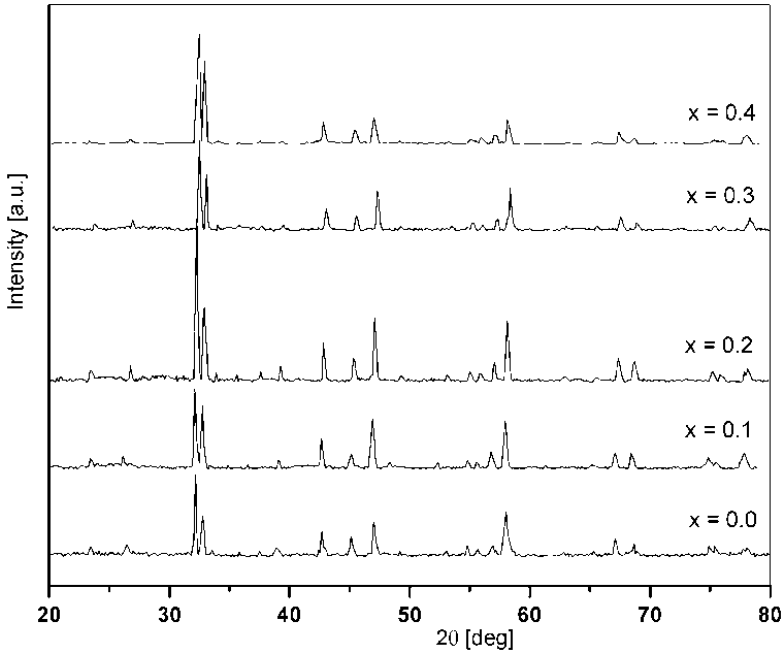

Fig. 1. XRD patterns of $La_{1.2}Sr_{1.8-x}Ca_xMn_2O_7$ (x = 0.0–0.4)

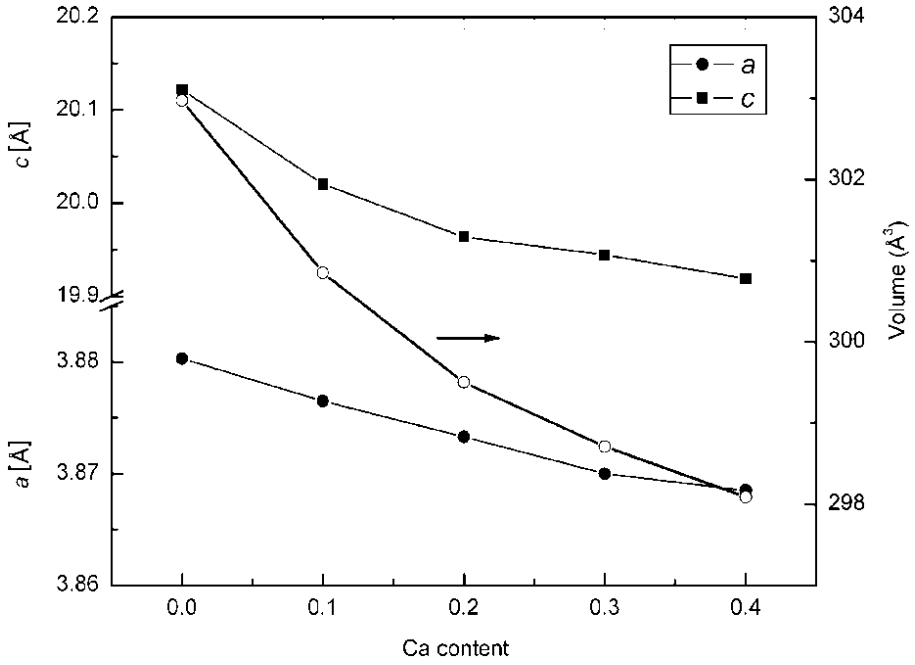

Fig. 2. Variation of lattice constants and cell volume with Ca content

Table 1. X-ray density (ρ_x), bulk density (ρ), pore fraction (C), longitudinal velocity (V_L), shear velocity (V_S), mean velocity (V_m), shear modulus (G), bulk modulus (B), Young's modulus (E), Poisson's ratio (σ) and acoustic Debye temperature(θ_D) of $La_{1.2}Sr_{1.8-x}Ca_xMn_2O_7$ (x = 0.0–0.4) system

x	ρ_x	ρ	C	V_L	V_S	V_m	G	B	E	σ	θ_D [K]
	[$\times 10^3$ kg/m^3]			[m/s]			[GPa]				
0.0	5.987	5.618	0.062	3860	2245	2491	28.31	45.97	70.47	0.244	311.7
0.1	5.977	5.599	0.063	3913	2275	2524	28.99	47.10	72.16	0.245	316.5
0.2	5.951	5.565	0.065	3967	2310	2562	29.69	48.00	73.84	0.244	321.55
0.3	5.914	5.490	0.072	4022	2345	2601	30.20	48.56	75.04	0.242	325.9
0.4	5.873	5.442	0.073	4079	2382	2642	30.88	49.39	76.66	0.241	331.0

Table 2. Elastic moduli corrected to zero porosity using HF and LD models and elastic moduli and acoustic Debye temperatures obtained from the MMM rule

x	Model	G_0 [GPa]	B_0 [GPa]	E_0 [GPa]	σ_0	θ_D [K]
0.0	HF	32.20	53.24	80.40	0.248	–
	LD	31.95	52.72	79.75	–	–
	MMMR	36.19	47.92	77.24	–	251.02
0.1	HF	33.09	54.78	82.62	0.249	–
	LD	32.81	54.21	81.92	–	–
	MMMR	36.21	47.99	77.44	–	252.66
0.2	HF	34.02	56.05	84.88	0.248	254.32
	LD	33.72	55.43	84.12	–	–
	MMMR	36.24	48.06	77.64	–	–
0.3	HF	35.14	57.67	87.62	0.247	–
	LD	34.76	56.90	86.65	–	–
	MMMR	36.26	48.13	77.84	–	255.98
0.4	HF	36.08	58.90	89.89	0.246	–
	LD	35.68	58.80	88.84	–	–
	MMMR	36.29	48.21	78.04	–	257.64

Recently, Modi et al. have developed a model, known as Modi's heterogeneous metal mixture rule (MMMR), to estimate the elastic constants of spinel ferrites [15], garnets [16], superconductors [17, 18] and La-based perovskites [9]. According to this model, the value of elastic constant or acoustic Debye temperature can be calculated from the following formula:

$$K^*_{pm} = \frac{1}{n} \sum_{i>0,\ n=1}^{\infty} C_{in} K_n$$

where K^*_{pm} is either the elastic modulus or acoustic Debye temperature of the composition to be estimated, n is the total number of metallic cations in the unit chemical formula (n = 5 in the present case), c_{in} is the concentration of the nth cation in the for-

mula unit, while K_n is the corresponding modulus or acoustic Debye temperature of the metallic element present in the system. The elastic moduli and acoustic Debye temperatures of the metallic elements are taken from the literature [19, 20] to estimate K^*_{pm}. The estimated values of elastic moduli and acoustic Debye temperatures using the MMM rule given in Table 2 are in good agreement with the values obtained from the UPT measurements.

The variation of elastic moduli with Ca content can be interpreted on the basis of the strength of interatomic bonding [21]. When larger Sr^{2+} ions (ionic radius – 1.31 Å) are replaced by smaller Ca^{2+} (ionic radius – 1.18 Å) ions, the length of the interatomic bonding decreases resulting in the increase of the strength of interatomic bonding, which in turn increases the magnitude of elastic moduli. The values of elastic moduli corrected to zero porosity and of porous materials show similar dependences on Ca concentration, which confirms the quality of the test samples and the validity of the method employed.

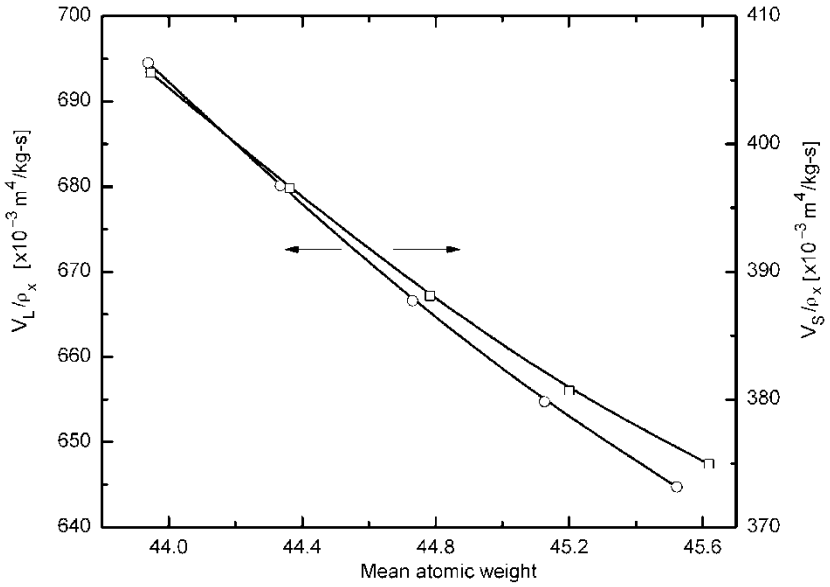

Fig. 3. Variation of V_L/ρ_x and V_S/ρ_x with the mean atomic weight (M/q)

The measured and corrected values of Poisson's ratios have been found to be in good agreement (Tables 1 and 2) and lie in the theoretical range from –1 to 0.5. Increasing Ca concentration results in the increase of the acoustic Debye temperature (Table 1) which suggests a hindrance in lattice vibrations with Ca substitution. This can be attributed to the increasing strength of interatomic bonding with increasing Ca content.

In the case of oxides having the same mean atomic weights (M/q) (M – molecular weight, q – number of atoms in a formula unit), it is proved that longitudinal and shear

wave velocities vary linearly with X-ray density [22, 23]. Hence, the variation in the mean atomic weight corresponds to the variation in the values of V_L/ρ_x and V_S/ρ_x because the product of M/q with V_L/ρ_x and V_S/ρ_x should be a constant [24, 25]. A similar behaviour can be seen from Fig. 3, thus establishing the fact that these materials behave like any other oxide materials described in the literature.

4. Conclusions

Based on the elastic constants determined by ultrasonic pulse transmission technique supported by heterogeneous metal mixture rule for $La_{1.2}Sr_{1-8-x}Ca_xMn_2O_7$ (x = 0.0–0.4), it is concluded that the observed increase of elastic constants and acoustic Debye temperature with Ca substitution suggests the strengthening of interatomic bonding and this may be due to the decrease in bond length by replacement of larger Sr^{2+} ions by smaller Ca^{2+} ions in the system. The elastic moduli, corrected to zero porosity with two different models, are in good agreement with each other and to those determined by metal mixture rule, confirming the consistency in the methods employed.

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