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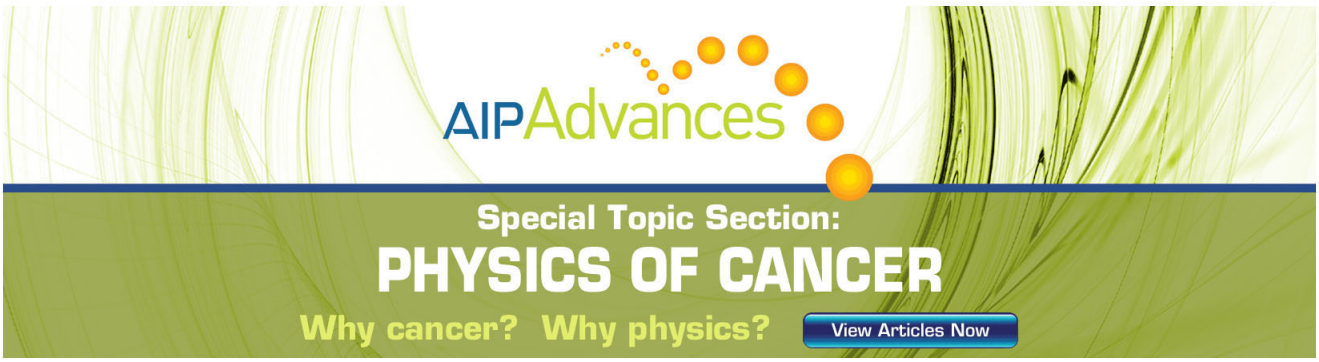

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Doping effects on the magnetic properties of $La_{0.5}Ba_{0.5}Co_{1-x}Ti_xO_3$

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A detailed magnetic study has been carried out for Ti-doped $La_{0.5}Ba_{0.5}Co_{1-x}Ti_xO_3$ ($x=0$, 0.05, 0.075, 0.10, 0.125, and 0.15) cobaltites. Ti doping suppresses the ferromagnetic interaction in $La_{0.5}Ba_{0.5}CoO_3$ and induces an antiferromagnetic phase in the system at $0.075 \leq x \leq 0.15$. The spin state of Co ions is not affected by the Ti doping and remains an intermediate-spin state at $x \leq 0.15$. At low temperatures, the system is in a reentrant spin glass state. Phase separation provides a phenomenological interpretation of these magnetic behaviors. A detailed phase diagram of $La_{0.5}Ba_{0.5}Co_{1-x}Ti_xO_3$ has been constructed. © *2011 American Institute of Physics*. [doi:10.1063/1.3561051]

I. INTRODUCTION

The fascinating magnetic and transport properties of cobaltites[1–5] with the perovskite structure has been the object of numerous studies for the past ten years. $LaCoO_3$ (Refs. 1 and 2), which is a good illustration, has nonmagnetic Co^{3+} ($3d^6$) ions with the low-spin (LS) state configuration ($t_{2g}^3 \uparrow t_{2g}^3 \downarrow$, $S=0$) at low temperatures, along with either an intermediate-spin (IS) state ($t_{2g}^3 \uparrow t_{2g}^2 \downarrow e_g^1 \uparrow$, $S=1$) or a high-spin (HS) state ($t_{2g}^3 \uparrow t_{2g}^1 \downarrow e_g^2 \uparrow$, $S=2$) that becomes populated as temperature increases. This is caused by the competition between the crystal field splitting energy ΔC and the exchange energy ΔE. The physical properties of $LaCoO_3$ can be changed drastically by substitution of the La^{3+} ions with divalent earth-alkaline elements.[3–7] For example, the chemical substitution of Ba^{2+} for La^{3+} ions can induce a ferromagnetic state.[3–5,7] Several possible scenarios have been proposed to account for the magnetic coupling,[7–13] but it is still not clear and remains a subject of debate. The substitution of other ions for Co ions could more directly modify the magnetic ordering and could facilitate an understanding of the nature of the ferromagnetic state. In this paper, we select the tetravalent Ti^{4+} as a substitute for Co^{4+} in the $La_{0.5}Ba_{0.5}CoO_3$ system. The magnetic measurements under applied pressure suggest that both Co^{3+} and Co^{4+} ions are stabilized in the IS state. The substitution by a Ti ion with a large radius enlarges the crystal lattice and bond length of the Co–O, which suppresses the double-exchange interaction. A detailed phase diagram of $La_{0.5}Ba_{0.5}Co_{1-x}Ti_xO_3$ has been constructed.

II. EXPERIMENT

$La_{0.5}Ba_{0.5}Co_{1-x}Ti_xO_3$ samples with $x=0$, 0.05, 0.075, 0.1, 0.125, and 0.15 were prepared by conventional solid state reaction.[4] The x-ray diffraction (XRD) patterns were registered at room temperature on a Rigaku-D/max-γ A diffractometer using high intensity Cu K α radiation. The magnetic properties were measured under 1 kOe by using a Quantum Design MPMS XL7. An Easylab Mcell 10 pressure cell was used to generate hydrostatic pressure.

III. RESULTS AND DISCUSSION

Room-temperature XRD patterns for pure and $x=0.15$ samples are shown in Fig. 1. The results of the Rietveld analysis confirm that the $La_{0.5}Ba_{0.5}Co_{1-x}Ti_xO_3$ samples are in a pure single phase.

Figure 2 displays magnetization as a function of temperature for $La_{0.5}Ba_{0.5}Co_{1-x}Ti_xO_3$. Consistent with previous reports,[7,13] the undoped compound exhibits a paramagnetic (PM)–ferromagnetic (FM) transition at 185 K. The sample with $x=0.05$ is similar to the parent compound, but with the transition being suppressed to a low temperature. As the concentration of Ti^{4+} increases ($0.075 \leq x \leq 0.125$), the PM–FM transition is replaced by a peak on the M-T curve, which seems to be the transition for either the antiferromagnetic or the spin state. The difference between the ZFC and FC curves still exists, which indicates that the system exists in the reentrant spin glass state. The peak temperature T_P and the transition temperature T_g increase with increasing x. For the sample with $x=0.15$, the peak on the M-T curve is suppressed to a bump. For the whole system, the value of magnetization decreases gradually with increasing Ti content. The above results indicate that the Ti doping greatly suppress the FM interaction in the system.

In order to understand whether the nature of the peak on M-T curves for the $x \geq 0.075$ samples is the antiferromagnetic transition or the spin state transition, we first fitted the $1/\chi - T$ above T_C to determine the spin state of the Co ions in the high temperature paramagnetic domain, which is still an open issue.[7,11,14,15] From Fig. 3(a), it can be seen that the $1/\chi$ −T curves of $La_{0.5}Ba_{0.5}Co_{1-x}Ti_xO_3$ above T_C can be linearly fitted very well, suggesting that the system is in the PM state at high temperatures. The effective moment of the Co ions was then obtained and is plotted in Fig. 3(b). On the

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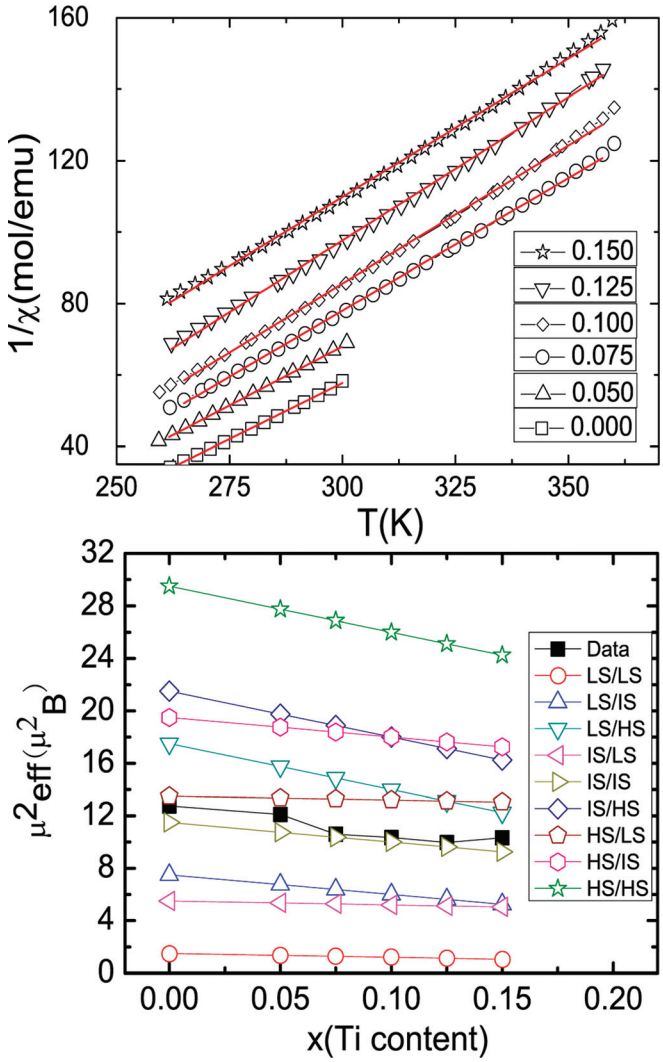

FIG. 3. (Color online) (a) The $1/\chi$ −T curves of $La_{0.5}Ba_{0.5}Co_{1-x}Ti_xO_3$ above 260 K. (b) The calculated effective moment according to different combinations of spin-state configurations compared with the experimental data. (For example, the spin-state configuration IS/HS means that the Co^{3+} exists in the IS state and the Co^{4+} exists in the HS state).

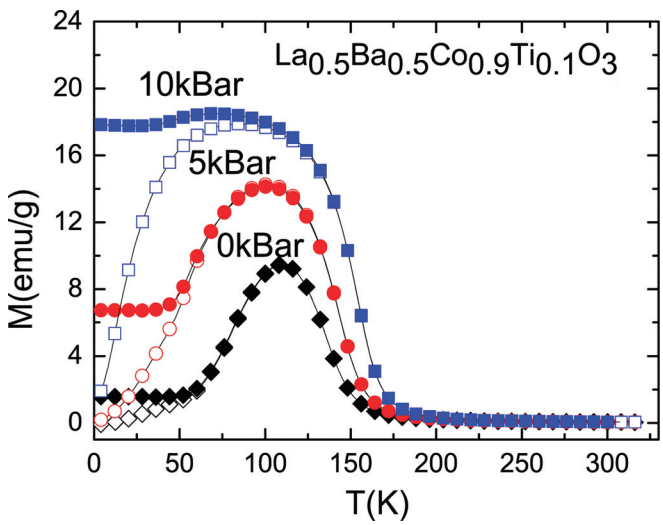

FIG. 4. (Color online) The ZFC (open symbols) and FC (solid symbols) magnetization as a function of temperature under different external pressures for the sample $x = 0.1$.

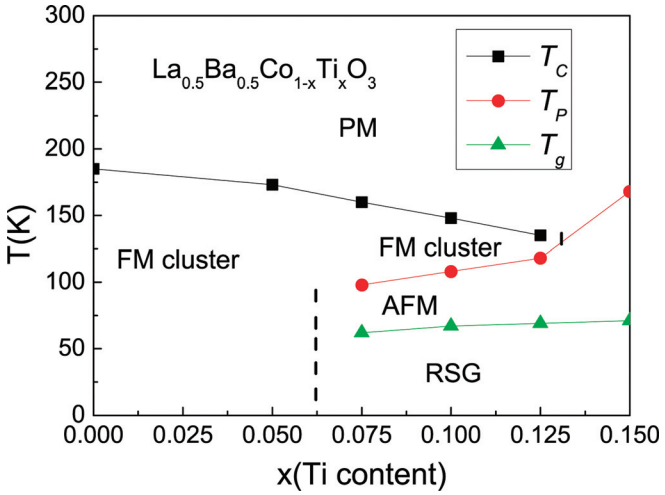

FIG. 5. (Color online) Phase diagram of $La_{0.5}Ba_{0.5}Co_{1-x}Ti_xO_3$.

Combining the above analysis and the experimental results of the magnetic measurements, a detailed phase diagram of $La_{0.5}Ba_{0.5}Co_{1-x}Ti_xO_3$ can be constructed as shown in Fig. 5. For the whole system, T_C decreases while T_P and T_g (slightly) increase with increasing x.

IV. CONCLUSION

In this paper, the Ti doping effect on the magnetic properties of $La_{0.5}Ba_{0.5}CoO_3$ has been studied. The magnetic measurements suggest that both Co^{3+} and Co^{4+} ions are stabilized in the IS state, and a detailed phase diagram has been constructed.

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