

Effect of Mo Doping on Thermodynamic Properties of $\text{SrCoO}_{3-\delta}$

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Abstract. The effects of doping Mo in $\text{SrCoO}_{3-\delta}$ on the elastic and thermal properties have been studied at temperature $10\text{K} \leq T \leq 1000\text{K}$ by using Modified Rigid Ion Model (MRIM). The model has been applied to describe the temperature dependence of specific heat and thermal expansion coefficient. Also, the calculated bulk modulus (B), Reststrahlen frequency (ν), cohesive energy (ϕ), Debye temperature (θ_D) and Gruneisen parameter (γ) are reported and discussed.

INTRODUCTION

The introduction of Mo as a substitution for Co in $\text{SrCoO}_{3-\delta}$ leads to a change from a hexagonal to a tetragonal perovskite structure at room temperature. The electrical conductivity is largely enhanced by the introduction of Mo at intermediate temperature due to the stabilization of the 3D-perovskite structure. However, the increase in Mo content decreases the total conductivity probably due to partial disruption of the electronic pathway. The use of these materials as cathodes in a solid-oxide fuel cell (SOFC) and as anodes in a solid oxide electrolyzer (SOE) have been evaluated [1], showing low values of electrode polarization resistances in both configurations over the intermediate temperature range. The good performance of the $\text{SrCo}_{1-x}\text{Mo}_x\text{O}_{3-\delta}$ compounds in both cathodic and anodic conditions makes this system a promising candidate for reversible oxygen electrodes in cells that could operate as both SOFC and SOE.

Recently we have successfully described the thermal properties of some perovskite manganites and other compounds over a fairly wide range of temperatures [2-4] by means of MRIM. Motivated by the unusual thermodynamic behavior and spin transitions of orthocobaltate, we have applied modified rigid ion model (MRIM) and successfully explored the specific heat (C), thermal expansion (α), cohesive energy (ϕ), molecular force constant (f), Reststrahlen frequency (ν), Debye temperature (θ_D) and Gruneisen parameter (γ) of the $\text{SrCo}_{1-x}\text{Mo}_x\text{O}_{3-\delta}$ perovskites. The study of the lattice thermal properties of these compounds may be taken as starting point for the consistent understanding of the more complex physical properties of the rare earth orthocobaltate. The essentials of the MRIM formalism and the results obtained from its application are discussed below.

MATHEMATICAL MODELING

The formalism of Modified Rigid Ion Model (MRIM) has been derived for the following effective interatomic potential [2-4].

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

The symbols involved are in it are the same as those defined in our earlier papers [2-4]. Here, k (k') denotes the positive (negative) ions and the sum is taken over all the ions (k, k') and the $\beta_i^{kk'}$ is the Pauling coefficient [5] given by:

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

where Z_k ($Z_{k'}$) and N_k ($N_{k'}$) are the valence and the number of electrons in the outermost orbit of the k (k') ion, respectively. The contributions of van der Waals (vdW) attraction for the dipole-dipole interaction are determined by using Slater- Kirkwood Variational (SKV) method [6].

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

Here e and m are the charge and mass of the electron, α_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') ions, respectively. The model parameters, hardness (b) and range (ρ) are determined from the equilibrium condition:

$$\left[d\phi/dr \right]_{r=r_0} = 0, \quad (4)$$

and the bulk modulus,

$$B = 1/9Kr_0 \left[d^2\phi/dr^2 \right]_{r=r_0}, \quad (5)$$

where K is the crystal structure-dependent constant and r_0 is the equilibrium nearest neighbour distance. The model parameters (b and ρ) obtained from the Eqn. (4) and (5) have been used to compute the thermodynamic properties of $\text{SrCo}_{1-x}\text{Mo}_x\text{O}_{3-\delta}$ perovskites. The lattice specific heat is calculated using the formula

$$C_{v(\text{lattice})} = 9R \left(\frac{T}{\theta_D} \right)^3 \int_0^{\theta_D/T} \frac{e^{-x} x^4}{(e^{-x} - 1)^2} dx. \quad (6)$$

And at very low temperature ($T < \theta_D / 50$) the specific heat is calculated by using

$$C_{v(\text{lattice})} = \frac{12\pi^4}{5} \left[Nk_B \left[\frac{T}{\theta_D} \right]^3 \right] p, \quad (7)$$

here p is the number of atoms in one formula unit, N is the Avogadro number, k_B the Boltzmann constant, R is the universal gas constant and θ_D is Debye temperature. The cohesive energy for $\text{SrCo}_{1-x}\text{Mo}_x\text{O}_{3-\delta}$ is calculated using equation (1) and other thermal properties such as the Debye temperature (θ_D), Reststrahlen frequency (ν), molecular force constant (f), Gruneisen parameter (γ), and thermal expansion (α) are computed using the expression given in our earlier publication [2-4]. The results are thus obtained and discussed below.

RESULTS & DISCUSSION

To decipher the exotic properties of these technologically important materials, input data are taken from refs. [1] for the calculation of model parameters (b_1 , ρ_1 and b_2 , ρ_2), for the desired compositions (x) and listed them in Table 1. As the cation radius decreases down the series, the tolerance factor $t = (r_{Sr} + r_o) / \sqrt{2} (r_{Co/Mo} + r_o)$, where r_{Sr} is the ionic radius of Sr site, $r_{Co/Mo}$ is the ionic radius of cobalt and molybdenum and r_o in the ionic radius of oxygen, whose value for $\text{SrCoO}_{3-\delta}$ cubic structure is around 1, also reduces (Table 1), so the structure progressively deviates from the cubic to the tetragonal form. From Table 1, all compositions could form a stable perovskite structure, but

the stability showed a trend to decrease slightly with increasing Mo doping. The cations-size disorder parameter (σ^2) calculated on the lines of our previous work [2-4] is depicted in Table 1. The thermal properties, such as cohesive energy (ϕ), molecular force constant (f), Debye temperature (θ_D), Reststrahlen frequency (ν) and Gruneisen parameter (γ) have been calculated and their values are listed in Table 2. Due to the lack of experimental and theoretical data, we could not compare them.

TABLE 1. Tolerance factor, variance model parameters of $\text{SrCo}_{1-x}\text{Mo}_x\text{O}_{3-\delta}$ system.

Doping concentration x	Tolerance Factor t	Variance σ^2 (\AA^2)	Model Parameters			
			$b_1 \times 10^{-19}$ (J) (Co/Mo-O)	$b_2 \times 10^{-19}$ (J) (Sr-O)	ρ_1 (\AA) (Co/Mo-O)	ρ_2 (\AA) (Sr-O)
0.05	1.036	0.026718	1.94	5.36	0.233	0.423
0.10	1.032	0.150625	2.03	5.41	0.240	0.435

TABLE 2. Values of bulk modulus, cohesive and thermal properties of $\text{SrCo}_{1-x}\text{Mo}_x\text{O}_{3-\delta}$ compounds.

Doping concentration x	Bulk modulus B (GPa)	Cohesive Properties		Thermal Properties			
		ϕ (eV) (MRIM)	ϕ (eV) (Kapustinskii equation)	f (N/m)	ν (THz)	θ_D (K)	γ
0.05	177.0	-157.4	-157.2	35.05	10.4	503.1	2.98
0.10	169.2	-156.4	-155.6	33.57	10.2	490.5	2.92

On the basis of above discussion we have also calculated the specific heat for $\text{SrCo}_{1-x}\text{Mo}_x\text{O}_{3-\delta}$ compounds over the temperature range $1\text{K} \leq T \leq 300\text{K}$ and the results are displayed in Fig. 1(a). From Fig. 1(a) it is clear that the nature of graph satisfies the well known relation $C=3R$ at higher temperature. The nature of specific heat curve in this work is found to be similar to other available results. The conclusion is supported by thermal expansion as depicted in Fig. 1(b) and observed to be increasing with increase in Mo concentration in $\text{SrCoO}_{3-\delta}$.

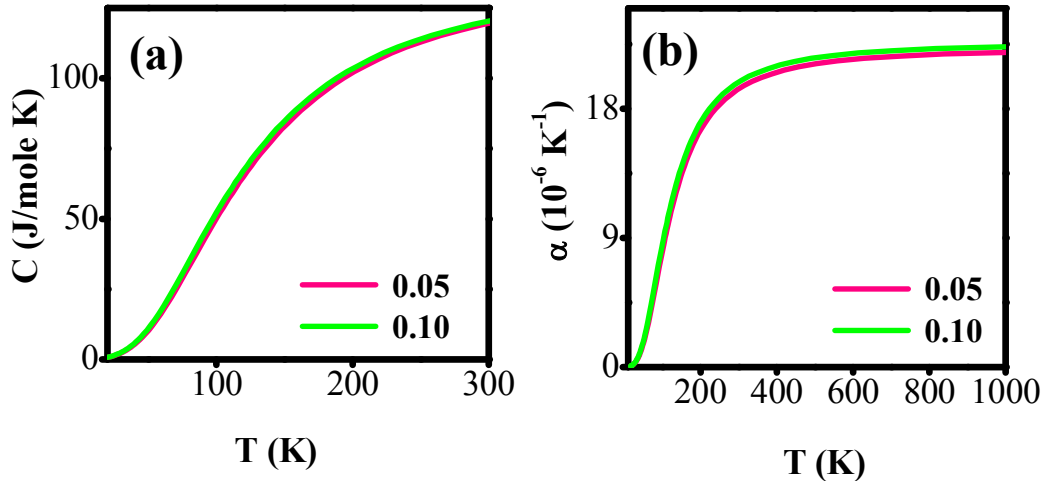


FIGURE 1. (a) Lattice specific heat of $\text{SrCo}_{1-x}\text{Mo}_x\text{O}_{3-\delta}$ in 1K to 300K temperatures and (b) Variation of thermal expansion of $\text{SrCo}_{1-x}\text{Mo}_x\text{O}_{3-\delta}$ in 10K to 1000K temperatures.

We have found that in B-site doped oxygen deficient cobaltates, the Debye temperature (θ_D) decreases with increasing level of doping (x) in $\text{SrCo}_{1-x}\text{Mo}_x\text{O}_{3-\delta}$. The specific heat correspondingly increases with increasing doping levels. The decrease in θ_D indicates that an anomalous softening of the lattice or increase in T^3 -term in specific heat occurs with the increase of doping. Our results are probably, the first reports of lattice specific heat at these temperatures and compositions.

ACKNOWLEDGEMENT

The author Rasna Thakur is thankful to UGC, New Delhi for the award of Post-Doctoral Fellowship.

REFERENCES

1. A. Aguadero, D. Perez-Coll, J.A. Alonso and S.J. Skinner, J. Kilner, *Chem. Mater.* **24**, 2655(2012).
2. Rasna Thakur, Rajesh K. Thakur and N.K. Gaur, *J. Alloys and Compd.* **661**, 257-267(2016).
3. Rasna Thakur, Rajesh K. Thakur and N.K. Gaur, *Thermochim. Acta* **584**, 79-82(2014).
4. Rasna Thakur, Rajesh K. Thakur and N.K. Gaur, *Appl. Phys. A* **118**, 869-876(2015).
5. L. Pauling, *Nature of the Chemical Bond*, NY: Cornell University Press, Ithaca, 1945.
6. J.C. Slater and J.G. Kirkwood, *Phys. Rev.* **37**, 682-697(1931).