

Theoretical Investigations of Complex Perovskite Oxides with Tetravalent Cation Doping at A-site to Establish the Role of Lattice Distortions

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Abstract. We have investigated the lattice distortions due to charge and size mismatch in complex oxides $(La, Y)_{1-x}(Te^{4+}, Zr^{4+})_xMnO_3$ and its effect on elastic and thermal properties of these complex perovskite manganites. The revealed data on specific heat, thermal expansion, Debye temperature and Bulk modulus studied as a function of lattice distortions using a novel atomistic approach of Atom in Molecules (AIM) theory and Modified Rigid Ion Model (MRIM) are presented for some concentrations (x) of $(La, Y)_{1-x}(Te^{4+}, Zr^{4+})_xMnO_3$ in a wide temperature range. Studied compounds exhibit anomalous increase in Bulk modulus and Debye temperature with increase in doping concentration of tetravalent Te^{4+} and Zr^{4+} cations at A-site. These compounds give us an unique opportunity to observe the effect of charge and size variance at A-site in perovskite structure without the effect of JT distortions due to occurrence of these compounds in Rhombohedra and hexagonal symmetry with high variance.

INTRODUCTION

Doped perovskite oxides are a class of materials having the general formula $(R_{1-x}A_x)(Mn_{1-y}B_y)O_3$, which can adopt the some of the most distorted variant of ideal cubic structure of perovskite $GdFeO_3$. They are found with varying degree of distortions with spectacular range of physical and magnetic properties. The most common distortions observed in these oxides are due to charge and size mismatch of cations at A and B-site, buckling of super-exchange angle (B-O-B), and Jahn-Teller (JT) distortions of MnO_6 octahedron within the intertwined structure of cations and octahedrons. These distorted oxides are potential candidates for new magnetic recording devices, cathode materials for Solid Oxide Fuel Cells (SOFC), gas sensors, magnetic refrigerant, gas separation membranes, optoelectronic materials *etc.* [1-3]

It is established that a reduction of r_A ("chemical" pressure) by substituting a smaller cation at A-site leads to a decrease of the insulator-metal transition temperature T_{I-M} and finally to a complete destabilization of the ferromagnetic metallic ground state. Small ionic radius of Zr^{4+} ($r = 1.04\text{\AA}$, CN=12) and of Te^{4+} ($r = 1.07\text{\AA}$, CN 12) compared to La^{3+} ($r = 1.36\text{\AA}$, CN=12) will introduce large A-site cation size variance and, charge variance hence expected to give some new results. The effect of this doping is to decrease drastically the e_g one electron bandwidth too. The insulator-metal transition temperature T_{I-M} is expected to decrease and possible destabilization of ferromagnetic state even at lower temperature is possible. At the same time, substitution of trivalent cation by a tetravalent cation induces two Mn^{3+} cations to change to divalent Mn^{2+} state. Thus the double exchange mechanism is expected between the Mn^{3+} -O- Mn^{2+} bridges.

This communication reports the investigation of lattice distortions, that is caused by the substitution of non-lanthanide tellurium ion and Zirconium ion for La/Y ions in the rare earth manganese oxide perovskite structure. Among these complex oxides $La_{1-x}Te_xMnO_3$ is an electron-doped CMR material, which has exhibited excellent physical and chemical properties. The studies indicated that ferro-paramagnetic and metal-insulator transition arose from the double exchange between Mn^{3+} -O- Mn^{2+} in $La_{0.9}Te_{0.1}MnO_3$. Experimental results suggest that

$\text{La}_{0.9}\text{Te}_{0.1}\text{MnO}_3$ has the characteristic of CMR effect and spin-glass state. As exploration in this field is still new, so the results of this investigation can help the researchers of this field in the coming years.

Table 1. The average cation radius at A-site (r_A), variance, charge, size mismatch and model parameters for $\text{La}/\text{Y}_{1-x}\text{Te}/\text{Zr}_x\text{MnO}_3$ system at room temperature.

Doping concentration n x	r_A (\AA)	Cation Variance σ^2 (\AA^2)	A-site charge mismatch σ_c	A-site size mismatch σ_m	Model Parameters			
					$b_1 \times 10^{-19}$ (J) (Mn-O)	$b_2 \times 10^{-19}$ (J) (La/Te/Zr-O)	ρ_1 (\AA) (Mn-O)	ρ_2 (\AA) (La/Te/Zr-O)
LaMnO_3	1.36	0.00	1.00	1.00	1.398	1.630	0.368	0.642
$\text{La}_{0.9}\text{Te}_{0.1}$	1.191	54.46	0.935	1.7956	0.064	0.368	0.099	0.191
$\text{La}_{0.8}\text{Te}_{0.2}$	1.167	96.83	0.875	1.7109	0.007	0.101	0.060	0.116
$\text{La}_{0.7}\text{Te}_{0.3}$	1.142	127.08	0.818	1.6305	0.001	0.024	0.042	0.081
$\text{La}_{0.9}\text{Zr}_{0.1}$	1.328	92.16	0.935	2.00	0.002	0.043	0.048	0.093
$\text{Y}_{0.9}\text{Zr}_{0.1}$	1.002	29.16	0.935	1.5102	0.164	0.559	0.136	0.241
$\text{Y}_{0.8}\text{Zr}_{0.2}$	0.984	51.84	0.875	1.4428	0.048	0.282	0.093	0.168
$\text{Y}_{0.7}\text{Zr}_{0.3}$	0.966	68.04	0.818	1.3790	0.013	0.131	0.070	0.126
YMnO_3	0.960	0.00	1.00	1.00	0.083	0.494	0.162	0.284

To the best of our knowledge, no systematic investigation of effect of lattice distortions on thermal properties of these doped manganites has been carried out in the past, whereas it is well established that distortions are one of the most relevant contributions in explaining the underlying physics of these semiconducting manganites. The main focus of the present paper is to quantify the role of distortions due to charge and size mismatch and their effect on the thermal properties of La/YMnO_3 , and it is probably the first time that this has been done. Recently, we have successfully portrayed the thermodynamic and elastic properties of some Manganites, Cobaltates *etc.* [4-8] by using a modified rigid ion model (MRIM) and a novel approach of Atoms in Molecules Theory. The formulas to quantify the distortions, MRIM formalism and the results are presented in subsequent sections.

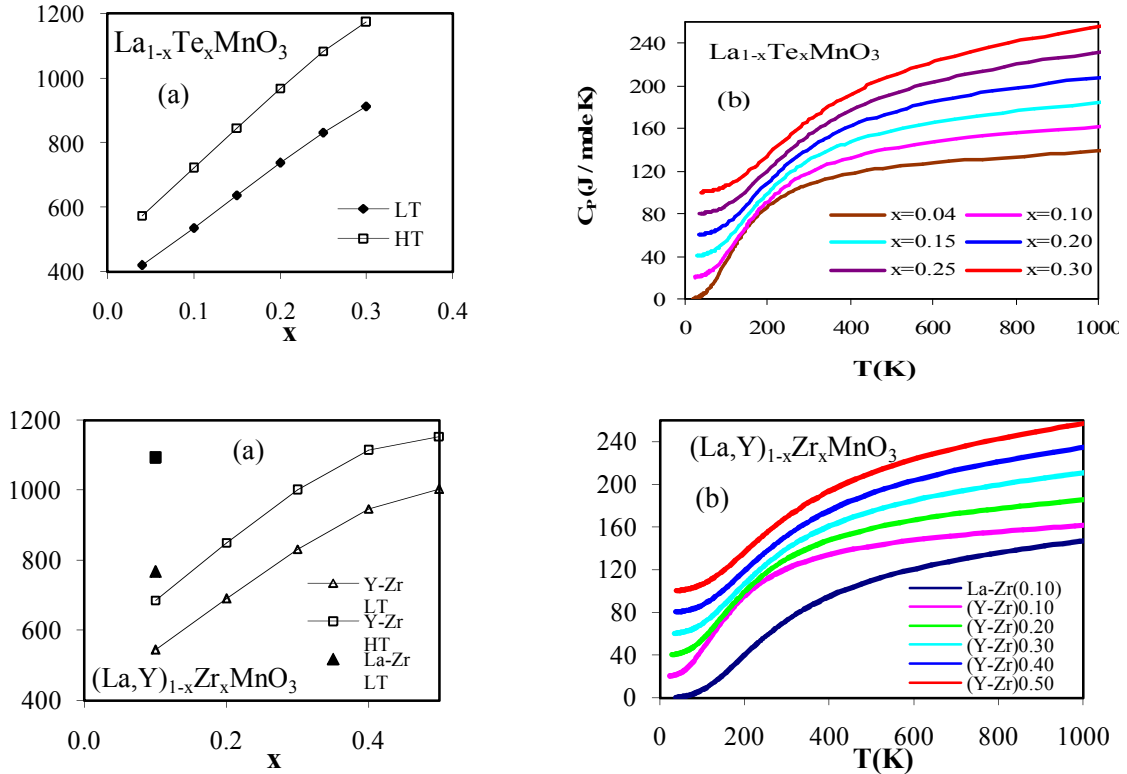


Figure 1 (a) Debye temperature of $\text{La}_{1-x}(\text{Te}/\text{Zr})_x\text{MnO}_3$ in (LT) and (HT) region against doping level x of Tellurium/Zirconium at A-site and (b) Lattice specific heat (C_p) of $\text{La}_{1-x}(\text{Te}/\text{Zr})_x\text{MnO}_3$ in 20K to 1000K temperature interval.

MODEL FORMALISM

We have formulated the modified rigid ion model (MRIM) by keeping the effect of long-range (LR) Coulomb attractions, the short-range (SR) Hafemeister–Flygare-type (HF) [9] overlap repulsion effective up to the next nearest neighbour atoms and the van der Waals attraction due to dipole–dipole (d–d) interactions. The potential describing the formalism of MRIM is expressed as

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

Here all the symbols have the usual meaning as described earlier [4, 5]. The bulk modulus is calculated using the Atom in Molecules (AIM) Theory [10]. Here $\beta_i^{kk'}$ is the Pauling coefficient [11]. The contribution of van der Waal's (vdW) attraction for the dipole-dipole interaction is determined by using the Slater- Kirkwood Variational (SKV) method [12] on the lines of our earlier papers. The model parameters, hardness (b) and range (ρ) are determined from the equilibrium condition and the bulk modulus:

$$\left[\frac{d\Phi}{dr} \right]_{r=r_0} = 0 \quad B = \frac{1}{9kr_0} \left[\frac{d^2\Phi}{dr^2} \right]_{r=r_0} \quad (2)$$

Where K is the crystal structure-dependent constant and r_0 is the equilibrium nearest neighbor distance. One of the important input parameter employed in critical determination of our model parameters is isothermal bulk modulus of the compound. We calculated bulk modulus of the $(La/Y)_{1-x}(Te/Zr)_xMnO_3$ systematically on the basis of formulations of atoms in molecules (AIM) theory [10]. The effect of various lattice distortions are incorporated in determining the bulk modulus of the compounds as they are observed to change the unit cell volume of the compound and the cell symmetry which in turn changed the bulk modulus of the compound. We considered the effect of charge and size mismatch along with the octahedral distortions due to rotation of MnO_3 octahedra on the bulk modulus of the compounds. The size and charge mismatch, bulk modulus, cohesive, elastic and thermal properties like specific heat and thermal expansion of the distorted perovskite manganite are calculated on the lines of our previous papers [4]. The model parameters obtained from the equations (2) and (3) have been used to compute the cohesive and thermal properties for these complex oxides. The results thus obtained are presented and discussed below.

Table 2 Bulk modulus B_0 (AIM), B_T (distorted structure), Cohesive energy (ϕ), Force Constant (f), Reststrahlen Frequency (ν), Debye temperature (θ_D), Gruneisen Parameter (γ) and volume thermal expansion (α) of $(La/Y)_{1-x}(Te/Zr)_xMnO_3$.

Compound, structure	B_0 (GPa) (AIM)	Bulk modulus		ϕ (eV)	f (N/m)	ν (THz)	θ_D		γ	$\alpha \times 10^{-5}$ (K ⁻¹) at 300K	
		B_T (GPa) LT	HT				(K) LT	(K) HT			
LaMnO ₃	R	85.6	109.7	173.6	-133.4	17.03	6.6	316.6	447.9	2.05	5.66
Earlier reports	R	85.4 ^a	108 ^b	182 ^c	-139.7 ^d			302 ^e	470 ^f , 650 ^g	2-3 ^h	
La _{0.9} Te _{0.1}	R	105.2	242.1	438.3	-151.7	48.70	11.2	536.5	721.9	4.03	3.76
La _{0.8} Te _{0.2}	R	106.0	463.3	798.3	-161.2	91.76	15.4	737.8	968.5	6.32	2.78
La _{0.7} Te _{0.3}	R	109.4	704.8	1166	-164.7	139.97	19.1	912.9	1174.0	9.07	2.18
La _{0.9} Zr _{0.1}	R	92.9	496.4	1005	-160.2	98.32	16.0	767.9	1092.8	6.78	2.44
Y _{0.9} Zr _{0.1}	H	150.5	206.3	327.0	-148.5	40.91	11.4	544.9	686.1	3.63	4.03
Y _{0.8} Zr _{0.2}	H	153.9	332.4	503.4	-155.7	65.84	14.4	691.0	850.4	5.08	3.27
Y _{0.7} Zr _{0.3}	H	157.2	483.5	699.8	-160.5	95.67	17.4	832.6	1001.7	6.78	2.72
YMnO ₃	H	153.0	164.0	295.1	-143.8	32.59	10.2	486.5	652.6	3.15	4.37
								425 ⁱ			

^a ref. [20], ^b ref. [21], ^c ref. [22], ^d ref. [19], ^e ref. [23], ^f ref.[24], ^g ref.[25], ^h ref.[23], ⁱ ref.[26]

RESULTS AND DISCUSSIONS

Taking the unit cell parameters (a , α) of rhombohedra/hexagonal compounds and some interionic distances are taken from refs. [13-18] for $La/Y_{1-x}Te/Zr_xMnO_3$ and the model parameters, lattice distortions, elastic and thermal properties of the compounds are determined on the similar lines as described earlier [4] and results are presented in table 1. The vdW coefficients $C_{kk'}$ were calculated using SKV method [12] for the present manganites. The values of model parameters (b_1 , b_2 , ρ_1 and ρ_2), various lattice distortions for various compositions (x) of $(La/Y)_{1-x}(Te/Zr)_xMnO_3$ and A-site cation variance, value of size and charge mismatch are listed in Table 1. Table 2 reports the bulk modulus on the basis of AIM theory (B_0), bulk modulus of the distorted structure (B_T), cohesive and thermal properties of the complex oxides. The negative values of cohesive energy show the stability of these compounds. The experimental values of cohesive energy for $(La/Y)_{1-x}(Te/Zr)_xMnO_3$ are not available but our calculated values are close to the reported value $-139.70eV$ for the compound $LaMnO_3$ [19]. The JT distortion is not observed in the rhombohedra and hexagonal variant of the perovskite structure hence high cation variance is the dominant factor affecting the interactions among the constituent atoms of these compounds. Zr/Te^{4+} ions at A-site increase the charge at this position of the structure. Thus the charge mismatch factor now attains the value less than 1, as expected, and octahedral tilting increases with the successive substitution of larger La/Y cation by much smaller Te/Zr ion. The large cation variance leads to very sharp increase in the cohesive and thermal properties of these manganites (Table 2). The Debye temperature increases to high values and such high values are reported by some researchers found in their experimental and *ab initio* investigations [27]. The reported values are compared successfully to the available data in table 2. All the calculated properties show an increasing trend with increase in concentration of Te/Zr ions in $La/YMnO_3$. Specific heat is found to decrease with increase in Te/Zr content of crystal signifying some hardening of the lattice and so do the volume thermal expansion. The calculated values of specific heat of $La_{1-x}(Zr/Te)_xMnO_3$ and $Y_{1-x}Zr_xMnO_3$ in the $20K < T < 1000K$ temperature range are presented in Fig. 1. The reported results for elastic and thermal properties are in contrast to the variation observed for monovalent and divalent doping in manganites perovskite where the bulk modulus is observed to be decreasing with increasing molar cell volume. [4,5,19].

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