

Elastic Properties of Colossal Magneto-resistive Manganites

$R_{0.67}Sr_{0.33}MnO_3$ ($R = Pr, Nd, Gd$)

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The polycrystalline bulk samples of $R_{0.67}Sr_{0.33}MnO_3$ ($R = Pr, Nd, Gd$) were prepared by solid state reaction method and characterized by powder X-ray diffraction. The room temperature elastic behavior of these materials was investigated by employing ultrasonic pulse transmission technique at 1 MHz. The values of elastic constants were computed from longitudinal and shear velocities. The measured values were corrected to zero porosity using Hasselman and Fulrath's formulae. The variation of elastic moduli with the size of rare earth ion is interpreted in terms of strength of interatomic bonding.

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1. Introduction

The doped rare earth manganites have been attracting the attention of materials scientists across the world owing to their colossal magnetoresistance (CMR). The cubic perovskite manganites with general compositional formula $R_{1-x}A_xMnO_3$ (R is trivalent rare earth ion and A is divalent alkaline earth ion) and double layered manganites in the form $R_{2-2x}Sr_{1+2x}Mn_2O_7$ are suitable for many technological applications which are based on CMR [1–5]. The term CMR refers to the large decrease in electrical resistance when magnetic field is applied (Fig. 1).

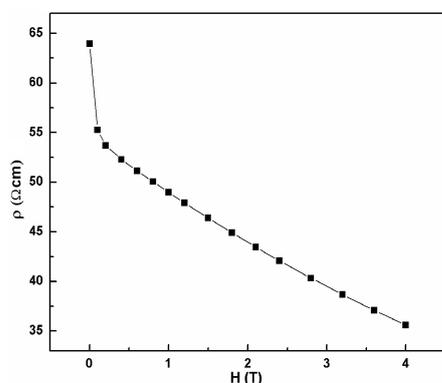


Fig. 1. An illustrative example of effect of applied magnetic field on electrical resistivity of a manganite sample.

When a material is subjected to an external magnetic field, stress will develop in the material. Therefore, a CMR material must be evaluated with respect to its elastic behavior before it is put into any application [6, 7]. The elastic properties along with electric and magnetic

properties are important to decide the suitability of a material for a specific application. Also, the determination of elastic constants is necessary to understand the nature of binding forces of the solids and the response of the materials to the mechanical stress. Further, the knowledge of the effect of porosity on elastic constants will help us to improve the mechanical properties of the materials to the best possible level.

In this paper, we report the results of elastic constants of $R_{0.67}Sr_{0.33}MnO_3$ ($R = Pr, Nd, Gd$) measured by ultrasonic pulse transmission (UPT) technique at room temperature and the variation of elastic constants with the size of rare earth ion is discussed. The zero porosity corrections are also done to know the effect of porosity on the elastic constants of the materials. This work may be helpful in understanding the effect of temperature and porosity on elastic constants of manganites.

2. Experiment

Polycrystalline perovskite manganite samples of $R_{0.67}Sr_{0.33}MnO_3$ ($R = Pr, Nd, Gd$) were prepared by the solid state reaction method. High purity powders of respective rare earth oxides, $MnCO_3$ and $SrCO_3$ weighted in appropriate proportions were used to obtain the nominal compositions of $R_{0.67}Sr_{0.33}MnO_3$ ($R = Pr, Nd, Gd$). The starting materials were mixed and ground thoroughly and calcined in air at 1100°C for 8 h with intermediate grinding. Then, the resultant powders were pressed into pellets of ≈ 12 mm diameter and ≈ 3 mm thickness and sintered in air at 1200°C for 6 h. The structural characterization was done by powder X-ray diffraction (XRD) using M/s PANalytical X-ray diffractometer giving $Cu K_\alpha$ radiation ($\lambda = 0.154056$ nm) in 2θ range of $20^\circ - 80^\circ$.

The values of bulk density (ρ) of the samples were estimated employing the Archimedes principle, with xylene as buoyant. The equation for bulk density is given by $\rho = \frac{W_a}{W_a - W_b} \times d_b$, where W_a is weight of the sample in air, W_b is weight of the sample in buoyant and d_b is density of the buoyant (0.865 g/cm³). The values of X-ray

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densities (ρ_x) were calculated from the lattice parameters using the formula: $\rho_x = \frac{z \times M}{V \times 0.6023}$, where z is number of chemical units in one unit cell of the crystal (in the present case, $z = 4$), M is molecular weight (for one unit of the chemical formula) of the sample in atomic weight units and V is volume of the crystalline unit cell as determined by the powder XRD ($V = a \times b \times c$ for orthorhombic unit cell). From the values of bulk and X-ray densities, porosity fraction (C) has been calculated using the formula: $C = 1 - \rho/\rho_x$.

The ultrasonic measurements were carried out by the UPT technique at room temperature [7]. Longitudinal and shear velocities have been measured using X -cut and Y -cut quartz transducers, respectively, with a fundamental frequency of 1 MHz. The rf pulses generated by the pulse oscillator were applied to the transmitting transducer, which converts them into acoustic pulses. These acoustic pulses, after propagating through the test sample, were converted back into electrical signals by the receiving transducers. The amplified output signal was displayed on a 100 MHz digital storage oscilloscope (Tektronix model No. 2221). The difference in time ΔT between two overlapping received pulse trains was noted using a timer. The velocity of sound was measured using the equation $V = t/\Delta T$, where t is the thickness of the sample. The overall accuracy of these measurements is $\pm 10 \text{ ms}^{-1}$.

3. Results and discussion

The powder XRD patterns of $\text{R}_{0.67}\text{Sr}_{0.33}\text{MnO}_3$ ($\text{R} = \text{Pr}, \text{Nd}, \text{Gd}$) are shown in Fig. 2 and they indicate the single phase formation of the samples with orthorhombic structure. As expected, the values of lattice constants and cell volume decrease with decreasing size of rare earth ion (Table I). Here, the Shannon ionic radii values ($\langle R \rangle$) of rare earth ions are considered (coordination number 9) [8].

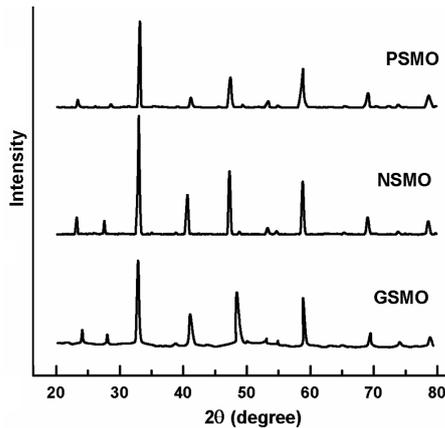


Fig. 2. Powder XRD patterns of $\text{R}_{0.67}\text{Sr}_{0.33}\text{MnO}_3$ ($\text{R} = \text{Pr}, \text{Nd}, \text{Gd}$).

As the samples under the present investigation are polycrystalline, the elastic constants are determined by applying the standard isotropic elastic medium

TABLE I

Crystallographic data of $\text{R}_{0.67}\text{Sr}_{0.33}\text{MnO}_3$ ($\text{R} = \text{Pr}, \text{Nd}, \text{Gd}$).

Sample	a [Å]	b [Å]	c [Å]	V [Å ³]	$\langle R \rangle$ [Å]	ρ_x		C
						[$\times 10^3$]	[g/cm ³]	
PSMO	5.4401	7.9910	5.5491	241.23	1.179	6.229	5.632	0.096
NSMO	5.4312	7.9781	5.5216	239.26	1.163	6.342	5.665	0.107
GSMO	5.4006	7.9303	5.4911	235.18	1.107	6.698	5.961	0.110

approximation. The values of elastic constants are determined with the help of the following formulae [9]. The values of longitudinal sound velocity (V_L) and shear sound velocity (V_S) obtained from UPT technique are used in these formulae.

$$\text{Longitudinal modulus } L = \rho V_L^2.$$

$$\text{Shear modulus } G = \rho V_S^2.$$

$$\text{Bulk modulus } B = L - \frac{4}{3}G.$$

$$\text{Poisson's ratio } \sigma = \frac{3B - 2G}{6B + 2G}.$$

$$\text{Young's modulus } E = (1 + \sigma)2G.$$

The values of acoustic Debye temperature (θ_D) are determined using Anderson equation

$$\theta_D = \frac{h}{k_B} \left(\frac{3\rho N_A q}{4\pi M} \right)^{1/3} V_m,$$

where h is the Planck constant, k_B is the Boltzmann constant, ρ is bulk density of the sample, N_A is the Avogadro number, q is number of atoms in the unit formula (in the present case $q = 5$), M is molecular weight and V_m is mean sound velocity and is given by the equation

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

The measured values of elastic constants are summarized in Table II.

TABLE II

Longitudinal velocity (V_L), shear velocity (V_S), mean velocity (V_m), longitudinal modulus (L), shear modulus (G), bulk modulus (B), Young's modulus (E), Poisson's ratio (σ) and acoustic Debye temperature (θ_D) for $\text{R}_{0.67}\text{Sr}_{0.33}\text{MnO}_3$ ($\text{R} = \text{Pr}, \text{Nd}, \text{Gd}$).

Sample	V_L	V_S	V_m	L	G	B	E	σ	θ_D
	[m/s]			[GPa]					
PSMO	3552	2078	2304	71.07	24.32	38.64	60.31	0.240	289.2
NSMO	3601	2101	2331	73.47	25.02	40.10	62.14	0.242	292.2
GSMO	3799	2205	2447	86.03	28.98	47.39	72.23	0.246	308.1

The present DL manganite samples are porous and hence the measured elastic constants are corrected to zero porosity using the following Hasselman and Fulrath's (HF) formulae [10] and the values, thus obtained, are given in Table III.

TABLE III

Shear modulus (G_0), bulk modulus (B_0), Young's modulus (E_0) and Poisson's ratio (σ_0) corrected to zero porosity using HF and Shear modulus (G^*), bulk modulus (B^*) and Young's modulus (E^*) estimated using MMMR.

Sample	G_0	B_0	E_0	σ_0	G^*	B^*	E^*
	[GPa]				[GPa]		
PSMO	30.08	48.89	74.59	0.240	44.16	57.86	94.22
NSMO	31.80	52.40	78.98	0.242	44.67	58.87	95.60
GSMO	37.16	62.77	92.61	0.246	46.51	60.91	100.08

$$\frac{1}{E_0} = \frac{1}{E} \left(1 - \frac{3C(1-\sigma)(9+5\sigma)}{2(7-5\sigma)} \right),$$

$$\frac{1}{G_0} = \frac{1}{G} \left(1 - \frac{15C(1-\sigma)}{(7-5\sigma)} \right),$$

$$B_0 = \frac{E_0 G_0}{3(3G_0 - E_0)},$$

$$\sigma_0 = \frac{E_0}{2G_0} - 1.$$

Here G , B and E represent the experimental values of shear, bulk and Young's moduli; and G_0 , B_0 and E_0 represent corrected shear, bulk and Young's moduli, respectively. σ and σ_0 are the measured and corrected values of Poisson's ratio, respectively.

Further, the elastic constants of the present system are also estimated by Modi's heterogeneous metal-mixture rule (MMMR) [6, 11]. This model is based on the idea that the density and elastic parameters of polycrystalline oxide compositions depend upon the density and elastic parameters of individual metallic cations present in the system. According to this model "the elastic constant and acoustic Debye temperature value of polycrystalline oxide material is equal to the average of stoichiometric compositional addition of elastic constant and acoustic Debye temperature values of metallic elements present in the material". Our earlier studies on cubic perovskite and DL manganite samples indicate that MMM rule is a valid model for the estimation of elastic constants of these materials [7, 12].

In MMMR model, the value of elastic constant or acoustic Debye temperature can be calculated by using the following formula:

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

where K_{pm}^* is either elastic modulus or acoustic Debye temperature of the composition to be estimated, n is total number of metal cations in unit chemical formula ($n = 2$ in the present case), C_{in} is concentration of the n -th cation in the formula unit, while K_n is the corresponding modulus or acoustic Debye temperature of the metallic element. The values of elastic moduli and acoustic Debye

temperature of the metallic elements are taken from the literature to estimate K_{pm}^* [13, 14]. The values of elastic moduli estimated using MMM rule and obtained from UPT show the similar trend with the change of the size of rare earth ion. However, the values of elastic moduli obtained from UPT show a large variation with size of rare earth ion as compared to moderate change predicted by MMM rule (Table III).

The variation in elastic parameters with size of rare earth ion can be interpreted in terms strength of interatomic bonding [15]. As the size of rare earth ion decreases, the length of interatomic bonding decreases and this results in the increase in strength of interatomic bonding and therefore the values of elastic moduli increase. From the above results, it can be seen that both the measured and the corrected values of elastic moduli change in the same manner.

The measured and the corrected values of Poisson's ratio are found to be in good agreement (Tables II and III) and lie in the theoretical range from -1 to 0.5 . The decreasing rare earth ion size results in the increase in the acoustic Debye temperature (Table II), which suggests the reduction in lattice vibrations with decreasing rare earth ion size [6]. This can also be attributed to the increase of strength of interatomic bonding with decrease of rare earth ion size.

TABLE IV

Mean atomic weight (M/q), V_L/ρ_x and V_S/ρ_x for $R_{0.67}Sr_{0.33}MnO_3$ ($R = Pr, Nd, Gd$).

Sample	M/q	V_L/ρ_x	V_S/ρ_x
		[m ⁴ kg ⁻¹ s ⁻¹]	
PSMO	45.25	0.570	0.334
NSMO	45.69	0.568	0.331
GSMO	47.44	0.567	0.329

In oxide materials with nearly equal mean atomic weight (M/q), the variation in the mean atomic weight corresponds to the variation in the values of V_L/ρ_x and V_S/ρ_x [12, 16]. Table IV indicates such behavior and confirms that these rare earth manganese oxide materials exhibit ultrasonic behavior similar to the many other oxide materials.

4. Conclusion

The room temperature elastic properties of polycrystalline DL manganite samples $R_{0.67}Sr_{0.33}MnO_3$ ($R = Pr, Nd, Gd$) synthesized by solid state reaction method were studied by UPT. The lattice parameters and cell volume are found to decrease with decreasing rare earth ion size. The values of elastic constants calculated from longitudinal and shear velocities increase with decreasing rare earth ion size. The values of elastic constants corrected to zero porosity using HF formulae and estimated using MMMR formula also show similar compositional dependence. The variation of elastic moduli with the size of the rare earth ion is interpreted in terms of strength of interatomic bonding.

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