The Effect of Potassium Doping on Specific Heat of Rare Earth Manganite $RMnO_3$(R=La, Pr).

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Abstract

We probe the physical properties of rare earth manganites $R_{1-x}K_xMnO_3$(R=La, Pr) like thermal expansion and Specific heat for their possible use as magnetic refrigerant material. Effect of Potassium doping (K^+ at the A-site) on the thermal properties of perovskite $RMnO_3$ has been considered in this investigation using the Modified Rigid Ion Model (MRIM)). The specific heat of magnetocaloric compounds $La_{1-x}K_xMnO_3$, and $Pr_{1-x}K_xMnO_3$ as a function of temperature ($20K \leq T \leq 1000K$) is reported. In addition, the results on the cohesive energy (ϕ), molecular force constant (f), Reststrahlen frequency (ν_o), Debye temperature (Θ_D) and Gruneisen parameter (γ) are also discussed. The monovalent cation (K^+) doping results in anomalous change in Debye temperature for heavily doped $La_{1-x}K_xMnO_3$ beyond x=0.5. The Specific heat decreases with increase in content of potassium doping in $La_{1-x}K_xMnO_3$ compound and it comes to a minimum for x=0.5 and then specific heat increases with further increase in doping concentration of Potassium in the $LaMnO_3$.

Keywords: Specific Heat, Magnetocaloric compounds, Thermal Properties, Bulk modulus, Colossal Magnetoresistance material, Manganites.

Introduction

Perovskite rare earth manganites doped with bivalent or monovalent cations $R_{1-x}A_xMnO_{3+\delta}$ (where R is rare earth cation and A is doping cation) were intensively studied over last decade as materials possessing Colossal Magnetoresistance and Magnetocaloric effect. $La_{1-x}K_xMnO_3$ compounds possess a magnetocaloric effect (MCE) around room temperature, which is comparable to that of Rare Earth element and its compounds. The relative cooling power (RCP) of $La_{1-x}K_xMnO_3$ compounds is estimated to be about one-third of that of the prototype magnetic refrigerant material (pure Gd) [1]. It was reported that substitution of monovalent ions (K^+, Rb^+, Na^+, Ag^+) for La in $LaMnO_3$ results in increased magneto-resistance [2] and magneto-caloric effect [3].

Colossal Magnetoresistive (CMR) or Magnetocaloric behaviour of manganese perovskite can be understood in terms of the coupling between the carriers and the lattice and it is established that it can be substantially modulated by doping [4]. The conduction mechanism in manganites is through the Double Exchange (DE) interaction and Super Exchange (SE) interactions which is affected by buckling of Mn-O-Mn angle or the so called tilting of MnO_6 Octahedra. Change in the ionic radius of the A and B site in ABO_3 perovskite type manganese oxides due to doping of another cation of different valence and size modifies the bond angle Mn-O-Mn.

The monovalent potassium is found to be substitutional for Lanthanum and Praseodymium and enters the A-site of the manganite perovskite structure. Substitution of K^+ ion for R^{3+} in $R^{3+}K^+MnO_3$ (R=La, Pr) forces two Mn^{3+} ions to change their valence state to Mn^{4+}, thus facilitating the double exchange interactions and stabilizing the ferromagnetic state at lower temperatures.

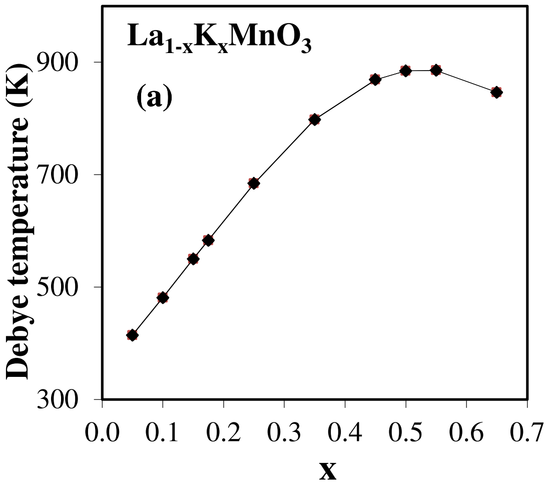

Figure 1 (a) Variation of Debye temperature of La$_{1-x}$K$_x$MnO$_3$ in low temperature (LT) and high temperature (HT) region against doping level x of potassium.

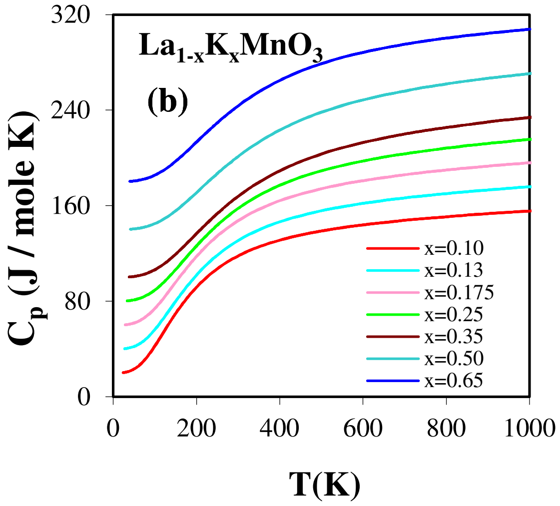

Fig 1(b) Lattice specific heat at constant pressure (C_p) of La$_{1-x}$K$_x$MnO$_3$ (x=0.10, 0.13, 0.175, 0.25, 0.35, 0.50, 0.65) in 20K to 1000K.

The valence states of manganese further changes from Mn^{4+} to Mn^{5+} with K-doping beyond the doping level of 50% (for x> 0.5) and then, much smaller radius of Mn^{5+} and Jahn-Teller effects strengthening with Mn^{5+} content respectively lead to the lattice parameters lowering [5].

However, monovalent Potassium doping in place of trivalent Lanthanum or Praseodymium cation in $LaMnO_3$/$PrMnO_3$ introduces charge mismatch at A-site that changes the interaction potential at the local site. The size mismatch at A-site is significantly high due to large size of K^+ (1.60Å) compared to lanthanides La/Pr (1.36 Å /1.16 Å). This local potential created in the vicinity of potassium by difference of the ionic radii and valency of Pr^{3+} and K^+ ions traps the charge carriers and lead to insulating behaviour [6] in $Pr_{0.85}K_{0.15}MnO_3$ that register absence of I-M transition despite 30% of Mn^{4+} cation. However, the K doped $LaMnO_3$ compounds show sharp metal–insulator transition and the conductivity of the system enhances with increase in K doping. The Curie temperature (T_C) is enhanced from 260 to 310K with K substitution [7] in $LaMnO_3$. This contrast behaviour is quite intriguing and warrants some atomistic investigations to understand the factors responsible for such results.

Apart from magnetic studies, some results on the specific heat and structural investigation were reported recently for the $La_{1-x}K_xMnO_3$ and $Pr_{1-x}K_xMnO_3$ compounds. These results served as input data for our investigation using MRIM (Modified Rigid Ion Model) in deciphering the thermal and elastic behaviour of these manganites. Recently MRIM has been applied successfully for several Manganites[8-10], Cobaltates [11] and Silicates [12] by our group and results are in agreement with the previously published results. So, we thought of making a systematic investigation of elastic, cohesive and thermal properties of these compounds to chalk out the effect of size and charge mismatch and tilt of MnO_6 octahedra on them. We studied the effect of change in valence and size of dopant cation on the thermal and elastic properties of manganites with the help of MRIM model. The present study suggests that the large size mismatch between La^{3+}/Pr^{3+} and K^+ play a major role in altering the local lattice environment that affect the carrier transport properties in perovskite manganites. These results are the first reports on physical properties of these compounds using MRIM. Since no results exist on elastic properties on these manganites so the presented results can work as reference data for the future workers.

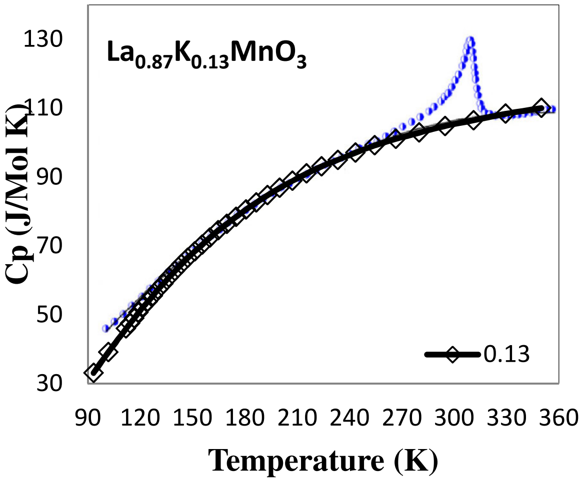

Fig. 3 Lattice specific heat of $Pr_{0.85}K_{0.15}MnO_3$ and its comparison with experimental values of Hejtmanek et al. [6].

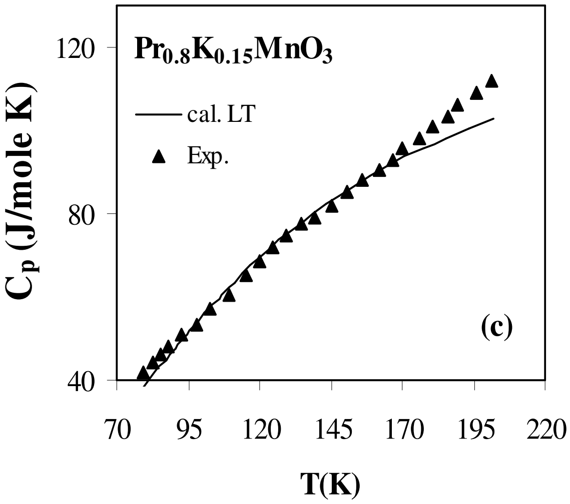

Fig. 4 Lattice specific heat of $Pr_{0.85}K_{0.15}MnO_3$ and its comparison with experimental values of Hejtmanek et al. [6].

All studied samples of $La_{1-x}K_xMnO_3$ are Rhombohedra in structure within R3c space group in the entire doping range (from x=0.05 to 0.65) whereas $Pr_{1-x}K_xMnO_3$ belong to orthoperovskites of the Pbnm symmetry with cooperative tilting of MnO_6 octahedra (so-called buckling) [1, 5-7]. However, for $Pr_{1-x}K_xMnO_3$, the maximum solubility of potassium in $PrMnO_3$ is estimated to be around x=0.175 due to larger size mismatch between Pr (1.16 Å, CN 12) and K^+ (1.60Å, CN 12). The interaction potential used in this investigation for these monovalent doped compounds is presented in next section and results obtained with the applications of our model potential are revealed and discussed in the subsequent sections.

Interaction Potential

Modified Rigid Ion Model (MRIM) have the effect of long-range Coulomb attractions, the short-range Hafemeister-Flygare-type [13] overlap repulsion effective up to the next nearest neighbour atoms and the van der Waals attraction due to dipole-dipole interactions. The potential describing the formalism of MRIM is expressed

$$\phi_{kk'}(r) = -\frac{e^2}{2}\sum_{kk'} Z_k Z_{k'} r_{kk'}^{-1}$$

as
$$+\sum_i n_i b_i \beta_{kk'} \exp\{(r_k + r_{k'} - r_{kk'})/\rho_i\} \qquad (1)$$
$$+\frac{n_i'}{2} b_i \left[\begin{array}{l}\beta_{kk}\exp\{(2r_k - r_{kk})/\rho_i\} \\ +\beta_{k'k'}\exp\{(2r_{k'} - r_{k'k'})/\rho_i\}\end{array}\right]$$

Here, first term is attractive long range (LR) coulomb interactions energy. The second term represents the contributions of van der Waal's (vdW) attraction for the dipole-dipole interaction and is determined by using the Slater- Kirkwood Variational (SKV) method [14] as defined in our earlier papers [8-10]. The third 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. b_i and ρ_i are the hardness and range parameters for the i^{th} cation-anion pair (i = 1, 2) respectively and $\beta_i^{kk'}$ is the coefficient given by Pauling [15]

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

Table 1 The A-site average cation radius (r_A), bulk Modulus and model parameters for $La_{1-x}K_xMnO_3$ and $Pr_{1-x}K_xMnO_3$ system. R and O indicates rhombohedra structure.

Doping concentration x/Structure		**r_A (Å)**	**Bulk modulus B_O (GPa)**	**Model Parameters**			
$La_{1-x}K_xMnO_3$				**b_1x10^{-19} (J) (Mn-O)**	**b_2 x10^{-19} (J) (La /K-O)**	**ρ_1 (Å) (Mn-O)**	**ρ_2 (Å) (La /K-O)**
0.10	R	58.1	1.389	0.074	0.493	0.114	0.212
0.13	R	49.7	1.400	0.036	0.305	0.093	0.175
0.175	R	46.1	1.406	0.027	0.249	0.086	0.161
0.25	R	37.6	1.424	0.011	0.142	0.070	0.132
0.35	R	29.8	1.447	0.005	0.090	0.059	0.112
0.50	R	22.2	1.483	0.006	0.099	0.058	0.109
0.65	R	17.2	1.518	0.027	0.236	0.071	0.133
$Pr_{1-x}K_xMnO_3$							
0.05	O	1.199	97.3	0.190	0.569	0.181	0.265
0.100	O	1.217	80.8	0.152	0.522	0.164	0.247
0.15	O	1.236	68.1	0.135	0.506	0.154	0.237

Table 2 Lattice distortions and A-site cation variance of $La_{1-x}K_xMnO_3$ and $Pr_{1-x}K_xMnO_3$ compounds

Doping concentration X	Variance σ^2 (Å^2)	Lattice Distortions			
		Jahn- Teller distortion Δ_{JT} x10^{-3}	A-site charge mismatch σ_c	A-site size mismatch σ_m	octahedral rotation ϕ_S
0.100	49.70	0.00	1.143	2.23	0.977
0.150	70.41	0.00	1.222	2.29	0.977
0.175	79.73	0.00	1.264	2.33	0.977
0.250	103.55	0.00	1.400	2.42	0.977
0.350	125.64	0.00	1.609	2.56	0.977
0.500	138.06	0.00	2.000	2.80	0.977
0.650	125.64	0.00	2.529	3.23	0.977
$Pr_{1-x}K_xMnO_3$					
0.05	65.03	41.23	1.069	1.89	0.975
0.10	123.21	4.12	1.143	1.96	0.980
0.15	174.55	4.80	1.222	2.02	0.982

Table 3 Cohesive and thermal properties of $La_{1-x}K_xMnO_3$ and $Pr_{1-x}K_xMnO_3$ system at low temperatures. R and O indicates Rhombohedra and Orthorhombic structure.

Doping x and structure		Cohesive Properties		Thermal Properties				
$La_{1-x}K_xMnO_3$		Φ (eV) MRIM	Φ (eV) Kapustinskii equation	f N/m	ν THz	Θ_D (K)	γ	α x 10^{-7} (K^{-1}) at 10K
0.10	R	-151.1	-147.6	36.11	9.9	473.6	3.18	0.440
		-139.7[a]				532[b]	(2-3)[c]	
0.13	R	-156.2	-152.2	44.46	11.1	532.9	3.63	0.286
						559[b]		
0.18	R	-158.8	-153.9	48.31	11.7	559.5	3.79	0.239
0.25	R	-164.7	-158.7	59.61	13.3	635.3	4.35	0.151
0.35	R	-170.7	-163.1	69.22	14.7	706.1	4.76	0.104
0.50	R	-176.6	-166.2	67.77	15.3	734.6	4.55	0.090
0.65	R	-178.6	-168.5	52.56	14.3	684.1	3.70	0.117
$Pr_{1-x}K_xMnO_3$								
0.05	O	-143.2	-143.3	25.18	8.1	389.2	2.56	0.969
0.10	O	-147.2	-145.9	27.79	8.7	414.5	2.67	0.768
0.15	O	-150.2	-147.8	29.31	9.0	431.6	2.72	0.662

[a] ref.[18] , [b] ref.[7], [c] ref.[19]

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 two equilibrium condition:

$$[d\phi/dr]_{r=r_0} = 0 \quad \text{and} \quad B = 1/9Kr_0\left[d^2\phi/dr^2\right]_{r=r_0} \qquad (3)$$

where B is Bulk modulus, K is the crystal-structure-dependent constant and r_0 is the equilibrium nearest neighbour distance. The AIM (Atoms in Molecules) theory by Pendas et al. [16] is the used to determine the bulk modulus for the these manganites which in turn is used in Eqn. (3) to determine the equilibrium conditions of the lattice as explained in our previous papers [8-10].

When we consider the doping at the A-site in $RMnO_3$ (R=La, Pr) compounds then the local compressibility of impurities with respect to host ions are governed by the size difference and tuned by the formal charge mismatch between host and guest cations. We considered the effect of charge and size mismatch along with the octahedral distortions due to Jahn-Teller effect on the bulk modulus of the compounds. These factors will determine the change in the unit cell volume that in turn will change the global bulk modulus of the compound on the lines of our previous papers [8-10]

The values of bulk modulus of Potassium doped rare earth manganites obtained by the application of AIM theory are presented in table 1 and they are used for the determination of model parameters

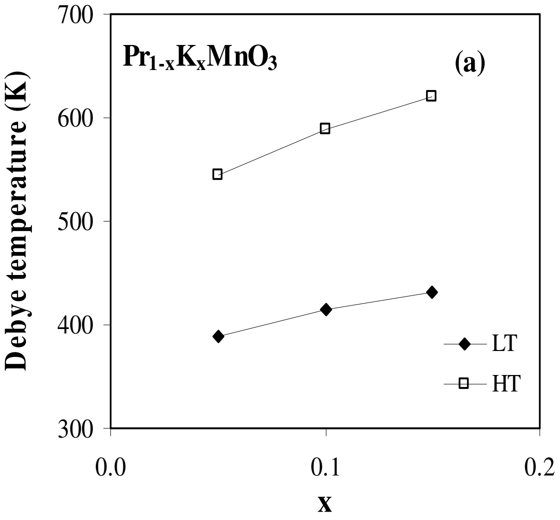

Figure 4 (a) Variation of Debye temperature of $Pr_{1-x}K_xMnO_3$ in low temperature (LT) and high temperature (HT) region against doping level x of potassium at A-site

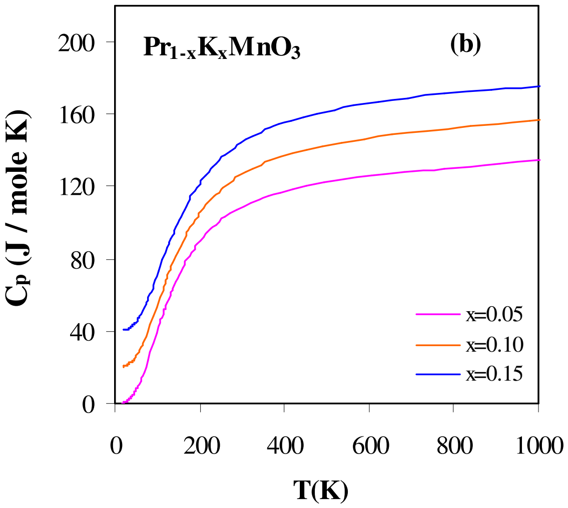

Fig.4 (b) Lattice specific heat at constant pressure (C_p) of $Pr_{1-x}K_xMnO_3$ (x= 0.05, 0.10, 0.15,) in 20K to 1000K temperature. All the curves have been shifted by 20J each from the preceding curve for clarity. The curve for x=0.05 is undisplaced.

through equation 3. The cohesive energy for $(Pr/La)_{1-x}K_xMnO_3$ is calculated using equation (1) and other thermal properties, the molecular force constant (f), Reststrahlen frequency (ν_o), Debye temperature (θ_D), Gruneisen parameter (γ) are computed using the expression given in our previous papers [8-10].

The expression for calculating lattice specific heat is

$$C_{V\,(lattice)} = 9R\left(\frac{T}{\theta_D}\right)^3 \int_0^{\frac{\theta_D}{T}} \frac{e^x x^4}{e^x - 1} dx \qquad (6)$$

where R is the universal gas constant and θ_D is the Debye temperature.

Results and Discussions

The values of input data like unit cell parameters (a, b, c) and some interionic distances are taken from refs. [1,5-7] for $La_{1-x}K_xMnO_3$ and $Pr_{1-x}K_xMnO_3$ and the model parameters, lattice distortions, elastic and thermal properties of the compounds are determined on the similar lines as described earlier and results are presented in Table 1, 2 and 3. Presented results are the first reports on specific heat, thermal and elastic properties of these compounds using the MRIM. Our results on Debye temperature at low doping concentrations in spin ordered state are comparable to the reported value of Das et al., [7]. Also, Fig.1 (a) presents the variation of Debye temperature of $La_{1-x}K_xMnO_3$ in spin ordered low temperature region against doping level x of potassium at A-site and Fig.1(b) presents the lattice specific heat at constant pressure (C_p) of $La_{1-x}K_xMnO_3$ (x= 0.10, 0.13, 0.175, 0.25, 0.35, 0.50, 0.65) in 20K to 1000K temperature interval. Fig. 2 shows the match of calculated specific heat for $La_{1-x}K_xMnO_3$ (x=0.13) with experimental data of Gamzatov et al.[17] and the match is satisfactory in the temperature range of 100K to 360K except for the peak observed in the experimental results around the Curie temperature Tc of the compound due to spin ordering. This peak can be reproduced in the calculate value by taking the term representing the spin interactions within the framework of MRIM. Fig 3 presents the lattice specific heat of $Pr_{0.85}K_{0.15}MnO_3$ and its comparison with experimental values of Hejtmanek et al[6]. Presented results for $Pr_{1-x}K_xMnO_3$ are the first reports on specific heat, thermal and elastic properties of these compounds using the MRIM. Figure 4 (a) depicts the variation of Debye temperature of $Pr_{1-x}K_xMnO_3$ in spin ordered low temperature (LT) and high temperature paramagnetic (HT) region against doping level x of potassium at A-site and Figure 4(b) presents the lattice specific heat at constant pressure (C_p) of $Pr_{1-x}K_xMnO_3$ (x= 0.05, 0.10, 0.15,) in 20K to 1000K temperature interval.

Conclusions

We studied the doped $La_{1-x}K_xMnO_3$ (x=0.10-0.65) and $Pr_{1-x}K_xMnO_3$(x=0.05-0.175) and reported the static thermal, elastic and cohesive properties along with specific heat of the compounds in the temperature range 20K to 1000K using the Debye approach. We have found that in Potassium-doped materials, the Debye temperature increases with increasing potassium doping up to x=0.5 that is up to 50% doping and it decreases after this doping. This behaviour is unique for this monovalent doping and no such anomalous softening of lattice is observed for divalent, trivalent or tetravalent doping in manganites. The specific heat also increases with increasing doping level (x) up to x=0.5. The decrease in θ_D indicates that an anomalous softening of the lattice occurs with the increase of potassium content in heavily doped compounds. Our results are probably the first reported values of lattice specific heat at these temperatures and doping and some of our reported results show satisfactory match with experimental data. We have also reproduced systematically cohesive and elastic properties of the lattice with varying potassium content of the lattice. Also, the negative value of lattice energy shows the stability of the compound. the results on cohesive energy were found to be in good agreement with the results using well known Kapustinskii equation for ionic crystals. Our present results show that more potassium doped compounds are less stable. On the basis of above discussion it can be concluded that heavy potassium cation doping (above x=0.5) at the A-site changes the thermal properties of $LaMnO_3$ in a very significant manner. The compound becomes less stable by heavy doping and its Debye temperature reduces appreciably.

A satisfactory prediction of the temperature-dependent thermal properties of potassium doped $LaMnO_3$ ans $PrMnO_3$ and close match with experimental data is remarkable in view of inherent simplicity and less parametric nature of modified rigid ion model (MRIM). Present results can further be improved by incorporating the effect of the magnetic interactions due to spin ordering and charge ordering in the modified RIM.

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