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Thermodynamic Properties of Ni-substituted $LnCoO_3$ Perovskite

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Abstract

With the objective of exploring the unknown thermodynamic properties of Ni-substituted $LnCoO_3$ perovskite, we present here an investigation of the temperature-dependent (10K < T < 300K) specific heat of $LnCo_{0.95}Ni_{0.05}O_3$ (Ln=Pr and Nd) family. We report here probably for the first time the specific heat along with other elastic and thermal properties of Ni doped perovskite cobaltate $LnCoO_3$ (Ln=Pr and Nd). In addition, the results on the cohesive energy (ϕ) in orthorhombic perovskite phase, molecular force constant (f), Reststrahlen frequency (υ_o) and Gruneisen parameter (γ) are also presented.
Keywords: Specific heat, Bulk modulus, Perovskite cobaltate

1. Introduction

Cobaltates 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 $LaCoO_3$ perovskite 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 and the second one is from IS to high spin (HS) state leading to an insulator-metal (I-M) transition around 500 K [3]. Throughout the $LnCoO_3$ series, only $LaCoO_3$ has been analyzed with rhombohedral symmetry 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. Recently, we have applied the modified rigid ion model (MRIM) to study the specific heat and thermal expansion of cobaltates and manganites [4-6]. Motivated from the applicability and versatility of MRIM, we have applied MRIM to investigate the temperature dependence of the specific heat, elastic and thermal properties of $LnCo_{0.95}Ni_{0.05}O_3$ (Ln= Pr, Nd). It is found that the model is successful in describing temperature dependent (10K<T<300K) specific heat (C), cohesive energy (ϕ), molecular force constant (f), Reststrahlen frequency (υ), Debye temperature (θ_D) and Gruneisen parameter (γ) of $LnCo_{0.95}Ni_{0.05}O_3$ (Ln= Pr, Nd) perovskites.

This study is organized as follows: in Sect. 2, we briefly describe the computational method used in this study. Results and discussion of the elastic and thermodynamic properties will be presented and compared with the available experimental data and theoretical results in Sect. 3. Finally, conclusions and remarks are given in Sect. 4.

2. Computational details

The effective interionic potential corresponding to the modified rigid ion model (MRIM) frame work is expressed as [4-6]:

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

Here, first term is attractive long range (LR) coulomb interactions energy. 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 [7]. 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 eqn. (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 ith cation-anion pair (i = 1, 2) respectively and $\beta_{kk'}$ is the Pauling coefficient [8] expressed as:

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

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

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

and the bulk modulus

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

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 $LnCo_{0.95}Ni_{0.05}O_3$ (Ln= Pr, Nd) is calculated using equation (1) and other thermal properties such as the Debye temperature (θ_D), Reststrahlen frequency (υ), molecular force constant (f), Gruneisen parameter (γ) and specific heat (C) are computed using the expressions given in our papers [4-6]. The results are thus obtained and discussed below.

3. Results and discussion

Input data like unit cell parameters (a, b, c) and other interionic distances are taken from refs. [9] for $LnCo_{0.95}Ni_{0.05}O_3$ (Ln= Pr, Nd) for the evaluation of model parameters (b_1, ρ_1) and (b_2, ρ_2) using eqn. (2) and (3) and listed them in Table 1. We have determined the bulk modulus of $LnCo_{0.95}Ni_{0.05}O_3$ (Ln= Pr, Nd) systematically on the basis of formulations of atoms in molecule (AIM) theory [10] and found to be good agreement with earlier report [11]. We have applied MRIM to compute the cohesive and thermal properties of these cobaltates and reported them in Table 2. Due to lack of experimental data on cohesive energy of these compounds the value can only be compared with the value -144.54 eV for $SmCoO_3$ [12] indicating that the compounds are stable at room temperatures. As a check we calculated the cohesive energy of these compounds using the Generalized Kapustinskii Equation [13]. The values are found to be in close agreement with our calculated values.

Table 1. The tolerance factor (t) and model parameters of $LnCo_{1-x}Ni_xO_3$ (Ln=Pr and Nd) perovskites.

Compound	t	ρ_1 (Å) (Co/ Ni-O)	$b_1 \times 10^{-19}$ (J) (Co/ Ni-O)	ρ_2 (Å) (Ln -O)	$b_2 \times 10^{-19}$ (J) (Ln -O)
$PrCo_{0.95}Ni_{0.05}O_3$	0.9296	0.225	1.602	0.396	4.769
$NdCo_{0.95}Ni_{0.05}O_3$	0.9238	0.207	1.438	0.367	4.604

Table 2. Cohesive and Thermal properties of $LnCo_{1-x}Ni_xO_3$ (Ln=Pr and Nd) perovskites.

Compound	B_T (Gpa) (AIM)	ϕ (eV) (MRIM)	ϕ (eV) (Kapustinskii equation)	f (N_n^{-1})	υ (THz)	θ_D (K)	γ
$PrCo_{0.95}Ni_{0.05}O_3$	191.6	-150.3	-148.9	36.6	9.56	459.6	3.09
$NdCo_{0.95}Ni_{0.05}O_3$	213.2	-152.1	-151.0	40.7	10.00	482.4	3.32
Others	211.8[a]		-144.54[b]		8.58[c]		(2-3)[d]

[a] Ref. [11], [b] Ref. [12], [c] Ref. [14], [d] Ref. [15]

The Reststrahlen frequency of these compounds is close to reported value of 8.58 THz for manganites [14] and the value of Gruneisen parameter is close as reported earlier [15] but lack of experimental results on these properties restrict us in predicting the accuracy of these values. Besides, we studied the temperature evolution of the lattice specific heat (Cp) of $PrCo_{0.95}Ni_{0.05}O_3$ (Fig. 1(a)) and of $NdCo_{0.95}Ni_{0.05}O_3$ over the temperature range $10K \leq T \leq 300K$ (Fig. 1(b)).

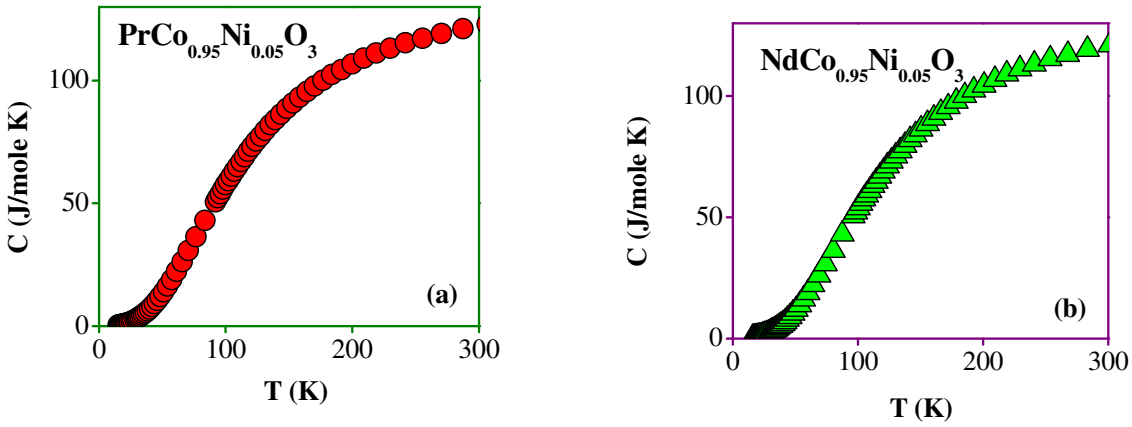

Fig. 1. The variation of calculated specific heat of (a) $PrCo_{0.95}Ni_{0.05}O_3$ and (b) $NdCo_{0.95}Ni_{0.05}O_3$ as a function of temperature ($10 \leq T \leq 300$ K).

Our results are probably, the first reports of lattice specific heat at these temperatures and compositions. It can be concluded that MRIM is successful in predicting the thermal and elastic properties of $LnCo_{0.95}Ni_{0.05}O_3$ (Ln=Pr, Nd) and the findings indicate that Debye temperature increases and cohesive energy decreases with the decrease of tolerance factor. The increase in θ_D indicates that an anomalous hardening of the lattice or decrease in T^3-term in the specific heat occurs as we move from $PrCo_{0.95}Ni_{0.05}O_3$ to $NdCo_{0.95}Ni_{0.05}O_3$ cobaltates.

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References

[1] T. Inagaki, K. Miura, H. Yoshida, R. Maric, S. Ohara, X. Zhang, K. Mukai, T. Fukui, J. Power Sources 86 (2000) 347.

[2] C.H. Chen, H.J.M. Bouwmeester, R.H.E. van Doorn, H. Kruidhof, A.J. Burggraaf, Solid State Ionics 98 (1997) 7.

[3] S. Yamaguchi, Y. Okimoto, H. Taniguchi, Y. Tokura, Phys. Rev. B 53 (1996) R2926.

[4] Rasna Thakur, Archana Shrivastava, Rajesh K. Thakur, N.K. Gaur, J. Alloys Comp. 516 (2012) 58-64.

[5] Rasna Thakur, N.K. Gaur, J. Solid State Chem. 201 (2013) 107-114.

[6] Rajesh K. Thakur, Rasna Thakur, S. Shanmukhrao Samatham, N. Kaurav, N.K. Gaur, V. Ganesan, G.S. Okram, J. Appl. Phys. 112 (2012) 104115.

[7] J.C. Slater, J.G. Kirkwood, Phys. Rev. 37 (1931) 682.

[8] L. Pauling, Nature of the Chemical Bond (Ithaca, NY: Cornell University Press, 1945).

[9] M. H. Aguirre, R. Robert, D. Logvinovich, A. Weidenkaff, Inorg Chem. 46 (2007) 2744-2750.

[10] A.M. Pendas, A. Costales, M.A. Blanco, J.M. Recio, V. Luana, Phys. Rev. B 62 (2000) 13970-78.

[11] A.S. Verma, A. Kumar, J. Alloys Comp. 541 (2012) 210–214.

[12] M.A. Farhan, M.J. Akhtar, J. Phys.: Condens. Matter 22 (2010) 075402.

[13] L. Glasser, Inorg. Chem. 34 (1995) 4935.

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