Research Article

Thermodynamic Properties of $\text{La}_{1-x}\text{Sm}_x\text{CoO}_3$

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We have investigated the bulk modulus and thermal properties of $\text{La}_{1-x}\text{Sm}_x\text{CoO}_3$ ($0 \leq x \leq 0.2$) at temperatures $1 \text{ K} \leq T \leq 300 \text{ K}$ probably for the first time by incorporating the effect of lattice distortions using the modified rigid ion model (MRIM). The calculated specific heat, thermal expansion, bulk modulus, and other thermal properties reproduce well with the available experimental data, implying that MRIM represents properly the nature of the pure and doped cobaltate. The specific heats are found to increase with temperature and decrease with concentration (x) for the present. The increase in Debye temperature (θ_D) indicates an anomalous softening of the lattice specific heat because increase in T^3 -term in the specific heat occurs with the decrease of concentration (x).

1. Introduction

Cobaltites of rare-earth elements with the chemical formula LnCoO_3 are important agile and multifunctional materials, which are very promising for high temperature oxygen separation membranes and cathodes in solid oxide fuel cells (SOFCs), heterogeneous catalysts, and gas sensors [1, 2]. The LaCoO_3 ceramic is at present the best studied representative of the rare-earth cobaltite family. LaCoO_3 exhibits two spin state transitions as the temperature increases. The first transition is from low temperature low spin (LS) to intermediate spin (IS) state near 100 K characterized by a steep jump of magnetization at the transition [3–5] and the second one is from IS to high spin (HS) state leading to an insulator-metal (I-M) transition around 500 K [3, 5]. Throughout the ACoO_3 series, only LaCoO_3 has been analyzed with rhombohedral symmetry [6]; the rest of the members of the family with the ionic radius of the rare-earth smaller than the ionic radius of La exhibit an orthorhombic crystallographic structure [7]. A structural transition from rhombohedral ($R\bar{3}C$) to orthorhombic ($Pbnm$) symmetry with Sm doping level $x > 0.08$ is found from the X-ray diffraction data in $\text{La}_{1-x}\text{Sm}_x\text{CoO}_3$ [8].

Recently, we have applied the modified rigid ion model (MRIM) to study the specific heat of cobaltates and manganites [9, 10]. Motivated from the applicability and versatility of MRIM, we have applied MRIM to investigate the temperature

dependence of the specific heat, thermal expansion, and elastic and thermal properties of $\text{La}_{1-x}\text{Sm}_x\text{CoO}_3$ ($0 \leq x \leq 0.2$). It is found that the model is successful in describing temperature dependent ($1 \text{ K} < T < 300 \text{ K}$) specific heat (C), cohesive energy (ϕ), molecular force constant (f), Reststrahlen frequency (ν), Debye temperature (θ_D), and Gruneisen parameter (γ) of $\text{La}_{1-x}\text{Sm}_x\text{CoO}_3$ ($0 \leq x \leq 0.2$). The various properties in $\text{La}_{1-x}\text{Sm}_x\text{CoO}_3$ ($0 \leq x \leq 0.2$) are affected by the exchange of the A ions due to their different ionic radii. The paper is organized in the following way.

The computational details of model formalism are given in Section 2. In Section 3, we discuss the elastic and thermal properties of $\text{La}_{1-x}\text{Sm}_x\text{CoO}_3$ ($0 \leq x \leq 0.2$). The calculated results are compared with the available experimental results in the same section. Finally, in Section 4, the findings of the present study are concluded.

2. Formalism of MRIM

The effective interionic potential corresponding to the modified rigid ion model (MRIM) frame work is expressed as [9, 10]

$$\phi(r) = -\frac{e^2}{2} \sum_{kk'} Z_k Z_{k'} r_{kk'}^{-1} - \sum_{kk'} C_{kk'} r_{kk'}^{-6} + \left[n_i b_i \beta_{kk'} \exp \left\{ \frac{(r_k + r_{k'} - r_{kk'})}{\rho_i} \right\} \right] + \frac{n'_i}{2} b_i$$

TABLE 1: Values of average cation radius at A-site, tolerance factor, critical radius, and model parameters of $\text{La}_{1-x}\text{Sm}_x\text{CoO}_3$ ($0.0 \leq x \leq 0.2$).

Compound	r_A (Å) (A-site)	Tolerance factor (t)	r_{cr} (Å)	Model parameters			
				$b_1 \times 10^{-19}$ (J)	ρ_1 (Å)	$b_2 \times 10^{-19}$ (J)	ρ_2 (Å)
LaCoO_3	1.360	0.9958	0.9148	1.662	1.114	0.225	0.404
$\text{La}_{0.98}\text{Sm}_{0.02}\text{CoO}_3$	1.357	0.9953	0.9159	1.636	1.105	0.222	0.399
$\text{La}_{0.96}\text{Sm}_{0.04}\text{CoO}_3$	1.355	0.9947	0.9164	1.605	1.095	0.219	0.394
$\text{La}_{0.94}\text{Sm}_{0.06}\text{CoO}_3$	1.352	0.9941	0.9168	1.596	1.093	0.218	0.392
$\text{La}_{0.92}\text{Sm}_{0.08}\text{CoO}_3$	1.350	0.9936	0.9168	1.551	1.071	0.213	0.383
$\text{La}_{0.88}\text{Sm}_{0.12}\text{CoO}_3$	1.205	0.9420	1.0102	1.317	1.757	0.197	0.364
$\text{La}_{0.84}\text{Sm}_{0.16}\text{CoO}_3$	1.202	0.9413	1.0143	1.288	1.751	0.192	0.355
$\text{La}_{0.80}\text{Sm}_{0.20}\text{CoO}_3$	1.199	0.9407	1.0169	1.269	1.751	0.190	0.351

FIGURE 1: The variation of bulk modulus, size mismatch, tolerance factor, and A-site variance of $\text{La}_{1-x}\text{Sm}_x\text{CoO}_3$ ($0.0 \leq x \leq 2.0$) with the radius of A-site cation.

$$\times \left[\beta_{kk} \exp \left\{ \frac{(2r_k - r_{kk})}{\rho_i} \right\} + \beta_{k'k'} \exp \left\{ \frac{(2r_{k'} - r_{k'k'})}{\rho_i} \right\} \right] \quad (1)$$

Here, first term is attractive long range (LR) coulomb interactions energy. The second term represents the contributions of van der Waals (vdW) attraction for the dipole-dipole interaction and is determined by using the Slater-Kirkwood Variational (SKV) method [11]. The third term is short range (SR) overlap repulsive energy represented by the Hafemeister-Flygare-type (HF) interaction extended up to the second neighbour. In (1), $r_{kk'}$ represents separation between the nearest neighbours, while r_{kk} and $r_{k'k'}$ appearing in the next terms are the second neighbour separation. r_k ($r_{k'}$) is the ionic radii of k (k') ion. n (n') is the number of nearest (next nearest neighbour) ions. The summation is performed over all the kk' ions. b_i and ρ_i are the hardness

and range parameters for the i th cation-anion pair ($i = 1, 2$), respectively, and $\beta_{kk'}$ is the Pauling coefficient [12] expressed as

$$\beta_{kk'} = 1 + \left(\frac{Z_k}{N_k} \right) + \left(\frac{Z_{k'}}{N_{k'}} \right) \quad (2)$$

with Z_k ($Z_{k'}$) and N_k ($N_{k'}$) as the valence and number of electrons in the outermost orbit of k (k') ions, respectively. The model parameters (hardness and range) are determined from the equilibrium condition

$$\left[\frac{d\phi(r)}{dr} \right]_{r=r_0} = 0 \quad (3)$$

and the bulk modulus

$$B = \frac{1}{9Kr_0} \left[\frac{d^2\phi(r)}{dr^2} \right]_{r=r_0} \quad (4)$$

The symbol K is the crystal structure constant, r_0 is the equilibrium nearest neighbor distance of the basic perovskite cell, and B is the bulk modulus. The cohesive energy for $\text{La}_{1-x}\text{Sm}_x\text{CoO}_3$ ($0 \leq x \leq 0.2$) is calculated using (1) and other thermal properties such as the Debye temperature (θ_D), Reststrahlen frequency (ν), molecular force constant (f), Gruneisen parameter (γ), specific heat (C), and thermal expansion (α) are computed using the expressions given in [9, 10]. The results are thus obtained and discussed below.

3. Results and Discussion

3.1. Model Parameters. The values of input data like unit cell parameters and interionic distances for Sm doped LaCoO_3 are taken from [8], for the evaluation of model parameters (b_1 , ρ_1) and (b_2 , ρ_2) corresponding to the ion pairs $\text{Co}^{3+}\text{-O}^{2-}$ and $\text{La}^{3+}/\text{Sm}^{3+}\text{-O}^{2-}$. The values of model parameters (b_1 , b_2 , ρ_1 and ρ_2) are listed in Table 1. The tolerance factor t ($t = (r_A + r_O)/(2(r_B + r_O))$) for these compounds is reported in Table 1, which satisfies the condition that t for a stable perovskite phase is above 0.84 [16]. Depending on the composition of the perovskite, critical radius (r_{cr}) can be calculated by using (5) (Table 1) which describes the maximum size of the mobile ion to pass through. Consider

$$r_{cr} = \frac{a_0 \left((3/4) a_0 - \sqrt{2} r_B \right) + r_B^2 - r_A^2}{2(r_A - r_B) + \sqrt{2} a_0} \quad (5)$$

TABLE 2: Values of bulk modulus, cohesive and thermal properties of $\text{La}_{1-x}\text{Sm}_x\text{CoO}_3$ ($0.0 \leq x \leq 0.2$).

Compound	B_T (GPa)	Cohesive property		Thermal property			
		ϕ (eV) MRIM	ϕ (eV) Kapustinskii Eqn.	f (N/m)	ν (THz)	θ_D (K)	γ
LaCoO_3	180.6	-148.5	-147.5	35.20	9.40	451.9	3.08
$\text{La}_{0.98}\text{Sm}_{0.02}\text{CoO}_3$	184.2	-148.8	-147.9	35.87	9.49	456.0	3.12
$\text{La}_{0.96}\text{Sm}_{0.04}\text{CoO}_3$	187.8	-149.2	-148.2	36.56	9.57	460.2	3.15
$\text{La}_{0.94}\text{Sm}_{0.06}\text{CoO}_3$	189.5	-149.4	-148.4	36.85	9.61	461.9	3.17
$\text{La}_{0.92}\text{Sm}_{0.08}\text{CoO}_3$	195.9	-150.0	-148.9	38.05	9.76	469.1	3.23
$\text{La}_{0.88}\text{Sm}_{0.12}\text{CoO}_3$	211.1	-151.4	-150.5	41.23	10.2	487.9	3.40
$\text{La}_{0.84}\text{Sm}_{0.16}\text{CoO}_3$	217.5	-151.7	-151.1	42.50	10.3	495.1	3.47
$\text{La}_{0.80}\text{Sm}_{0.20}\text{CoO}_3$	221.3	-152.1	-151.5	43.25	10.4	499.1	3.52
Others	180 ^a	-144.54 ^b				480 ^c	

^areference [13], ^breference [14], and ^creference [15].

where r_A and r_B are the radius of the A ion and B ion, respectively, and a_0 corresponds to the lattice parameter ($V^{1/3}$). The condition that critical radius does not exceed 1.05 Å [17] for typical perovskite material is satisfied in our compounds. The values of ionic radii and atomic compressibility for La^{3+} , Sm^{3+} , Co^{3+} , and O^{2-} are taken from [18, 19]. We defined the variance of the La/Sm ionic radii as a function of x , $\sigma^2 = \sum(x_i r_i^2 - r_A^2)$. Here, x_i , r_i , and r_A are the fractional occupancies, the effective ionic radii of cation of La and Sm, and the averaged ionic radius ($r_A = (1-x)r_{\text{La}^{3+}} + xr_{\text{Sm}^{3+}}$), respectively. The effect of ionic radii on tolerance factor and A-site variance is shown in Figure 1. In $\text{La}_{1-x}\text{Sm}_x\text{CoO}_3$, the A-site cation radius reduces with decrease in x , and the buckling of Co-O-Co angle progressively increases with x , which leads to increased distortions of the lattice. Here, we have computed the bulk modulus (B) on the basis of Atoms in Molecules (AIM) theory [20] which emphasizes the partitioning of static thermophysical properties in condensed systems into atomic or group distributions. The computed values of bulk modulus for $\text{La}_{1-x}\text{Sm}_x\text{CoO}_3$ ($0.02 \leq x \leq 0.2$) are in good agreement with value predicted by Cornelius et al. [13].

3.2. Cohesive Energy. The cohesive energy (ϕ) is a measure of the strength of forces that bind atoms together in the solid states and is descriptive in studying the phase stability. The cohesive energy of Sm doped LaCoO_3 is computed using (1) and is reported in Table 2. The negative value of the ϕ indicates that these compounds are stable at ambient temperature. The calculated cohesive energy of $\text{La}_{1-x}\text{Sm}_x\text{CoO}_3$ is quite comparable with the reported value of the lattice energy for SmCoO_3 , -144.54 eV [14]. The variation of the cohesive energy (ϕ) of $\text{La}_{1-x}\text{Sm}_x\text{CoO}_3$ ($0 \leq x \leq 0.2$) as a function of A-site ionic radius is displayed Figure 2. Further, to ascertain the validity of the MRIM, we have used the generalized Kapustinskii equation [21]. The lattice energy obtained using the Kapustinskii equation is close to the MRIM. According to generalized Kapustinskii equation, the lattice energies of crystals with multiple ions are given as

$$U/\text{KJ mol}^{-1} = -\frac{1213.9}{\langle r \rangle} \left(1 - \frac{\rho}{\langle r \rangle}\right) \sum n_k z_k^2, \quad (6)$$

FIGURE 2: Variation of cohesive energy with radius of A-site cation for $\text{La}_{1-x}\text{Sm}_x\text{CoO}_3$ ($0.0 \leq x \leq 0.2$).

where $\langle r \rangle$ = weighted mean cation-anion radius sum and ρ is the average value of model parameters ρ_1 and ρ_2 .

3.3. Thermal Properties. We have also predicted the molecular force constant (f), Reststrahlen frequency (ν), and Gruneisen parameter (γ) for Sm doped LaCoO_3 (Table 2). In the Debye approach, we consider the vibrations of the collective positive ion lattice with respect to the negative ion lattice. The frequency of vibration obtained by this model is also reported here as Reststrahlen frequency. This is clear from Table 2 that as the Sm doping increases the Reststrahlen frequency increases. The Debye temperature estimated for the analysis of specific heat is also reported in Table 2. Our calculated values of Debye temperature for $\text{La}_{1-x}\text{Sm}_x\text{CoO}_3$ ($0.02 \leq x \leq 0.2$) are close to reported value of LaCoO_3 which is 480 K [15]. Since the ionic radius of Sm is larger than that of La, the bulk modulus and other thermal properties systematically increase with increasing x (Table 2). We have

FIGURE 3: Variation of Debye temperature (θ_D) for $\text{La}_{1-x}\text{Sm}_x\text{CoO}_3$ ($0.0 \leq x \leq 2.0$) with molar volume (cm^3) of the basic perovskite cell.

displayed the variation of the Debye temperature (θ_D) of Sm doped LaCoO_3 as a function of molar volume in Figure 3 and the θ_D is observed to be increasing with increasing basic perovskite molar cell volume.

3.4. Specific Heat and Thermal Expansion. The specific heat in the normal state of the material is usually approximated by the contribution of the lattice specific heat. The temperature dependence ($10 \text{ K} \leq T \leq 300 \text{ K}$) of specific heat for $\text{La}_{1-x}\text{Sm}_x\text{CoO}_3$ ($0 \leq x \leq 0.2$) is computed as displayed in Figure 4. We find that when the temperature is below 300 K the specific heat (Figure 4) is strongly dependent on temperature which is due to the anharmonic approximation. However, at higher temperatures, the anharmonic effect on C is suppressed, and C is almost constant at high temperature. The computed results on specific heat for LaCoO_3 compared with the experimental work of Tsubouchi et al. [22] in temperature range ($10 \text{ K} \leq T \leq 300 \text{ K}$) are displayed in the inset of Figure 4. The calculated dependence of C on temperature does not show any anomalous behavior and is in good agreement with the other experimental data [22].

Encouraged by the specific heat results, we tried to compute the thermal expansion coefficient (α) as a function of temperature using the well-known relation, $\alpha = \gamma C / B_T V$, where B_T , V , and C are the isothermal bulk modulus, unit formula volume, and specific heat at constant volume, respectively, and γ is the Gruneisen parameter. It is important to note that in Figure 5 (for 10 K) that thermal expansion shows a significant decrease due to the doping of Sm in LaCoO_3 . Our results on volume thermal expansion coefficients will certainly serve as a guide to experimental workers in future.

4. Conclusion

On the basis of an overall discussion, it may be concluded that the description of the thermodynamic properties of Sm

FIGURE 4: The variation of calculated specific heat of $\text{La}_{1-x}\text{Sm}_x\text{CoO}_3$ ($0.0 \leq x \leq 0.2$) as a function of temperature ($10 \leq T \leq 300 \text{ K}$). The curves of higher cation doping are shifted upward by 10 J each from the preceding curve for clarity. Inset shows the specific heat of LaCoO_3 in the temperature interval ($10 \text{ K} \leq T \leq 300 \text{ K}$) and its comparison with the experimental values [22]. The solid line (—) and open square ($\square$) represent the model calculation and experimental curve, respectively.

FIGURE 5: The variation of thermal expansion (α) with composition (x) in $\text{La}_{1-x}\text{Sm}_x\text{CoO}_3$ ($0.0 \leq x \leq 0.2$) at 10 K.

doped LaCoO_3 given by us is remarkable in view of the inherent simplicity and less parametric nature of the modified rigid ion model (MRIM). Our results are probably the first reports of specific heat and thermal expansion at these temperatures for $\text{La}_{1-x}\text{Sm}_x\text{CoO}_3$ ($0.02 \leq x \leq 0.2$). To the best of our knowledge, the values on bulk modulus, cohesive and lattice

thermal properties for $\text{La}_{1-x}\text{Sm}_x\text{CoO}_3$ ($0.0 \leq x \leq 0.2$) have not yet been measured or calculated, hence our results can serve as a prediction for future investigations.

Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

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