Influence of La doping on elastic and thermodynamic properties of SrMoO$_3$

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ABSTRACT

The elastic and thermodynamic properties for Sr$_{1-x}$La$_x$MoO$_3$ (x = 0.0, 0.05, 0.1, 0.15, and 0.2) with temperature have been investigated, probably for the first time, by using modified rigid ion model (MRIM). The computed results on the elastic constants (C_{11}, C_{12}, and C_{44}) are the first report on them. Using these elastic constants we have computed other elastic properties such as B, β, G', G, E, σ, B/G ratio, Cauchy pressure ($C_{12} - C_{44}$) and Lame's parameters (μ, λ). We have also reported the thermodynamic properties such as ϕ, f, θ_D, θ_{D1}, υ_0, υ_1, γ, and α. The values of Young's modulus, shear modulus and compressibility for SrMoO$_3$ are in good agreement with the available experimental data. The concentration (x) dependence of θ_D in Sr$_{1-x}$La$_x$MoO$_3$ suggests that increased La doping drives the system effectively away from the strong electron–phonon coupling regime. Specific heat is reported in the wide temperature range and compared with the respective experimental data available in the literature. The thermal expansion coefficient of SrMoO$_3$ is in good agreement with the other theoretical data.

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1. Introduction

Transition-metal oxides (TMOs) have attracted a lot of attention for a long time because of their importance in both the fundamental aspects of condensed-matter physics and the potential for technological applications. The A$_{n+1}$B$_n$O$_{3n+1}$-type perovskite 3d TMO attracted considerable attention due to the discovery of high-temperature superconductivity (SC) in cuprates [1] and colossal magnetoresistance (CMR) [2] in manganites.

With the passage of time, the scope of research has broadened to include 4d/5d TMOs from 3d TMOs. The central characteristic of these 4d and 5d shell-based TMOs is more extended d orbitals of transition-metal ions as compared to those of 3d-shell ions [3]. It has been generally believed that the electrons in these orbitals feel rather weak on-site Coulomb repulsion energy and the 4d orbitals hybridize more strongly with their neighbouring orbits, e.g., O 2p orbitals, than the 3d orbitals. As a result, the physical properties of these 4d or 5d TMOs are sensitive to perturbations, such as magnetic fields, pressure or chemical doping.

SrMoO$_3$, a 4d TMO has been widely studied due to its interesting physical properties in the past few years. It is a cubic perovskite showing Pauli paramagnetism, and metallic conductivity [4–6]. The metallic conductivity of SrMoO$_3$ is related to the 4d^2 delocalized electrons of Mo^{4+} cations which act as carriers in the material [7], its high conductivity and low raw-material costs are attractive for practical applications [8]. And the charge-transfer energy ($\Delta_{pd} \sim 5$ eV) of SrMoO$_3$ is so large that it can be classified as a possible superconducting material according to the criterion established by Goodenough [9] and [10]. However, no observation of a superconducting transition has been observed down to 36 mK in SrMoO$_3$ single crystal due to the extremely small electron–phonon interaction [7].

Zhang et al. have done a systematic study of many pure and doped perovskite molybdate oxides such as SrMo$_{1-x}$B$_x$O$_3$ (B = Mn, Cu, Cr) [11–13] and Sr$_{1-x}$A$_x$MoO$_3$ (A = La and Pr) [14,15] on the structural, electronic transport and magnetic properties. Agarwal et al. [4] have done calorimetric investigations of SrMoO$_3$ and BaMoO$_3$ compounds. Lee et al. reported the systematic inves-

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tigations on the thermal, electrical, and mechanical properties of barium and strontium series perovskite-type oxides, such as $Ba(Zr,Ce)O_3$ [16,17], $BaMoO_3$ [18], $Sr(Hf,Ru)O_3$ [19] and 4d $SrMO_3$ (M = Zr, Mo, Ru, and Rh) [3] using optical conductivity analyses. Structural and magnetic properties of $SrFe_xMo_{1-x}O_3$ were reported by Kawachi et al. [20]. Recently Macquart et al. [21] studied phase transition in SrMoO3 using neutron diffraction. Logvinovicha et al. [22] have reported the synthesis procedure for higher level substituted oxynitrides of the composition $SrMoO_{3-x}N_x$ and characterised them for crystallographic structure and physical properties by neutron diffraction (ND) XRD, X-ray absorption near edge spectroscopy, Seebeck coefficient and electrical conductivity measurements. But no efforts have been made to study the elastic properties of these molybdates. Therefore, in this paper, probably for the first time, we have made an attempt to carry out systematic study the elastic and thermodynamic properties of $SrMoO_3$ and the effect of La substitution on these properties by using modified rigid ion model (MRIM).

Recently, we have successfully shown the thermodynamic behaviour of manganites [23–27] and diborides [28,29], by using MRIM. The major contribution to the pair potential of MRIM is of the long-range (LR) Coulomb attraction, which is counterbalanced by the short-range (SR) overlap repulsion having their origin in the Pauli exclusion principle. This SR interaction is expressed by a Hafemeister–Flygare (HF) [30] type overlap repulsion effective up to the second neighbour ions. This potential also incorporates the effects of the van der Waals (vdW) attraction (Tosi and Fumi [31]) arising from the dipole–dipole (d–d) and dipole–quadrupole (d–q) interactions, whose coefficients are estimated from the Slater–Kirkwood variational (SKV) [32] approach, which treats both the ions (cations and anions) as polarizable. Motivated from such a realistic and qualitative representation of the interionic potential and its versatile applicability to describe the cohesive and physical properties of solids and alloys (Singh [33] and Varshney et al. [34]), we thought it is pertinent to apply this MRIM, probably for the first time, to explore the elastic and thermodynamic properties of the pure and doped $SrMoO_3$. The interaction potential of the MRIM is described in Section 2. The computed results are presented and discussed in Section 3.

2. Theoretical methods

2.1. Modified rigid ion model (MRIM)

The interionic potential of the rigid ion model (RIM) [29,33] is formulated on the basis of the simple Born model, according to which the ions are treated as the rigid (or unpolarisable) ions held together in crystals by the long-range (LR) Coulomb attraction and prevented from the collapsing by the short-range (SR) overlap repulsion. This potential was modified by Fumi and Tosi [31] by incorporating the effect of van der Waals (vdW) attraction due to the d–d and d–q interactions to reveal the cohesive properties of ionic solids. Also, the overlap repulsion was extended up to the second neighbour ions by Hafemeister and Flygare (HF) [30].

In the present investigation, we have modified the RIM potential by including the vdW attraction and HF type overlap repulsion to describe the elastic and thermodynamic properties of $Sr_{1-x}La_xMoO_3$ (x = 0.0, 0.05, 0.1, 0.15, and 0.2). The effective interionic potential corresponding to the MRIM framework is expressed as:

$$\phi = -\frac{e2}{2}\sum_{kk'} ZkZk'r - 1kk' - \sum_{kk'} ckk'r - 6kk' - \sum_{kk'} dkk'r - 8kk'$$
$$+ nb1\beta kk' \exp\left\{\frac{(r_k + r_{k'} - r_{kk'})}{\rho 1}\right\}$$
$$+ \frac{n'}{2}b2\left[\beta kk \exp\left\{\frac{2rk - rkk}{\rho 2}\right\} + \beta k'k' \exp\left\{\frac{2rk' - rk'k'}{\rho 2}\right\}\right] \quad (1)$$

Here, the first term represents the LR Coulomb energy. The second and third terms are the SR vdW energies due to d–d and d–q interactions, respectively. The last two terms are the SR repulsive energies due to the overlap repulsion between the nearest (kk') and the next nearest (nn) neighbour (kk and k'k') ions, respectively. Z_k ($Z_{k'}$) and r_k ($r_{k'}$) are the ionic charges and radii of k (k') ions. Also, $r_{kk'}$ and r_{kk} (= $r_{k'k'}$) are the interionic separations between the nearest k(k') and the next nearest kk(=k'k') neigh-

bour ions. The symbols $c_{kk'}$ and $d_{kk'}$ represent the vdW coefficients due to d–d and d–q interactions, respectively. b_1 (ρ_1) and b_2 (ρ_2) are the range (hardness) parameters corresponding to the Sr/La–O and Mo–O bond distances for these $Sr_{1-x}La_xMoO_3$ compounds. $\beta_{kk'}$ [=1 + (Z_k/n_k) + ($Z_{k'}/n_{k'}$)] are the Pauling coefficients [35]. The vdW coefficients ($c_{kk'}$ and $d_{kk'}$) are evaluated from the Slater–Kirkwood variational (SKV) method [32].

The present interionic potential of MRIM contains two-model parameters b and ρ, which have been determined from the equilibrium condition,

$$\left(\frac{d\phi}{dr}\right)_{r=r_0} = 0 \quad (2)$$

and the bulk modulus,

$$B = (9Kr_0)^{-1}\left[\frac{d2\phi}{dr2}\right]_{r=r_0} \quad (3)$$

where K is the structure dependent constant. r_0 is the equilibrium interatomic separation. The model parameters b (ρ) when calculated corresponding to Sr/La–O and Mo–O bond distances then they effectively become four model parameters b_1 (ρ_1) and b_2 (ρ_2) for the $Sr_{1-x}La_xMoO_3$ compounds.

2.2. Elastic properties

Using Eq. (1), the expressions for second-order elastic constants (SOECs) [27,36] are expressed as:

$$C11 = 4.133T\beta BT + \frac{e2}{4r4}\left[\frac{A1}{6} - 1.7333B1 + \frac{A2}{2} - 2.0666B2\right] \quad (4)$$

$$C12 = 3.0666T\beta BT + \frac{e2}{4r4}\left[\frac{A1}{6} - 1.3666B1 + \frac{A2}{2} - 1.5333B2\right] \quad (5)$$

$$C44 = -2.0666T\beta BT + \frac{e2}{4r4}\left[\frac{A1}{6} - 1.3666B1 + \frac{A2}{2} - 1.5333B2\right] \quad (6)$$

$$T\beta BT = \frac{e2}{4r4}[0.3392\varepsilon 2 + B1 + B2] \quad (7)$$

where A_1, A_2, B_1 and B_2 are the short-range parameters [33], β is the volume thermal expansion coefficient and B_T is the isothermal bulk modulus. e is the electronic charge and $\in$ is the ionic charge.

For a cubic structure, the bulk modulus B and the shear modulus G are taken as:

$$B = \frac{C_{11} + 2C_{12}}{3} \quad (8)$$

$$G = \frac{3C_{44} + C_{11} - C_{12}}{5} \quad (9)$$

Also, the Young's modulus (E) and the Poisson's ratio (σ) are given by:

$$E = \frac{9BG}{3B + G} \quad (10)$$

$$\sigma = \frac{1}{2}\left(1 - \frac{E}{3B}\right) \quad (11)$$

Using Poisson's ratio σ the Lamé's coefficients (μ and λ), for $Sr_{1-x}La_xMoO_3$ have been obtained as:

$$\mu = \frac{E}{2(1+\sigma)} \quad (12)$$

$$\lambda = \frac{\sigma E}{(1+\sigma)(1-2\sigma)} \quad (13)$$

The shear and longitudinal sound velocities υ_s and υ_l are obtained from Navier's equation as follows [37]:

$$\upsilon s = \sqrt{\frac{G}{\rho}} \quad (14)$$

$$\upsilon l = \sqrt{\frac{B + (4/3)G}{\rho}} \quad (15)$$

The average sound velocity υ_m [38] is obtained from:

$$\upsilon_m = \left[\frac{1}{3}\left(\frac{2}{\upsilon_s^3} + \frac{1}{\upsilon_l^3}\right)\right] \quad (16)$$

where υ_s and υ_l are the shear and longitudinal sound velocities, respectively.

The Debye temperature may be estimated from the average sound velocity υ_m [38] as:

$$\theta D = \frac{h}{k}\left[\frac{3n}{4\pi}\left(\frac{NA\rho}{M}\right)\right]^{1/3}\upsilon m \quad (17)$$

where h is Planck's constants, k is Boltzmann's constant, N_A is Avogadro's number, n is the number of atoms per formula unit, M is the molecular mass per formula unit, and ρ is the density.