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Unusual electronic transport properties in $La_{0.96-x}Nd_xK_{0.04}MnO_3$

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Polycrystalline $La_{0.96-x}Nd_xK_{0.04}MnO_3$ has been studied by means of x-ray powder diffraction, dc magnetization, and electrical resistance measurement. $La_{0.96-x}Nd_xK_{0.04}MnO_3$ initially crystallizes in a rhombohedral distorted perovskite structure. However, an orthorhombic structure is obtained with increasing Nd content more than 20%. Both the rhombohedral and the orthorhombic phases show ferromagnetic order. However, the compound shows a magnetic inhomogeneity behavior with increasing Nd content. With increasing Nd doping, the ferromagnetic order is significantly weakened, and the second magnetic transition occurs at a low temperature and its peak intensity enhances. The resistivity of these compounds also exhibits an imhomogeneity behavior. The rhombohedral phase shows a metal–insulator (MI) transition but the MI transition peak intensity is obviously weakened and broadens with increasing Nd content and a low temperature insulator state is observed in the orthorhombic phase. It is interesting that the second magnetoresistance ratio peak appears at low temperature. It might be due to Nd induced low temperature phase separation between the ferromagnetic metallic and antiferromagnetic insulating state. © *2003 American Institute of Physics.* [DOI: 10.1063/1.1544482]

Colossal magnetoresistance (CMR)–a huge decrease in resistivity in mixed valent manganites of the formula $R_{1-x}A_xMnO_3$ (R = rare earth elements; A = Ca,Sr,Ba,Pb) by applied magnetic field—has triggered intense scientific activity in recent years.[1,2] Millis introduced an electron–lattice interaction model, which included double exchange interaction, Jahn–Teller effect, and the tolerance factor, to explain the CMR of manganese perovskites.[3] More recently, the investigation on the low temperature electronic transport has attributed great interest due to the coexistence of several magnetic phases. This phenomenon is interpreted by an electronic phase separation between ferromagnetic metallic and antiferromagnetic insulating state at low temperature.[4]

In $LaMnO_3$ doping La site by monovalent cation will create two holes (Mn^{4+}), however, in $R_{1-x}A_xMnO_3$ the divalent ion substitution for La create a single hole. So the alkaline metal doping in $LaMnO_3$ manganite saves doping ion content and easily achieve a high percentage of Mn^{4+} with the same doping level of divalent ion. However, some authors report special electronic transport property,[5,6] i.e., the existence of two transitions or resistivity shoulder in the temperature dependence of resistivity measurements. This phenomenon was first regarded as being due to phase inhomogeneity triggered by evaporation of K and Na at high temperature. But the second transition or resistivity shoulder could not be removed even after using different synthesis techniques such thin films or by changing sintering conditions.[7–9] In this article, we report our experimental results on crystal structures, electronic, magnetic, and magnetoresistance properties of polycrystalline $La_{0.96-x}Nd_xK_{0.04}MnO_3$ with a long sintering period.

Polycrystalline $La_{0.96-x}Nd_xK_{0.04}MnO_3$ ($x=0-0.4$) and $Nd_{0.96}K_{0.04}MnO_3$ were synthesized by solid-state reaction. The starting materials La_2O_3, Nd_2O_3, MnO_2, and K_2CO_3 were mixed in stoichiometeric proportions and were calcined at 1273 K for 20 h. The powder thus obtained was ground, pelletized, and sintered at 1473 K for 96 h. Chemical analysis have been performed for checking the element compositions. X-ray diffraction (XRD) was carried out by a Siemens D-5000 powder diffractometer Cu $K_{\alpha 1}$ radiation. Rietveld's powder diffraction profile-fitting technique[10] was employed to refine the crystal structure. The thermo-magnetic property was measured by a superconducting quantum interference device magnetometer from 1.5 to 400 K with an applied field of 50 G. The temperature dependence of magnetoresistance was measured by means of a standard four-probe resistance-temperature method at zero field, 1 T, and 5 T, respectively.

The XRD patterns of the calcined samples reveal that the structural transitions exist in the $La_{0.96-x}Nd_xK_{0.04}MnO_3$. For the first two samples with $x=0$, and 0.1, the compound has a rhombohedral structure with a space group of $R\text{-}3c$, and $Z=6$. A tetragonal-rhombohedral transition occurs in the sample with $x=0.2$. The corresponding lattice parameters are $a=3.890(6)$ Å and $c=3.941(4)$ Å. $La_{0.96-x}Nd_xK_{0.04}MnO_3$ compounds with $x=0.3$ and 0.4 as well as $Nd_{0.96}K_{0.04}MnO_3$ have an orthorhombic structure with space group of $Pbnm$, and $Z=4$. Figure 1 shows the

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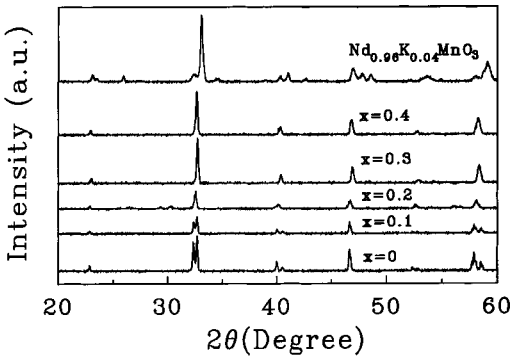

FIG. 1. The XRD patterns of $La_{0.96-x}Nd_xK_{0.04}MnO_3$.

XRD patterns. After the sintering process, the tetragonal phase decomposes to the rhombohedral and orthorhombic phase. According to the chemical composition analysis, the exact structural formulas have been calculated and they correspond to $La_{0.854}K_{0.038}MnO_{3.027}$, $La_{0.778}Nd_{0.095}K_{0.035}MnO_{2.994}$, $La_{0.674}Nd_{0.192}K_{0.033}MnO_{2.870}$, $La_{0.585}Nd_{0.286}K_{0.039}MnO_{2.890}$, $La_{0.491}Nd_{0.378}K_{0.037}MnO_{2.880}$ for the compounds from $x=0$ to 0.4.

The $La_{0.96-x}Nd_xK_{0.04}MnO_3$ compounds exhibit a magnetic inhomogeneity behavior as shown in Fig. 2. Nd doping weakens the ferromagnetic order and induces a low temperature antiferromagnetic phase, which is perhaps a spin glass phase. When La is totally substituted by Nd (i.e., in $Nd_{0.96}K_{0.04}MnO_3$), only an antiferromagnetic order is observed with $T_N=76$ K as shown in inset plot in Fig. 2. The magnetic phase relation implies that the magnetic inhomogeneity derives from the mixture between La-rich ferromagnetic phase and Nd-rich low temperature antiferromagnetic phase. The resistivity also exhibits an imhomogeneity behavior as shown in Fig. 3. The rhombohedral phase shows a metal–insulator (MI) transition near ferromagnetic transition temperature, although the MI transition peak intensity is weakened and widens with increasing Nd content. The orthorhombic phase exhibits a low temperature insulating state and a very weak ferromagnetic metallic state. The ferromagnetic metallic state melts with increasing Nd content. The resistivity behavior in the $La_{0.96-x}Nd_xK_{0.04}MnO_3$ compound might be explained as Nd induced phase separation between ferromagnetic metallic (FM) state and the antiferromagnetic insulating (AFI) state at low temperature. Therefore, Nd doping weakens the magnetic order and MI transition intensity; it results in the ferromagnetic spin alignment disorder; and increases the opportunity of spin-electron scattering that leads to the decrease of the FM phase in the compounds. It also induces a low temperature insulating state and enhances the resistivity significantly by increasing the AFI phase. When La is totally substituted by Nd, there is only the AFI phase, so the $Nd_{0.96}K_{0.04}MnO_3$ compound is the only compound exhibiting insulating behavior. The low temperature insulating state induced by Nd doping might be related to

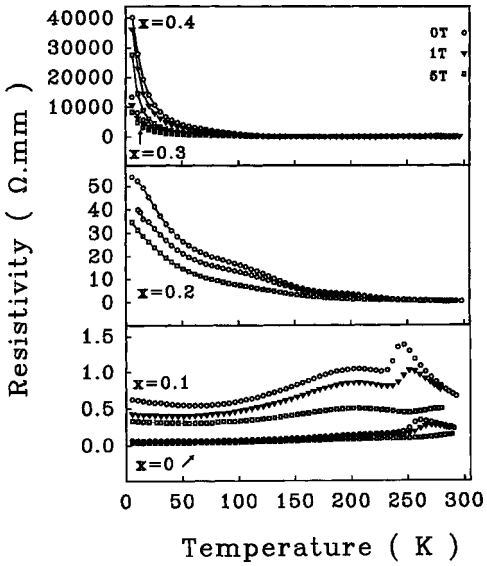

FIG. 3. Temperature dependence of resistivity of $La_{0.96-x}Nd_xK_{0.04}MnO_3$.

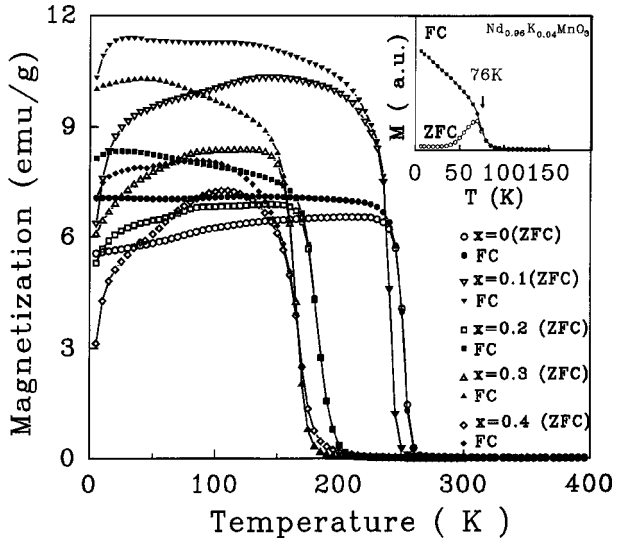

FIG. 2. The temperature dependence of magnetization of $La_{0.96-x}Nd_xK_{0.04}MnO_3$ compound in an applied field of 50 G. The inset plot gives measurement results for $Nd_{0.96}K_{0.04}MnO_3$.

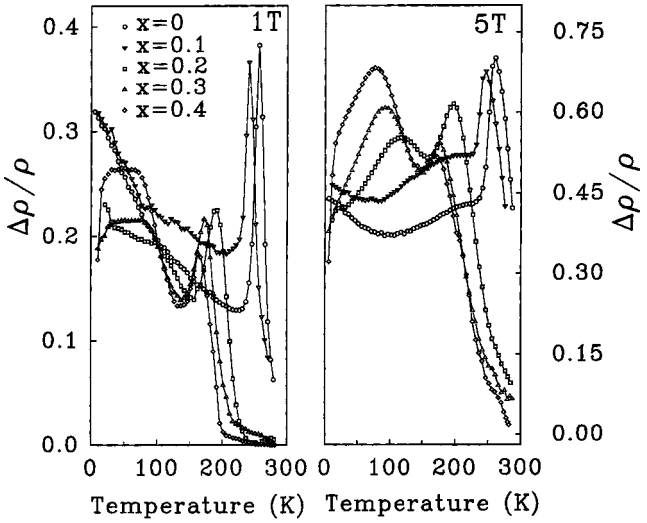

FIG. 4. The MR vs temperature measured at the applied field of 1 T (a) and 5 T (b).

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TABLE I. The refined structural parameters, the MnO_6 distortion (Mn–O bond lengths and Mn–O–Mn bond angles), and tolerance factors of $La_{0.96-x}Nd_xK_{0.04}MnO_3$ compounds. R_p, R_{wp}, and S are the residual factor, the weighted residual factor, and the goodness-of-fit factor, respectively.

Nd content (x)	0	0.1	0.2	0.3	0.4
S.G.	R-3c	R-3c	$Pbnm$	$Pbnm$	$Pbnm$
a (Å)	5.536(4)	5.526(7)	5.528(3)	5.508(4)	5.507(5)
b (Å)	···	···	5.488(4)	5.485(5)	5.480(1)
c (Å)	13.376(1)	13.364(3)	7.766(1)	7.758(8)	7.749(9)
⟨Mn–O⟩ (Å)	1.968	1.961	1.969	1.972	1.968
Mn–O–Mn	164.0(3)^o	165.6(8)^o	161.2(3)^o	162.3(3)^o	161.6(0)^o
Tolerance factors	0.896	0.908	0.891	0.885	0.888
R_p	8.1%	10.3%	8.5%	9.1%	9.4%
R_{wp}	11.2%	10.6%	11.6%	11.8%	11.9%
S	1.6	1.7	1.5	1.6	1.6

Nd $4f$ electrons. According to Hwang's report,[11] the ferromagnetic order was significantly weakened by substitution of Pr for La. The resistivity enhances quickly when La was totally substituted by Pr, where the compound showed an insulating behavior.[11] This experimental result was interpreted by size effect at the La site. However, if the $4f$ electrons are taken into account, one can find a relationship between the $4f$ electron and the electronic transport. In the alkaline metal doped $LaMnO_3$ perovskites, since there is no $4f$ electron in La ion, there is no second magnetic transition at low temperature. However, the number of the $4f$ electrons in the Nd cation is 3, and there could be a weak effect of the crystal field interaction between Nd $4f$ electrons and Mn $3d$ electrons at low temperature, i.e., the Ruderman–Kittel–Kasuya–Yosida (RKKY) effect. Since the RKKY interaction usually works at low temperature, if a long distance RKKY ordering is formed in the $La_{0.96-x}Nd_xK_{0.04}MnO_3$ compound at low temperature, the $3d-4f$ spin coupling will have the contribution to spin-electron scattering. We have measured the thermomagnetic property of $La_{0.96-x}Nd_xK_{0.04}MnO_3$ at 5 T. The low temperature magnetic transition, most likely induced by a weak $3d-4f$ interaction, disappeared due to strong applied magnetic field. The study on transport property of $(La,Gd)_{0.7}A_{0.3}MnO_3$(A=Sr,Ca) supports our results.[12,13] A special resistivity behavior in $Yb_xCa_{1-x}MnO_3$ compound also seems to be related to a low temperature RKKY effect in our recent study.[14]

Nd doping induced double peak phenomenon also appears in the temperature dependent magnetoresistance ratio (MR) as shown in Fig. 4. One MR peak denoted by FM–MR occurs near ferromagnetic metallic transition temperature, and the other one denoted by I–MR occurs near the insulating state temperature. With increasing Nd content, the FM–MR peak intensity is weakened and broadened, although the I–MR peak intensity enhances. This phenomenon might be due to weakening of ferromagnetic metallic transition by Nd substitution that also increases the low temperature antiferromagnetic insulating state.

Stoichiometric perovskite ABO_3 is cubic, but, most of divalent cation doped $RMnO_3$ compounds crystallize the distorted orthorhombic, rhombic, or tetragonal structure. One possible reason for the lattice distortion is the deformation of the MnO_6 octahedron arising from the Jahn–Teller (JT) effect, which is inherent to the high spin ($S=2$) Mn^{3+} with double degeneracy of e_g orbital. And the other one comes from the connection pattern of the MnO_6 octahedron in the pervoskite structure. In this case, the MnO_6 octahedron shows alternative bulking. Such a lattice distortion of the pervoskite is governed by a tolerance factor. In this article, the JT effect has been investigated by studying the MnO_6 octahedron distortion, which includes the Mn–O bond lengths and Mn–O–Mn bond angles. The tolerance factors also have been calculated based on the structural refinement. The calculated results about the nearest Mn–O bond lengths and Mn–O–Mn bond angles and tolerance factors have been listed in Table I. The distortion of MnO_6 octahedron shows that Nd doping tends to bend the average Mn–O–Mn bond angle from 164.14° to 161.60° in its spacing orientation. Such a distortion will affect the electron hopping and therefore affects the resistivity.

In conclusion, Nd doping results in a rhombohedral–orthorhombic structural transition in the $La_{0.96-x}Nd_xK_{0.04}MnO_3$ compound, and also induces magnetic and resistivity inhomogeneity. Nd doping weakens the ferromagnetic order and induces a low temperature magnetic transition. The resistivity exhibits MI transition and the insulating state near ferromagnetic transition temperature and low temperature magnetic transition temperatures, respectively. The Nd doping results in the formation of the second MR peak at low temperature. This special electronic transport property might be interpreted by the close coupling among lattice, electronic, and magnetic degrees of freedom, that has generally shown electronic phase separation between different magnetoelectronic states at low temperature.

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