

Increase of Magnetic Transition Temperatures by Reduction of Local Disorder for Perovskite Manganites

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ABSTRACT

We report the synthesis of $\text{Sr}_{1-x}\text{Ca}_x\text{MnO}_3$ and $\text{La}_{0.5}\text{Ba}_{0.5}\text{MnO}_3$ perovskites over extended cation and oxygen composition ranges and describe the dependence of their phase stability on the tolerance factor $t = t(x, T, \delta)$ that is a function of composition, temperature, and oxygen content. We show that magnetic transition temperatures depend strongly on the tolerance factor and charge disorder while dependence on the structural disorder is less important. By reducing charge and structural disorder we have significantly increased the Curie and Neel temperatures for perovskite manganites.

Perovskite manganites, AMnO_3 , have been recently studied in great detail because of very interesting magnetic and electronic properties resulting from competing charge, exchange, and phonon interactions [1]. The properties can be tuned over a wide range through the choice of the sizes and charges of the A-site cations that control the degree of structural distortions and the formal valance of Mn. The correlation of physical properties with the Mn–O–Mn bond-angle controlled electronic band-width has been clearly established for decades [2,3]. These correlations are also frequently described in terms of the average structure using a concept of tolerance factor $t = [\text{A-O}]/\sqrt{2}[\text{Mn-O}]$ [4]. Here, $[\text{A-O}]$ and $[\text{Mn-O}]$ are the average cation-oxygen interatomic distances of the A- and B-sites, respectively, the approximate values of which can be obtained from the ionic sizes that are tabulated for various coordination numbers and oxidation states at room temperature [5]. It was reported recently that the ferromagnetic transition temperatures can be better accounted for by using in addition to the tolerance factor the variance of sizes of the A-site ions, $s(x) = \sqrt{\sum_i \{x_i [\text{A}_i\text{-O}]^2 - [\text{A-O}]^2\}}$, where $[\text{A-O}] = \sum_i x_i [\text{A}_i\text{-O}]$,

and x_i is the fractional occupancy of atoms occupying the A-site [4]. The effects of local structural distortions have been studied most extensively for the mixed valent manganites $\text{La}_{1-x}\text{A}_x\text{MnO}_3$ ($\text{A} = \text{Ca}, \text{Sr}, \text{Ba}$) [6,7,8,9]. To date, studies of these materials were limited by the substitution level x_s of the A metal, beyond which formation of the perovskite phase was not possible because of the decreasing average size of the Mn^{3+x} ion and the unfavorable tolerance factor $t \geq 1$ of the desired composition.

With modified synthesis methods at reduced oxygen pressure we recently have been able to extend the solubility limits from $x_s = 0.6$ and 0.3 to $x_s = 1$ and 0.7 for $\text{La}_{1-x}\text{Sr}_x\text{MnO}_{3-\delta}$ and $\text{La}_{1-x}\text{Ba}_x\text{MnO}_{3-\delta}$, respectively [10,11]. These results are in disagreement with the much smaller values of $x_s = 0.46$, and 0.27 which are predicted for Sr, and Ba, respectively, based on tolerance-factor arguments using tabulated interatomic distances [5]. In this paper we report the synthesis of the $\text{Sr}_{1-x}\text{Ca}_x\text{MnO}_3$ and $\text{RE}_{0.5}\text{Ba}_{0.5}\text{MnO}_3$ compounds over an extended cation and oxygen composition range and describe the dependence of their phase stability on a newly calculated tolerance factor that explains the expanded solubility limits. We show that for a single-valent Mn^{4+} compound $\text{Sr}_{1-x}\text{Ca}_x\text{MnO}_3$ the variance of sizes of the A-site ions suppresses the antiferromagnetic transition temperature by a maximum of ~ 20 K at $x = 0.5$ where $s(x)$ is the largest. By comparing ferromagnetic transition temperatures of the two structural forms of $\text{RE}_{0.5}\text{Ba}_{0.5}\text{MnO}_3$ compounds studied by neutron diffraction, disordered (with randomly mixed RE/Ba) and ordered (forming Ba/RE/Ba layers along the c-axes), we show that a decrease of the local A-site charge disordering induces a large, ~ 80 K, increase of the ferromagnetic T_c .

To improve the calculation of the tolerance factor we have used neutron powder diffraction to precisely measure the A-O and Mn-O bond lengths and derive accurate interatomic distances [Ca-O], [Sr-O], [Ba-O], and [Mn-O] rather than relying on tabulated values [12]. The temperature dependence of the tolerance factor was then calculated from the measured bond lengths where weighted averages were defined to account for the unusual coordination. By using thermogravimetric measurements of oxygen deficiency δ and parameterizing the measured tolerance factor, we have obtained the functional dependence of the tolerance factor $t = t(x, T, \delta)$ on composition, temperature, and oxygen content. At a fixed oxygen content, the tolerance factor is an increasing function of temperature as a result of greater thermal expansion of the

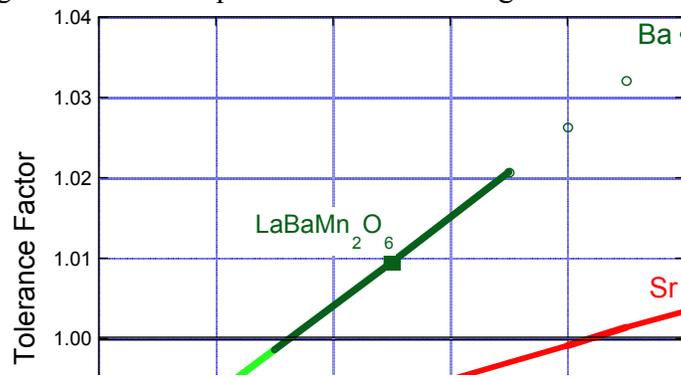


Fig. 1 Tolerance factor as a function of composition for $\text{La}_{1-x}\text{A}_x\text{MnO}_3$ system (A = Ba, Sr, Ca) at room temperature. Dark solid lines denote extended solid solution ranges for A = Ba and Sr.

average [A-O] bond relative to the average [Mn-O] bond. The stability of the perovskite phase at high temperature (where synthesis is done) is governed, as expected, by the magnitude of the tolerance factor ($t \leq 1$) which can be adjusted by controlling the average interatomic distance $[\text{Mn}^{4-2\delta}\text{-O}]$ as a function of the oxygen content $3-\delta$. This dependence of the tolerance factor on oxygen content and temperature has been utilized for the controlled formation of the $\text{Sr}_{1-x}\text{Ca}_x\text{MnO}_3$ and $\text{RE}_{0.5}\text{Ba}_{0.5}\text{MnO}_3$ phases. The synthesis have been done in two steps: Formation of the oxygen-deficient ($\text{O}_{2.5-2.8}$) perovskite framework at high temperature (1300 – 1400 C) and low oxygen pressure (Ar or H_2/Ar flow), followed by the complete oxygenation (air or O_2 flow) at a temperature low enough (below 500 C) that the cations do not diffuse. Formation of the well layered-ordered $\text{RE}_{0.5}\text{Ba}_{0.5}\text{Mn}_{3-\delta}$ phases at high temperatures required accurate control of the oxygen content at $\text{O}_{2.5}$.

Figure 1 shows the tolerance factor as a function of composition for the $\text{La}_{1-x}\text{A}_x\text{MnO}_3$ system at room temperature using our values of interatomic distances $[\text{Ca-O}] = 2.640$, $[\text{Sr-O}] = 2.691$, $[\text{La-O}] = 2.765$, $[\text{Ba-O}] = 2.783$, $[\text{Mn}^{4+}\text{-O}] = 1.896$, and $[\text{Mn}^{3+}\text{-O}] = 1.990 \text{ \AA}$. Our values of interatomic distances are similar to the sum of ionic radii obtained from tabulated values [5] for oxygen with La and Mn. For Ca, Sr, and Ba our interatomic distances are significantly smaller than those obtained from tables. As a result there is a considerable discrepancy between tolerance factors obtained from our values and from Shannon's tables [5]. The discrepancy is

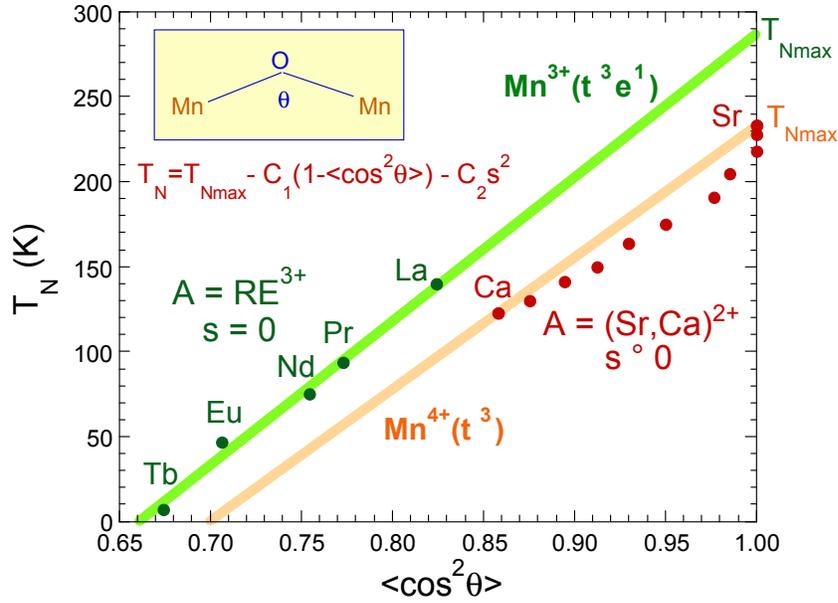


Fig. 2 Neel temperatures vs. average \cos^2 of the Mn-O-Mn bond angle for the solid solution system $\text{Sr}_{1-x}\text{Ca}_x\text{MnO}_3$ with a single valent Mn^{4+} (t^3) and REMnO_3 ($\text{RE} = \text{La}, \text{Pr}, \text{Nd}, \text{Eu}, \text{Tb}$) with the single valent Mn^{3+} ($t^3 e^1$) perovskites. The variance of sizes $s = 0$ and $s \neq 0$ for REMnO_3 and $\text{Sr}_{1-x}\text{Ca}_x\text{MnO}_3$, respectively ($s = 0$ for $\text{Sr}_{1-x}\text{Ca}_x\text{MnO}_3$ with $x = 0$ and 1).

even larger for the variance of sizes of the A-site ions $s(x)$. Our more accurate interatomic distances derived for manganites should be used for the purpose of correct calculation of $t(x)$ and $s(x)$. The unusually short lattice parameter ($a_0 = 3.805$) (and the interatomic distance of $[\text{Sr-O}] = a_0/\sqrt{2} \sim 2.69 \text{ \AA}$) for manganites when compared with the lattice parameters $a_0 = 3.869, 3.841,$ and 3.904 for several cubic perovskites SrBO_3 with $\text{B} = \text{Fe}, \text{V},$ and Ti , respectively, may be the cause of these discrepancies.

The two-step synthesis method allowed us to prepare the $\text{Sr}_{1-x}\text{Ca}_x\text{MnO}_3$ and $\text{La}_{0.5}\text{Ba}_{0.5}\text{MnO}_3$ compounds with the unusual tolerance factors $t \sim 1$ and investigate their structural and physical properties. Figure 2 shows Neel temperatures as a function of the Mn-O-Mn bond angle for solid solution system $\text{Sr}_{1-x}\text{Ca}_x\text{MnO}_3$ with single valent $\text{B} = \text{Mn}^{4+}$ (t^3). Magnetic superexchange interactions in ABO_3 perovskites are dependent on the B-O-B bond angle ϕ [3]. For single valent systems with $\text{B} = \text{Fe}^{3+}$ ($t^3 e^2$) and Cr^{3+} (t^3) it was determined that the antiferromagnetic $T_N \sim \langle \cos^2 \phi \rangle$ when there is only one kind of Rare Earth on the A-site. Fig. 2 shows that a similar relationship holds for the single valent Mn^{3+} ($t^3 e^1$) compounds. However, for the solid solution system $\text{Sr}_{1-x}\text{Ca}_x\text{MnO}_3$ with a single valent $\text{B} = \text{Mn}^{4+}$ (t^3), the structural disorder on the A-site introduces measurable deviation from this relation. The size

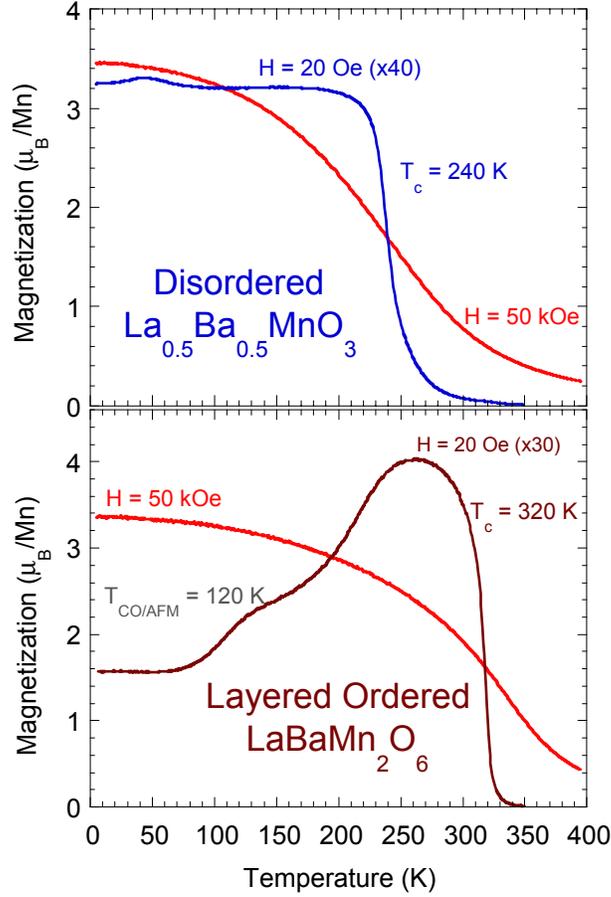


Fig. 3 dc magnetization in low magnetic field (20 Oe) and at 5 Tesla for disordered ($\text{La}_{0.5}\text{Ba}_{0.5}\text{MnO}_3$) and layer ordered ($\text{LaBaMn}_2\text{O}_6$) perovskites with mixed valent $\text{Mn}^{3.5+}$.

difference between interatomic distances of the iso-electronic Sr-O and Ca-O introduces local variance of the bond angles that suppresses T_N by ~ 20 K at $x = 0.5$ where the variance of sizes is the largest.

Fig. 3 shows much larger effects of the charge disorder on the ferromagnetic transition temperature observed for mixed valent perovskite manganites, $\text{La}_{0.5}\text{Ba}_{0.5}\text{MnO}_3$. Because our measured interatomic distances of [La-O] and [Ba-O] are quite similar, the variance of size, $s(x)$, is tiny, i.e., the effects of structural disorder are anticipated to be small. Nonetheless, we observe a large, ~ 80 K, difference of ferromagnetic T_c between the two structural forms. In addition to a higher $T_c = 320$ K the layered ordered phase displays novel $\text{Mn}^{3+}/\text{Mn}^{4+}$ charge/antiferromagnetic ordering at $T_{\text{CO/AFM}} = 120$ K. We attribute the different properties of the disordered and layered-ordered phases to the local A-site charge disordering that profoundly disturbs the coherent electronic states of the Mn-O bonds. The difference between T_c 's of the two structural forms increases with the increase of the variance of sizes for the smaller ionic size RE = La - Nd

showing that the structural order is also important to preserve the ferromagnetic and charge-ordered/antiferromagnetic phases. With a decrease of the RE-O interatomic distances, the T_c of the disordered phase decreases quickly, the T_c of the layered order phase decreases slowly, and the $T_{CO/AFM}$ increases rapidly. The layered ordered compounds with the ionic sizes of the RE smaller than Nd have $T_c < T_{CO/AFM}$; i.e., a novel metal-insulator transition is found that is similar to that observed for the disordered $RE_{0.5}Sr_{0.5}MnO_3$ perovskites and which was discussed in terms of the disordered-controlled quantum critical transition [13,14]. We have observed that by stabilizing structurally and charge ordered structures over a wide range of compositions around $x = 0.5$ a substantial increase of the Neel (520 K) and Curie (365 K) temperatures can be achieved. Similar effects of local structural/charge order no doubt have profound effects on the properties of other complex oxides; for example, copper oxide high temperature superconductors.

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