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Thermophysical properties of $Pr_{1-x}Ca_xCoO_3$

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ABSTRACT

In the present paper, the thermophysical properties of $PrCoO_3$ cobaltates is mapped here with reference to the changed local environment at A-site due to calcium doping for the first time using Rigid Ion Model (RIM). The specific heat and there by thermal expansion for temperature ($1\,K \leq T \leq 1000\,K$) of $Pr_{1-x}Ca_xCoO_3$ ($x = 0.0–0.5$) are presented. The trends of variation of our computed results on specific heat with temperature are in more or less similar with corresponding experimental data for almost all the compositions (x) of $Pr_{1-x}Ca_xCoO_3$. Strong electron–phonon interactions are present in these compounds which causes the variation of the lattice specific heat ($C_{v(\mathrm{lattice})}$) with cation doping of varying size and valence. In addition, we have computed the thermal expansion (α), bulk modulus (B), cohesive energy (ϕ), molecular force constant (f), and Restsrahalen frequency (υ) whose results are discussed in detail.

1. Introduction

Recently, physicists are interested in the research of cobaltate, due to a couple of unique properties; namely, the large magnetoresistance (MR) [1], enormous Hall effect [2], the existence of the spin-state transitions [3], and the unusual magnetic ground states of doped cobaltate [4] as well as metal–insulator transitions. The perovskite cobaltates $ACoO_3$ was discovered in 1950s. But they still attracted interest due to a key aspect of cobalt oxides that distinguishes them clearly from the transition metal oxides, i.e. the spin state degree of freedom of the $Co^{3+/III}$ and Co^{IV} ions: it can be low, intermediate and high spin state ($S = 0$, 1, 2 for $Co^{3+/III}$ and $S = 1/2$, 3/2, 5/2 for Co^{IV}). Perovskite cobaltite $ACoO_3$ (A: rare earth element) with a 3D network of corner-sharing CoO_6 octahedra often undergoes a spin state change from low-spin state (LS, $t_{2g}^6\, e_g^0, S = 0$) ground state to intermediate-spin state (IS, $t_{2g}^5\, e_g^1$, $S = 1$) or high-spin state (HS, $t_{2g}^4\, e_g^2$, $S = 2$) with increasing temperature [5]. A spin state transition was also proposed for $PrCoO_3$, for which the $\chi - T$ (χ denotes magnetic susceptibility; and T denotes temperature) curve exhibits a broad minimum at around 200 K [6].

The parent $PrCoO_3$ shows paramagnetic behavior down to 5 K [7]. Pandey el al. [8] studied the electronic states of $PrCoO_3$ using X-ray photoemission spectroscopy and LDA + U density of states calculation and found that $PrCoO_3$ was a charge transfer insulator. Yoshii and Nakamur [9] studied magnetic behavior and showed that $PrCoO_3$ exhibited no magnetic ordering down to 4.5 K. The properties of these materials are expected to be strongly dependent on the average radius of the A-site cation. Substitution of cations with different ionic radii, at the A-site, distorts the structure, introduces disorder, and enhances antiferromagnetic (AFM) superexchange interactions and change the spin state of Co ions. The compound $Pr_{0.7}Ca_{0.3}CoO_3$ has a semiconductor-like and a magnetic cluster-glass behavior [10] below 70 K. The physical properties of these compounds will depend on the average size of the A-site (Pr^{3+} and Ca^{2+}) cations, $\sigma^2 = \sum_i y_i r_i^2 - <r_A>^2$ (where y_i is the fractional occupancy of A-site ions, and r_i is the corresponding ionic radius). In the studies of 'half-doped' perovskite cobaltates, $Pr_{0.5}Ca_{0.5}CoO_3$ behaves anomalously. $Pr_{0.5}Ca_{0.5}CoO_3$ is the first compound in cobalt oxides which describes both the cooperative metal–insulator ($M–T$) and spin state transition in perovskite cobaltates and is considered a strongly correlated spin-crossover system [3,11]. At ambient temperature, they appear in the metallic $t_{2g}^5\sigma^*$ phase as expected but on cooling they undergo a sharp metal–insulator ($M–I$) transition at $T_{M–I} = 90\,K$, documented for the first time by Tsubouchi et al. [3,12]. The same transition was observed also on the less doped samples $Pr_{1-x}Ca_xCoO_3$ ($x = 0.3$) under high pressures or upon a partial substitution of praseodymium by smaller rare earth cations or yttrium [13]. It has been seen that the formal cobalt valency in $Pr_{0.5}Ca_{0.5}CoO_3$ is changed at $T_{M–I}$ from the mixed-valence $Co^{3.5+}$ toward pure Co^{3+} with strong preference for LS state, and the praseodymium valence is simultaneously increased from Pr^{3+} toward Pr^{4+}. $Pr_{0.5}Ca_{0.5}CoO_3$ shows a temperature-induced paramagnetic–paramagnetic

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spin-state transition accompanied by a simultaneous MIT ($T_{M-I} = 70$ K). Recent experiments have proved the possibility of generating metallic domains in the insulating low temperature phase of $Pr_{0.5}Ca_{0.5}CoO_3$ by ultrafast photoexcitation, making this material of interest in the area of ultrafast optical switching devices [14]. In this compound, a spin state transition from IS Co^{3+} to diamagnetic LS Co^{3+} and a charge-ordering of Co^{3+} ($S = 0$) and Co^{4+} sites was proposed as the origin of the MIT transition [3]. The magnetic measurements indicate that the Ca-doped samples ($x = 0$, 0.3, 0.5) have at low temperatures, similar properties to the frustrated magnetic materials. A semiconducting type behavior and high negative magnetoresistance was found for the Ca-doped compounds [15].

The crystal structure of given cobaltates with space group *Pbnm* have an orthorhombic structure and four formula units per unit cell [15]. However, the studies regarding the theoretical understanding of these lattice effects on the thermophysical properties have been initiated by very few researchers whereas it is important to know the effects of doping a cation with different charge and size compared to the host cation on heat conduction of these materials. Taking into consideration these results, the $Pr_{1-x}Ca_xCoO_3$ have been investigated to study their thermophysical properties, temperature dependence of the lattice contribution to the specific heat at constant volume ($C_{v(lattice)}$) and thermal expansion by varying x in the range $0.0 < x < 0.5$. To the best of our knowledge no systematic experimental or theoretical study of thermal properties of these calcium-doped cobaltates was undertaken in the past whereas it is well established that strong electron–phonon coupling is present in these compounds and this electron–phonon interaction is one of the most relevant contributions in determining the conduction mechanism in these cobaltates.

In order to do a systematic analysis of how the specific heat, thermal expansion, cohesive and thermal properties can be tuned by doping, the series of cobaltites $Pr_{1-x}Ca_xCoO_3$ ($0.0 \le x \le 0.5$) is studied as a function of temperature ($0 \le T \le 1000$ K) using RIM. The essentials of RIM formalism and the results obtained from its application are presented in subsequent sections.

2. RIM computations

The potential describing the formalism of RIM is expressed as [18–24]:

$$\phi^R_{kk'}(r) = -\frac{e^2}{2}\sum_{kk'} Z_k Z_{k'} r^{-1}_{kk'} + \sum_i n_i b_i \beta_{kk'} \exp\{(r_k + r_{k'} - r_{kk'})/\rho_i\} + \frac{n'_i}{2} b_i[\beta_{kk}\exp\{(2r_k - r_{kk})/\rho_i\} + \beta_{k'k'}\exp\{(2r_{k'} - r_{k'k'})/\rho_i\}] \quad (1)$$

Here, first term is attractive long-range (LR) coulomb interactions energy and the second term is overlap repulsive energy represented by the Hafemeister–Flygare-type (HF) interaction extended up to the second neighbour. Here, $r_{kk'}$ 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. In ABO_3 (such as $PrCoO_3$) perovskite structure, k represents cation (A, B) and k' denotes the (O_1, O_2) type of ions. b_i and ρ_i are the hardness and range parameters for the ith cation–anion pair (i = 1, 2) respectively and $(_i^{kk'}$ is the Pauling coefficient [25] given by

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

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 model parameters, hardness (b) and range (ρ) parameters are determined from the equilibrium condition:

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

and the bulk modulus:

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

where K is the crystal-structure-dependent constant and r_0 is the equilibrium nearest neighbor distance. The cohesive energy for $Pr_{1-x}Ca_xCoO_3$ ($0.0 \le x \le 0.5$) is calculated using Eq. (1) and other thermal properties, the molecular force constant (f), Restsrahalen frequency (υ), and Debye temperature (θ_D) are computed using the expression given in our previous papers [18–24]. The expression for calculating lattice specific heat is

$$C_{V(\mathrm{lattice})} = 9R\left(\frac{T}{\theta_D}\right)^3 \int_0^{\frac{\theta_D}{T}} \frac{e^x x^4}{(e^x - 1)^2} dx \quad (5)$$

In the above equation R is the universal gas constant and θ_D is the Debye temperature. C_P is formulated by taking into account the important role of the $\alpha^2 B_T VT$ term, which links the measured specific heat with the measured physical properties of solids at high temperature.

$$C_P = C_V + \alpha^2 B_T VT \quad (6)$$

where T is the temperature, B_T is the isothermal bulk modulus, V is the unit cell volume and α is the volume thermal expansion calculated by

$$\alpha = \frac{\gamma C_V}{B_T V} \quad (7)$$

Here B_T, V, C_V are the isothermal bulk modulus, unit formula volume and specific heat at Constant volume respectively and γ is the Gruneisen parameter. The results thus obtained are presented and discussed below.

3. Results and discussion

We have evaluated the model parameters (b, ρ) from Eqs. (3) and (4) by taking the values of the input data like unit cell parameters (a, b, c) and other interionic distances directly from Refs. [3,15–17]. The values of computed model parameters (b_1, ρ_1) and (b_2, ρ_2) corresponding to the ionic bonds Co—O and Pr/Ca—O as a function of temperature are listed in Table 1. The values of b and ρ show decreasing trend with increasing Ca doping. This decreasing trend of hardness parameter (b) with Ca doping indicates the decrease in the strength of the crystal with higher levels of doping. The unit cell parameter (a, b, c) taken from the reported data [3,15–17], are used to calculate the simple perovskie lattice cell parameter (r) in the space group Pbnm for the present compounds [15–17]. The values of ionic radii for Pr^{3+}, Ca^{2+}, Co^{3+}, Co^{4+} and O^{2-} are taken from ref. [26] and the data on atomic compressibility are taken from ref. [27]. In the ideal cubic perovskite structure, RE^{3+} occupies the centre of dodecahedron of oxygen and has an ideal unity value of tolerance factor. The Co—O—Co angle reaches the value 180° which facilitates the exchange interactions and electron hopping. But due to orthorhombic deformation of the lattice, the coordination number of Pr reduces to 9, as three oxygen atoms remain essentially non-bonded due to large Pr^{3+}—O distance. So we considered the ionic radii of A-site cations of coordination number 9 [26] in the