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Effect of Sodium Doping on Thermal Properties of Perovskite $RMnO_3$ for Potential Magnetoelectric Applications

Archana Srivastava
Department of Physics, Sri Sathya Sai College for Women, Bhopal 462024, India
Tel: 00917552660186 E-mail: archanasaran@rediffmail.com
Rasna Thakur
Department of Physics, Barkatullah University, Bhopal 462026, India
Tel: 00917552491821 E-mail: rasanathakur@yahoo.com
N.K.Gaur
Department of Physics, Barkatullah University, Bhopal 462026, India
Tel: 00917552491821 E-mail: srl_nkgaur@yahoo.co.in

Abstract
The partial replacement of rare earth cation by sodium introduces large size and charge mismatch at A-site affecting the bulk modulus and thermal properties of $RMnO_3$ which in turn makes them suitable candidates for thermoelectric applications. Thermal, elastic, cohesive properties of sodium doped Rare Earth manganites $R_{1-x}Na_xMnO_3$ (R^{3+}= La, Pr, Tb) has been studied by means of a Modified Rigid Ion Model (MRIM) and AIM theory. Lattice specific heat (C_p) of $Pr_{0.8}Na_{0.2}MnO_3$, and $Tb_{0.85}Na_{0.15}MnO_3$ as a function of temperature ($1K \leq T \leq 350K$) is found to be in agreement with the published data. The trend of variation of Debye temperature (θ_D), thermal expansion (α), bulk modulus (B) and cohesive energy (φ) with A-site cationic radius is predicted probably for the first time for these technologically important doped rare earth manganites.
Keywords: Thermal Expansion, Specific Heat, Thermal properties, Colossal Magnetoresistance Materials, Magnetoelectric materials.

1. Introduction

The multiferroic materials with the coexistence of (anti)ferromagnetic and (anti)ferroelectric properties are one of the best candidates to enhance the magnetoelectric (ME) effects. It is reported that substitution of monovalent ions (K^+, Rb^+, Na^+, Ag^+) for La in $LaMnO_3$ results in increased magneto-resistance and large magneto-caloric effect [Tao et al. 2000; Tang et al. 2000]. The ferroelectric polarization has been found to develop in $Tb_{0.85}Na_{0.15}MnO_3$ with the polarization vector pointing along the longest crystallographic direction [Chan, *et al.* 2007]. $Pr_{0.8}Na_{0.2}MnO_3$ is a charge ordered system which is a paramagnetic insulator at ambient conditions and exhibits an electrically insulating pseudo-CE type antiferromagnetic (AFM) state at low temperatures. Under high externe pressures, structural changes in $Pr_{0.8}Na_{0.2}MnO_3$ are accompanied by an insulator–metal transition [Hejtmaek, *et al.* 2001]. At normal conditions, the system undergoes a charge ordering transition at T_{CO} = 215 K, followed by an antiferromagnetic arrangement of the pseudo-CE type at T_N = 175 K. Experimentalists have studied the magnetic properties of these compounds well but no attempts were made to determine their thermal and elastic properties.

The ionic radius of Na^+Å (ionic radius =1.39Å CN 12) is larger than largest lanthanide La^{3+} (ionic radius =1.36Å CN 12) and the effect of this doping in $RMnO_3$ (R=La, Pr, Tb) is to increase the A-site cation radius and e_g one electron bandwidth of the manganites [Tao et al. 2000; Tang et al. 2000]. The insulator–metal transition temperature T_{I-M} is expected to increase and possible stabilization of ferromagnetic state at room temperature can be achieved paving the way for magnetoelectric applications. So, it seems worthwhile to investigate the static cohesive, elastic (bulk modulus (B)) and thermodynamic properties like Debye temperature (θ_D) Specific heat (Cp) and volume thermal expansion ( )) at low temperatures and at room temperature as well of these technologically important manganites.

We investigate here three potential magnetoelectric compounds $La_{0.85}Na_{0.15}MnO_3$, $Pr_{0.8}Na_{0.2}MnO_3$, and $Tb_{0.85}Na_{0.15}MnO_3$ for their elastic, cohesive and thermal properties. The studied samples of $Tb_{0.85}Na_{0.15}MnO_3$, $Pr_{0.8}Na_{0.2}MnO_3$ exhibited *Pbnm* symmetry within the orthorhombic setting and $La_{0.85}Na_{0.15}MnO_3$ showed rhombohedral symmetry [Malavasi , *et al*. 2005].

2. Interaction Potential

The potential to describe the interatomic interactions of these materials within modified Rigid Ion Model (MRIM) is formulated as

$$\phi = -\frac{e^2}{2}\sum_{kk'} Z_k Z_{k'} r_{kk'}^{-1} + \phi_{kk'}^{vdw} + \sum_i \left(\begin{array}{l} n_i b_i \beta_{kk'} \exp\{(r_k + r_{k'})/\rho_i + \\ \frac{n_i'}{2} b_i \left[\beta_{kk} \exp\{(2r_k - r_{kk}/\rho_i\} + \beta_{k'k'} \exp\{(2r_{k'} - r_{k'k'})/\rho_i\}\right] \end{array} \right) \quad (1)$$

Here $r_{kk'}$ appearing in the first term on the right represents separation between the nearest neighbours while r_{kk} and $r_{k'k'}$ appearing in the following two terms are the second neighbour seperation. $r_k (r_{k'})$ is the ionic radii of k (k') ion. n (n') is the number of nearest (next nearest neighbour) ions. In ABO_3 (like $CaMnO_3$) perovskite structure, k represent the cations (A, B) and k' denote the type of (O_1, O_2) ion. The summation is performed over the ion pair (A-O) and (B-O). b_i and ρ_i are the hardness and range parameters for the i^{th} cation-anion pair (i = 1, 2) respectively and $\beta_i^{kk'}$ is the Pauling coefficient (Pauling, 1945). Z_k ($Z_{k'}$) and N_k ($N_{k'}$) are the valence and the number of electrons in the outermost orbit of k(k') ion respectively. The $r_{kk'}$ and r_{kk} ($r_{k'k'}$) are obtained for some doping concentration (x) of Ln=La, Ce, Pr, Nd, Th, Bi by using the well known Vegard's law [24] using the cell parameters of undoped compounds like $CaMnO_3$ and $NdMnO_3$. The contributions of van der Waal's (vdW) attraction for the dipole-dipole interaction is determined by using the Slater- Kirkwood Variational (SKV) method (Slater and Kirkwood 1931)

$$\phi_{kk'}^{vdW} = C_{kk'} r_{kk'}^{-6} \quad \text{and}$$

$$C_{kk'} = \frac{3eh}{4\pi m}\alpha_k \alpha_{k'} \left[\left(\frac{\alpha_k}{N_k}\right)^{1/2} + \left(\frac{\alpha_{k'}}{N_{k'}}\right)^{1/2} \right]^{-1} \quad (2)$$

where e and m are the charge and mass of the electron respectively. $\alpha_k (\alpha_{k'})$ is the polarizability of k (k') ion. N_k ($N_{k'}$) are the effective number of electrons responsible for the polarization of k (k') ion.
The model parameters, hardness (b) and range (ρ) parameters are determined from the equilibrium condition

$$\left[\frac{d\phi}{dr}\right]_{r=r_0} = 0 \quad \text{and} \quad B = \frac{1}{9Kr_0}\left[\frac{d^2\phi}{dr^2}\right]_{r=r_0} \quad (3)$$

here K is the crystal-structure-dependent constant, B is bulk modulus and r_0 is the equilibrium nearest neighbor distance. Our other formulations are taken from our previous papers [Thakur et al. 2012: Srivastava et al. 2009]. The bulk modulus was calculated using the Atom in Molecules (AIM) Theory [Pendas, *et al*. 2000].

3. Results and Discussions

To reveal the specific heat, the values of input data like unit cell parameters (a, b, c) and some interionic distances are taken from refs. [Malavasi , *et al*. 2005, Yang, *et al*. 2008, Kozlenko *et al.* 2003] for $(La, Tb)_{0.85}Na_{0.15}MnO_3$, $Pr_{0.8}Na_{0.2}MnO_3$. We have applied MRIM to compute the model parameters and Debye temperature of these manganites and AIM theory [Pendas, *et al*. 2000] to compute bulk modulus on the similar lines as described earlier [Thakur *et al*. 2012: Srivastava *et al*. 2009]. The results are reported in Table 1 and are compared with the available data there [Srivastava et al. 2009; Kovaleva , *et al*. 2002, Kamilov, *et al*. 2007].
The cohesive energy is the measure of strength of the force binding the atoms together in solids. This fact is exhibited from our cohesive energy results which indicate increase in stability with decrease of A-site cation radius (Table 1). Besides, we studied the temperature evolution of the lattice specific heat (C_p) of $Tb_{0.85}Na_{0.15}MnO_3$over the temperature range 1K ≤ T ≤ 100K (Fig. 1(a)) and of $Pr_{0.8}Na_{0.2}MnO_3$ in 10K ≤ T ≤ 350K (Fig. 1(b)). It is found to show satisfactory match with the experimental values of Yang *et al*. (2006) and Hejtmaek *et al* (2001) at higher temperatures using HT Debye temperature and at low temperature using LT Debye temperature respectively which again establishes the validity of using two Debye temperature model [Thakur et al. 2012: Srivastava et al. 2009] to describe the specific heat of manganites. A sharp peak can be seen in Figure 1(b) in the experimental curves at their respective Neel temperature due to spin interactions. This feature can be revealed in the calculated curves by including the ferromagnetic spin interactions in the framework of our MRIM. It can be concluded that MRIM is successful in predicting the thermal properties of doped manganites and the findings indicate that cohesive energy decreases and Debye temperature increases with the decrease of A-site cation radius. The increase in θ_D indicates that an anomalous hardening of the lattice or decrease in T^3-term in the specific heat occurs with the decrease of A-site cation radius. The specific heat correspondingly decreases with decreasing A-site cation radius. These results of specific heat

and volume thermal expansion are crucial in deciding the compatibility of different components of thermoelectric devices and they reveal the electron lattice coupling as well of these compounds, suggesting strong coupling between their various degrees of freedom.

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TABLE 1. Cation radius at A-site, Bulk modulus, model parameters, cohesive and thermal properties of $R_{1-x}Na_xMnO_3$. R and O indicate Rhombohedra and Orthorhombic structure respectively.

R/x	r_A(Å) /Structure	(B) (GPa) (LT)	b_1 x 10^{-19} (J)	b_2 x 10^{-19} (J)	ρ_1 (Å)	ρ_2 (Å)	Φ (eV) (MRIM)	Θ_D (K) LT	Θ_D (K) (RT)	$(10^{-5}/K)$ (RT)
La/0.15	1.365/R	107.7	0.323	1.243	0.185	0.335	-139.0	371.3	560.5	4.53
For x=0		108 [a]					-139.4 [b]	370[c]		3.0[c]
Pr/0.2	1.192/O	125.0	0.212	1.027	0.180	0.353	-144.5	405.9	577.7	4.54
Tb/0.15	1.117/O	194.9	0.069	0.246	0.134	0.192	-155.8	491.9	692.0	3.87

[a] ref. (Srivastava *et al*. 2009), [b] ref. (Kovaleva, *et al*. 2002), [c] ref. (Kozlenko, *et al*. 2003) for $La_{0.85}Ag_{0.15}MnO_3$

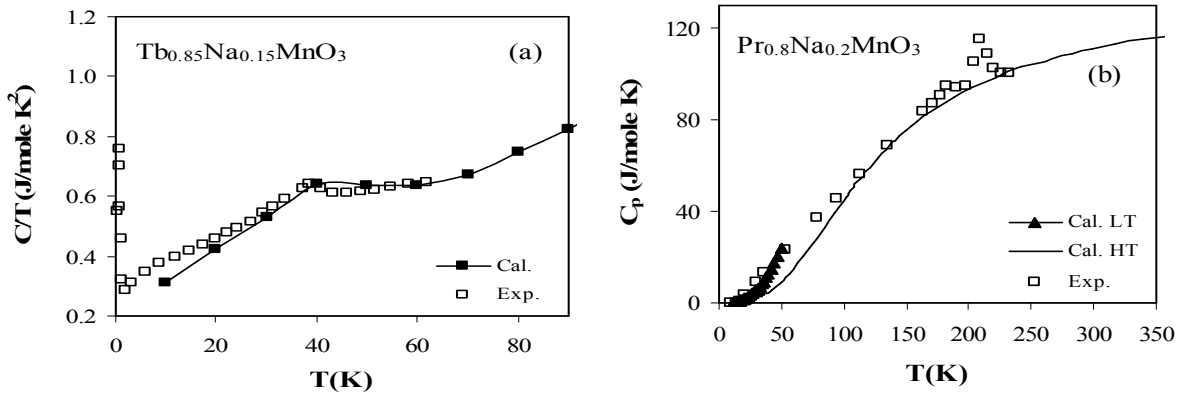

FIGURE 1. (a) C/T against temperature for $Tb_{0.85}Na_{0.15}MnO_3$ with the experimental data of Yang *et al* (2006) (b) Variation of C_p with temperature of $Pr_{0.8}Na_{0.2}MnO_3$ and experimental data of Hejtmaek *et al* (2001)

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