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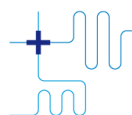
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Search for long-range ferromagnetism: Charge-spin co-doped $\text{Ba}_{1-x-y}\text{La}_{x+y}\text{Ti}_{1-x}\text{M}_x\text{O}_3$ ($\text{M} = \text{Cr, Fe, and Co}$)

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We investigate the structural, magnetic, and electrical properties of charge-spin co-doped $\text{Ba}_{1-x-y}\text{La}_{x+y}\text{Ti}_{1-x}\text{M}_x\text{O}_3$ ($\text{M} = \text{Cr, Fe, and Co}$). For $\text{Ba}_{1-x-y}\text{La}_{x+y}\text{Ti}_{1-x}\text{Cr}_x\text{O}_3$, carrier doping induces short-range ferromagnetism, and we find a large negative magnetoresistance in these compounds. However, for $\text{Ba}_{1-x-y}\text{La}_{x+y}\text{Ti}_{1-x}\text{M}_x\text{O}_3$ ($\text{M} = \text{Fe and Co}$), the magnetism does not seem to couple with the charge carriers. The transport properties of $\text{Ba}_{1-x-y}\text{La}_{x+y}\text{Ti}_{1-x}\text{Cr}_x\text{O}_3$ can be described by a three-dimensional variable-range-hopping model that implies itinerant charge carriers, whereas almost all the samples of $\text{Ba}_{1-x-y}\text{La}_{x+y}\text{Ti}_{1-x}\text{M}_x\text{O}_3$ ($\text{M} = \text{Fe and Co}$) exhibit high resistivity. It is known that only the itinerant charge carriers can enhance the coupling of two isolated magnetic ions. Therefore, there is almost no long-range ferromagnetism in the studied system. © 2013 American Institute of Physics. [<http://dx.doi.org/10.1063/1.4790869>]

I. INTRODUCTION

Spin electronics (also called spintronics or magnetoelectronics) has received much attention and developed rapidly through application of the charge and spin degree of freedom of electrons. If the electronic charge and spin degrees of freedom can be controlled by design, it is possible to engineer a next-generation device merging conventional electronics with magnetoelectronics.¹ Carrier-induced ferromagnetism, such as that described by the Ruderman-Kittel-Kasuya-Yosida (RKKY) interaction model,²⁻⁴ might be a solution.

According to the model, Katsufuji *et al.*⁵⁻⁸ designed the system $\text{Sr}_{1-x-y}\text{La}_{x+y}\text{Ti}_{1-x}\text{M}_x\text{O}_3$. The parent compound SrTiO_3 is a simple band insulator. Substituting La^{3+} for Sr^{2+} introduces Ti^{3+} with $3d^1$ configuration, which offers electrons to the conduction band (electron doping). Spins can be introduced by substituting other transition metal ions for Ti. The charge and spin degrees of freedom in the system are independently controllable,^{6,8} and ferromagnetic (FM) coupling between spins appears with increasing carrier concentration at low temperatures. Yang *et al.*^{9,10} reported a similar system, spin-charge co-doped $\text{Sr}_{1-x-y}\text{La}_{x+y}\text{Ti}_{1-x}\text{Co}_x\text{O}_3$, which has an unconventional magnetism at low temperatures. However, no long-range FM state has been observed in spin-charge co-doped bulk SrTiO_3 . Many researchers have, however, observed room-temperature ferromagnetism in diluted magnetic-ion doped conductive (La,Sr) TiO_3 films.¹¹⁻¹³ The idea of independently controlling the spin and charge degrees of freedom provides a new route in material design. Also, some functional materials, e.g., diluted semiconductors, can be made that way.

BaTiO_3 is a perovskite ferroelectric insulator similar to SrTiO_3 . High-temperature ferromagnetism can be found in diluted ion- (Fe- , Mn- , Co- , etc.) doped BaTiO_3 ,¹⁴⁻¹⁷ which

makes BaTiO_3 a candidate for a high-temperature diluted magnetic material. However, reported samples are insulators, and there are no carriers coupled with the magnetism. What happens if we introduce the carrier into BaTiO_3 ? In this research, we studied the system $\text{Ba}_{1-x-y}\text{La}_{x+y}\text{Ti}_{1-x}\text{M}_x\text{O}_3$ ($\text{M} = \text{Cr, Fe, and Co}$), where substituting La^{3+} for Ba^{2+} introduces charge carriers and the doping of transition ions introduces spins. We measured the structural, magnetic, and electrical properties. In $\text{Ba}_{1-x-y}\text{La}_{x+y}\text{Ti}_{1-x}\text{Cr}_x\text{O}_3$, a short-range FM appears upon doping of charge carriers. However, for $\text{Ba}_{1-x-y}\text{La}_{x+y}\text{Ti}_{1-x}\text{M}_x\text{O}_3$ ($\text{M} = \text{Fe and Co}$), there is no obvious coupling between charge and spin degrees of freedom, possibly because the system is localized by the doping of Fe and Co, and electrons cannot mediate magnetic ions.

II. EXPERIMENT

Polycrystalline $\text{Ba}_{1-x-y}\text{La}_{x+y}\text{Ti}_{1-x}\text{M}_x\text{O}_3$ ($0 \leq x \leq 0.2$, $0 \leq y \leq 0.2$) was prepared with a conventional solid-state method. Stoichiometric amounts of high purity BaTiO_3 , La_2O_3 , Ti_2O_3 , M_2O_3 ($\text{M} = \text{Cr, Fe, and Co}$) were mixed and grounded, and then calcined at 900°C for 7 days. The obtained powders were ground, pelletized, and sintered at 1300°C for 40 h with an intermediate grinding, and finally the furnace was cooled slowly to room temperature. The $y=0$ samples were synthesized under air, whereas the $y>0$ samples were sealed in an evacuated quartz tube during preparation to introduce Ti^{3+} ions.

The crystal structure was determined with powder x-ray diffraction (XRD) using $\text{Cu } K_\alpha$ radiation at room temperature. We determined the chemical composition of the samples with energy dispersive spectroscopy (EDS) quantitative analysis using a scanning electron microscope (AMRAY 1000B). The microstructure was characterized with a field-emission scanning electron microscope (FE-SEM, Sirion 200, FEI Company). The magnetic measurements were carried out with a Quantum Design Superconducting Quantum

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Interference Device (SQUID) ($2 \leq T \leq 400$ K, $0 \leq H \leq 5$ T). We used a Quantum Design Physical Property Measurement system (PPMS) to measure electrical resistivity with a conventional four-probe technique with sputtered gold as electrodes ($2 \leq T \leq 400$ K, $0 \leq H \leq 9$ T).

III. RESULTS

A. $\text{Ba}_{1-x-y}\text{La}_{x+y}\text{Ti}_{1-x}\text{M}_x\text{O}_3$ ($\text{M} = \text{Cr}$)

The powder XRD pattern at room temperature reveals that samples with $x \leq 0.2$ and $y \leq 0.2$ are single-phase with no detectable secondary phases (Fig. 1). We refined the structural parameters by using the program FULLPROF,¹⁸ and all samples can be indexed with a cubic lattice with the space group Pm3m. The lattice parameter a decreases with increasing concentration of charge carriers, as shown in the inset of Fig. 1. We confirmed the uniformity of the microstructure and composition for $\text{Ba}_{1-x-y}\text{La}_{x+y}\text{Ti}_{1-x}\text{M}_x\text{O}_3$ ($\text{M} = \text{Cr}$, Fe, and Co) by using EDS (not shown here) and FE-SEM. All the samples are relatively uniform and dense. As an example, Figs. 2(a)–2(c) shows the surface morphologies of $\text{Ba}_{0.7}\text{La}_{0.3}\text{Ti}_{0.9}\text{Cr}_{0.1}\text{O}_3$, $\text{Ba}_{0.7}\text{La}_{0.3}\text{Ti}_{0.9}\text{Fe}_{0.1}\text{O}_3$, and $\text{Ba}_{0.7}\text{La}_{0.3}\text{Ti}_{0.9}\text{Co}_{0.1}\text{O}_3$, respectively.

We measured the temperature dependence of magnetization, $M(T)$, in the zero-field-cooled (ZFC) and field-cooled (FC) modes at an applied field of 100 Oe. Figs. 3(a) and 3(b) show the temperature dependence of magnetization of the samples under an applied field of 100 Oe. All the samples show a Curie-Weiss-like paramagnetism. Moreover, the ZFC and FC susceptibility curves of each sample are nearly superposed. The susceptibilities are fitted with a modified Curie-Weiss model

$$\chi = \chi_0 + \frac{C}{T - \theta}, \quad (1)$$

where χ_0 is the temperature-independent susceptibility, C is the Curie constant, and θ is the paramagnetic (PM) Curie temperature. Table I lists the values of θ . Note that LaCrO_3

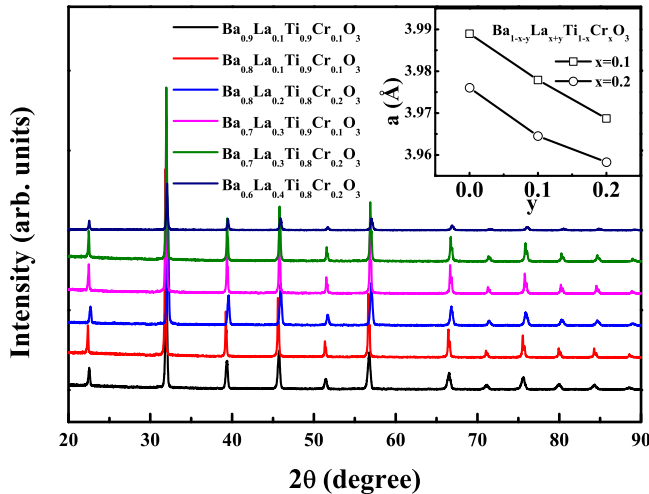


FIG. 1. XRD patterns of $\text{Ba}_{1-x-y}\text{La}_{x+y}\text{Ti}_{1-x}\text{Cr}_x\text{O}_3$ samples. The inset shows the fitted lattice parameters.

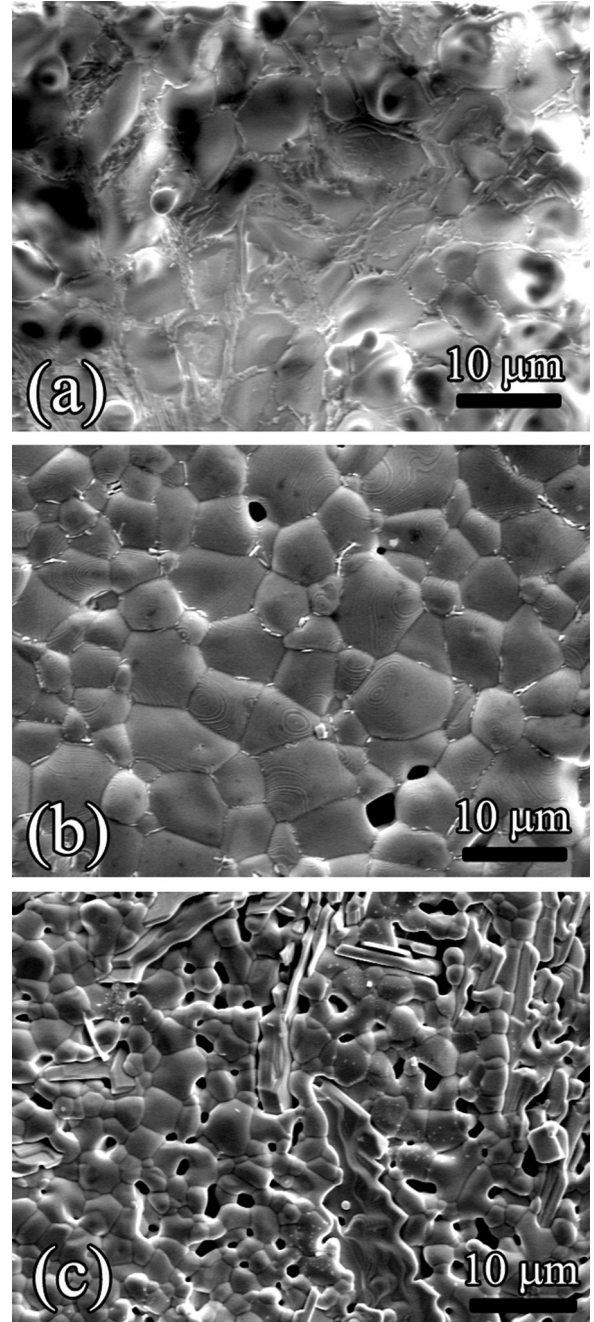


FIG. 2. SEM patterns of (a) $\text{Ba}_{0.7}\text{La}_{0.3}\text{Ti}_{0.9}\text{Cr}_{0.1}\text{O}_3$, (b) $\text{Ba}_{0.7}\text{La}_{0.3}\text{Ti}_{0.9}\text{Fe}_{0.1}\text{O}_3$, and (c) $\text{Ba}_{0.7}\text{La}_{0.3}\text{Ti}_{0.9}\text{Co}_{0.1}\text{O}_3$.

is an antiferromagnetic (AFM) insulator below 290 K.¹⁹ As a result, the negative Weiss temperature observed for $y = 0$ can be attributed to a simple superexchange coupling between Cr spins. When spin concentrations are fixed, the doping of charge carriers enhances the magnitudes of magnetic susceptibility and θ , implying that doping electrons into the conduction band induces some FM interactions between the localized spins on the Cr sites.

To characterize further the magnetic properties of $\text{Ba}_{1-x-y}\text{La}_{x+y}\text{Ti}_{1-x}\text{Cr}_x\text{O}_3$ at low temperatures, we measured the magnetic-field dependence of magnetization at 5 K (Figs. 3(c) and 3(d)). For the samples not doped with charge carriers ($y = 0$), the $M(H)$ plots exhibit a linear behavior, implying AFM characteristics. It seems that FM interactions

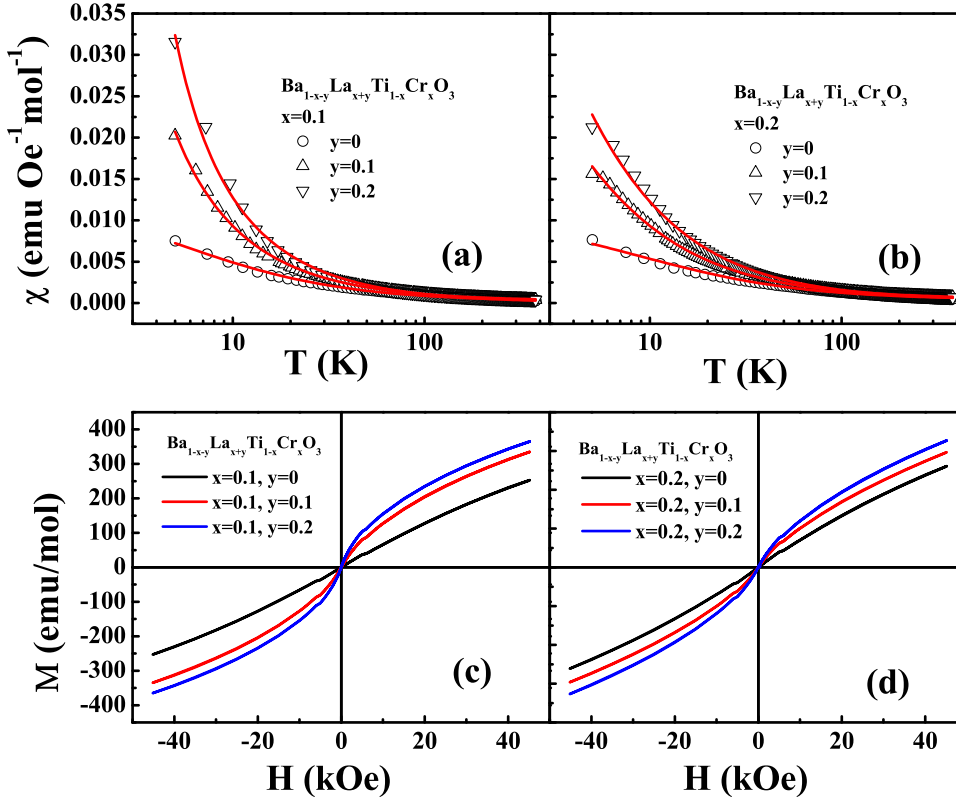


FIG. 3. Temperature dependence of magnetization for $\text{Ba}_{1-x-y}\text{La}_{x+y}\text{Ti}_{1-x}\text{Cr}_x\text{O}_3$ samples measured at $H = 100$ Oe for (a) $x = 0.1$ and (b) $x = 0.2$. The solid line is the Curie-Weiss fit. Magnetization as a function of field at 5 K for the samples with (c) $x = 0.1$ and (d) $x = 0.2$.

appear in the carrier-doped samples ($y > 0$). Increasing the doping level of charge carriers significantly enhances the magnetization, which is consistent with the results from Curie-Weiss fitting. In addition, the very small coercive field (H_c) and remnant magnetization (M_r) indicate that only short-range FM interactions exist in the samples with $y > 0$.

We measured the temperature dependence of the resistivity, $\rho(T)$ (Figs. 4(a) and 4(b)). The samples without charge-carrier doping ($y = 0$) are insulators. The charge-carrier doping efficiently improves the conductivity. However, for the same concentration of charge carriers, increasing the doping level of spins significantly increases the resistivity. These tendencies are similar to what is observed in $\text{Sr}_{1-x-y}\text{La}_{x+y}\text{Ti}_{1-x}\text{Cr}_x\text{O}_3$.^{5,7} Moreover, when applying a magnetic field of $H = 5$ T, we observed a negative magnetoresistance (MR) (Fig. 4(c)). This indicates that the magnetic state of $\text{Ba}_{1-x-y}\text{La}_{x+y}\text{Ti}_{1-x}\text{Cr}_x\text{O}_3$ dominated its transport properties. It should be noted that we found the most remarkable negative MR in the sample $\text{Ba}_{0.7}\text{La}_{0.3}\text{Ti}_{0.9}\text{Cr}_{0.1}\text{O}_3$ ($x = 0.1$, $y = 0.2$), which has the largest fitting Weiss temperature and the lowest resistivity. The MR decreases with increasing temperature. The magnitude of MR, almost 15% at 5 K, is comparable with that of $\text{Sr}_{1-x-y}\text{La}_{x+y}\text{Ti}_{1-x}\text{Cr}_x\text{O}_3$.⁵

To characterize further the electrical properties of $\text{Ba}_{1-x-y}\text{La}_{x+y}\text{Ti}_{1-x}\text{Cr}_x\text{O}_3$, we fit the resistivities at low

temperatures by using the three-dimensional variable-range-hopping (3D VRH) model: $\rho \sim \exp(T_0/T)^{1/4}$. In this model, T_0 is related to the localization length, ξ , and the density of state near Fermi energy level, $N(E_F)$, i.e., $k_B T_0 \approx 21/\xi^3 N(E_F)$.²⁰ According to the model, a larger T_0 indicates that the charge carriers are more localized. Table II shows the fitting results. The charge-carrier doping makes the carrier more itinerant, but the spin doping makes the carrier localized.

B. $\text{Ba}_{1-x-y}\text{La}_{x+y}\text{Ti}_{1-x}\text{M}_x\text{O}_3$ ($\text{M} = \text{Fe}$ and Co)

We refined the structural parameters of single-phase $\text{Ba}_{1-x-y}\text{La}_{x+y}\text{Ti}_{1-x}\text{M}_x\text{O}_3$ ($\text{M} = \text{Fe}$ and Co) (Fig. 5) by using the program FULLPROF, and all samples can be indexed with a cubic lattice with the space group Pm3m.

We measured the magnetic properties of $\text{Ba}_{1-x-y}\text{La}_{x+y}\text{Ti}_{1-x}\text{M}_x\text{O}_3$ ($\text{M} = \text{Fe}$, Co) under the same conditions as $\text{Ba}_{1-x-y}\text{La}_{x+y}\text{Ti}_{1-x}\text{Cr}_x\text{O}_3$ mentioned earlier. For $\text{Ba}_{1-x-y}\text{La}_{x+y}\text{Ti}_{1-x}\text{Fe}_x\text{O}_3$, all the samples show a Curie-Weiss-like PM behavior. The ZFC magnetic susceptibility and the FC susceptibility curves of each sample are nearly superposed (Figs. 6(a) and 6(b)). When the spin concentration is fixed at $x = 0.1$, the doping of charge carriers enhances the susceptibilities, which is similar to the case of $\text{Ba}_{1-x-y}\text{La}_{x+y}\text{Ti}_{1-x}\text{Cr}_x\text{O}_3$. Increasing the spin concentration to $x = 0.2$ brings the susceptibilities of $\text{Ba}_{0.7}\text{La}_{0.3}\text{Ti}_{0.8}\text{Fe}_{0.2}\text{O}_3$ ($y = 0.1$) and $\text{Ba}_{0.6}\text{La}_{0.4}\text{Ti}_{0.8}\text{Fe}_{0.2}\text{O}_3$ ($y = 0.2$) very close to each other, which indicates the carrier doping does not affect the magnetism anymore. For $\text{Ba}_{1-x-y}\text{La}_{x+y}\text{Ti}_{1-x}\text{Co}_x\text{O}_3$ (Fig. 7), we observed a spin-glass behavior for the sample with $x = 0.2$ and $y = 0$, implying that a short-range FM interaction appears. Detailed information on the spin-glass nature of this material has been reported elsewhere.²¹ The sample

TABLE I. Fitted Weiss temperature of $\text{Ba}_{1-x-y}\text{La}_{x+y}\text{Ti}_{1-x}\text{Cr}_x\text{O}_3$.

	$y = 0$	$y = 0.1$	$y = 0.2$
$x = 0.1$	$\theta = -5.13$ K	$\theta = 1.02$ K	$\theta = 1.76$ K
$x = 0.2$	$\theta = -8.70$ K	$\theta = -1.13$ K	$\theta = -0.67$ K

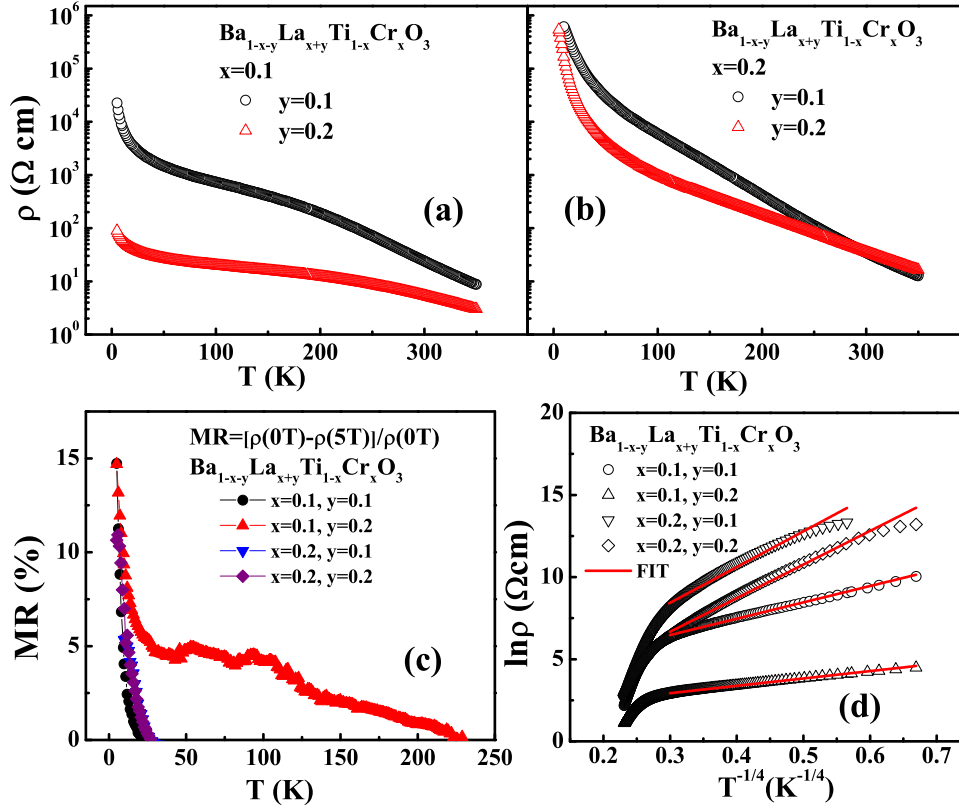


FIG. 4. Temperature dependence of resistivities for $\text{Ba}_{1-x-y}\text{La}_{x+y}\text{Ti}_{1-x}\text{Cr}_x\text{O}_3$ samples for (a) $x=0.1$ and (b) $x=0.2$. (c) Magnetoresistance of $\text{Ba}_{1-x-y}\text{La}_{x+y}\text{Ti}_{1-x}\text{Cr}_x\text{O}_3$ and (d) 3D VRH fit for $\text{Ba}_{1-x-y}\text{La}_{x+y}\text{Ti}_{1-x}\text{Cr}_x\text{O}_3$.

with $x=0.2$ and $y=0.1$ exhibits a Curie-Weiss-like PM again. The magnetizations increase with increasing y , whereas H_c and M_r are still very small. Table III lists the fitted Weiss temperatures found with Eq. (1). Except for $\text{Ba}_{0.8}\text{La}_{0.2}\text{Ti}_{0.8}\text{Co}_{0.2}\text{O}_3$, whose Weiss temperature is denoted by the spin-glass freezing temperature, 10.1 K, all other samples' Weiss temperatures are negative. Obviously, the doping of charge carriers does not affect Weiss temperature much.

We measured the temperature dependence of the resistivity. All samples except $\text{Ba}_{0.7}\text{La}_{0.3}\text{Ti}_{0.9}\text{Fe}_{0.1}\text{O}_3$ have a very large resistance, and the data overflowed during the measurements. Fig. 8 shows the resistivity of $\text{Ba}_{0.7}\text{La}_{0.3}\text{Ti}_{0.9}\text{Fe}_{0.1}\text{O}_3$. We again fit the resistivity at low temperatures with the 3D VRH model, and obtained $T_0 = 25\,924.45$ K. The MR of the sample is very small and can be neglected.

IV. DISCUSSION

In the RKKY model, the sign of the magnetic interaction depends on the relation between the Fermi wave number of conduction carriers and the distance between neighboring magnetic moments. The numbers of spins and carriers are the most important parameters for the coupling between spin and charge degrees of freedom. Theoretically, the RKKY interaction can be described by²²

TABLE II. Fitted T_0 of VRH model for $\text{Ba}_{1-x-y}\text{La}_{x+y}\text{Ti}_{1-x}\text{Cr}_x\text{O}_3$.

	$x=0.1$	$x=0.2$
$y=0.1$	$T_0 = 9787.79$ K	$T_0 = 224\,006.34$ K
$y=0.2$	$T_0 = 404.51$ K	$T_0 = 175\,259.65$ K

$$J_{ij}^{\text{RKKY}} = J_0 r^{-4} [\sin(2k_F r) - 2k_F r \cos(2k_F r)] , \quad (2)$$

where $r \propto n_s^{-1/3}$ is the spatial separation between the magnetically coupled magnetic atoms, corresponding to the spin density, n_s , which is decided by x ; $k_F \propto n_c^{1/3}$ is the Fermi wave vector corresponding to the carrier density, n_c , which is decided by y ; J_0 is the RKKY coupling strength and is positive. So the magnetism is fully decided by x and y . This magnetism requires itinerant charge carriers. The longer the itinerant distance of a carrier is, the easier it is the separated local magnetic ions can be mediated magnetically.

Let us recall the magnetic and transport properties of $\text{Ba}_{1-x-y}\text{La}_{x+y}\text{Ti}_{1-x}\text{M}_x\text{O}_3$ described earlier. For $\text{Ba}_{1-x-y}\text{La}_{x+y}\text{Ti}_{1-x}\text{Cr}_x\text{O}_3$, the T_0 obtained from VRH fitting shows a variation in the localization of each sample. For a fixed spin concentration, the carrier doping makes the system

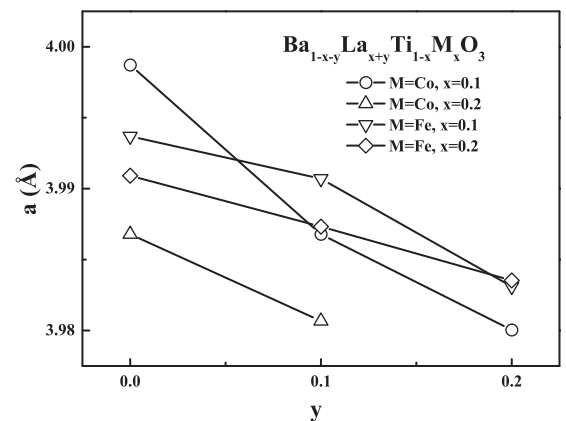


FIG. 5. Fitted lattice parameters of $\text{Ba}_{1-x-y}\text{La}_{x+y}\text{Ti}_{1-x}\text{M}_x\text{O}_3$ ($M = \text{Fe}$ and Co).

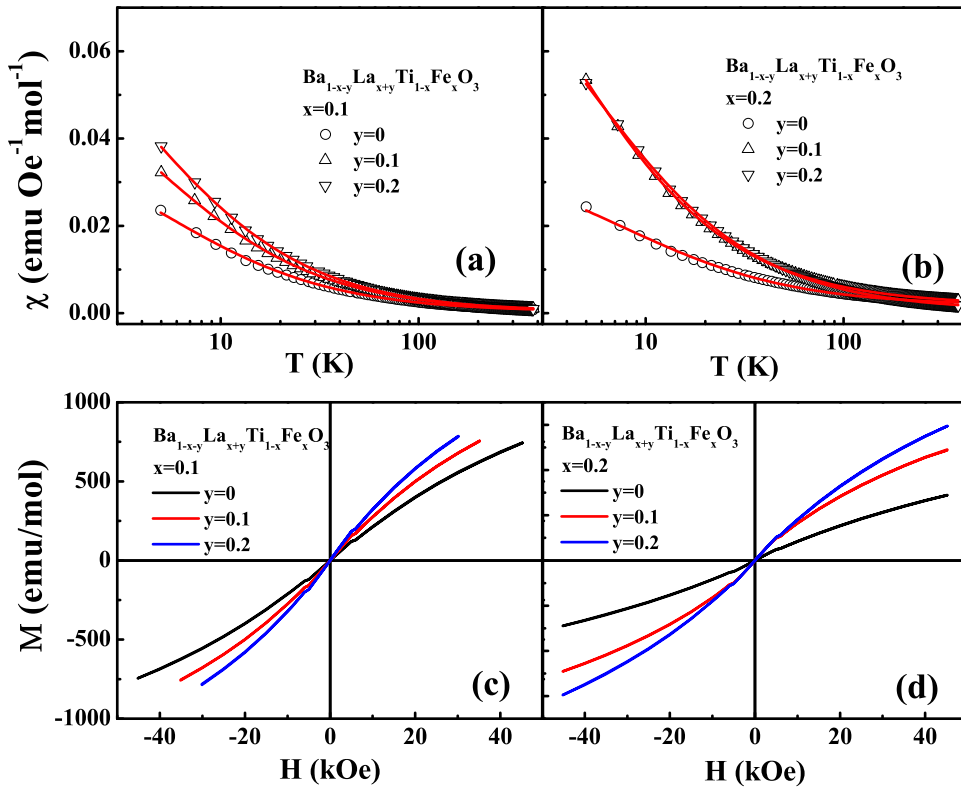


FIG. 6. Temperature dependence of magnetization for the samples $\text{Ba}_{1-x-y}\text{La}_{x+y}\text{Ti}_{1-x}\text{Fe}_x\text{O}_3$ measured at $H=100$ Oe for the samples with (a) $x=0.1$ and (b) $x=0.2$. The solid line is the Curie-Weiss fit. Magnetization as a function of field at 5 K for the samples with (c) $x=0.1$ and (d) $x=0.2$.

less localized. But when the charge carrier concentration is fixed, the spin doping makes the system more localized. The localization of carriers may originate from the disorder introduced by doping. The maximum Weiss temperature appears in the sample with $x=0.1$ and $y=0.2$. In this case, the sample exhibits the minimum resistivity and the largest localization length, implying that the charge carriers in this sample are most itinerant. The magnetic results for $\text{Ba}_{1-x-y}\text{La}_{x+y}\text{Ti}_{1-x}\text{Cr}_x\text{O}_3$ are qualitatively consistent with the sum of the carrier-independent

superexchange AFM interaction and the carrier-dependent RKKY interaction.

For the compounds with $M=\text{Fe}$ or Co , $\text{Ba}_{0.7}\text{La}_{0.3}\text{Ti}_{0.9}\text{Fe}_{0.1}\text{O}_3$ ($x=0.1$, $y=0.2$) has the minimum resistivity and most itinerant charge carrier. The parameter T_0 of the sample obtained from VRH fitting of this sample is 25924.45 K, which is almost 60 times larger than that for $\text{Ba}_{0.7}\text{La}_{0.3}\text{Ti}_{0.9}\text{Cr}_{0.1}\text{O}_3$. Also the other $\text{Ba}_{1-x-y}\text{La}_{x+y}\text{Ti}_{1-x}\text{M}_x\text{O}_3$ ($M=\text{Fe}$ and Co) samples are insulators with very large resistance. It suggests that

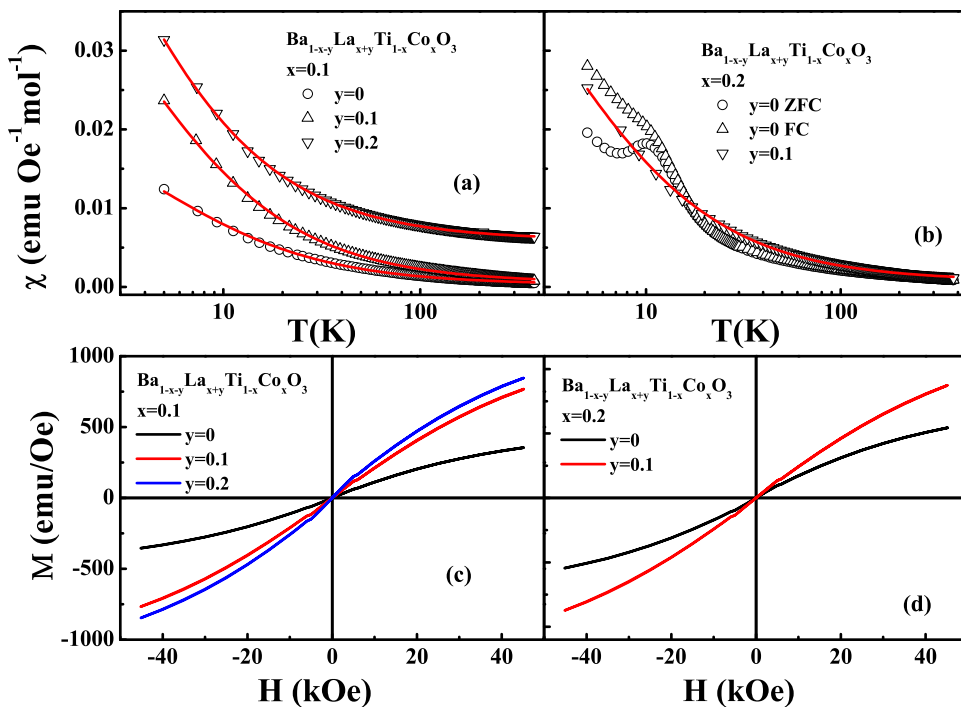


FIG. 7. Temperature dependence of magnetization for $\text{Ba}_{1-x-y}\text{La}_{x+y}\text{Ti}_{1-x}\text{Co}_x\text{O}_3$ samples measured at $H=100$ Oe for (a) $x=0.1$ and (b) $x=0.2$. The solid line is the Curie-Weiss fit. Magnetization as a function of field at 5 K for (c) $x=0.1$ and (d) $x=0.2$.

TABLE III. Fitted Weiss temperature of $\text{Ba}_{1-x-y}\text{La}_{x+y}\text{Ti}_{1-x}\text{M}_x\text{O}_3$ ($\text{M} = \text{Fe}$ and Co).

$\text{M} = \text{Fe}$	$y = 0$	$y = 0.1$	$y = 0.2$
$x = 0.1$	$\theta = -4.97 \text{ K}$	$\theta = -4.19 \text{ K}$	$\theta = -3.63 \text{ K}$
$x = 0.2$	$\theta = -7.58 \text{ K}$	$\theta = -3.46 \text{ K}$	$\theta = -4.96 \text{ K}$
$\text{M} = \text{Co}$	$y = 0$	$y = 0.1$	$y = 0.2$
$x = 0.1$	$\theta = -4.16 \text{ K}$	$\theta = -2.83 \text{ K}$	$\theta = -2.04 \text{ K}$
$x = 0.2$	$\theta = 10.1 \text{ K}$	$\theta = -3.14 \text{ K}$	...

the carriers in these samples are completely localized. Why is there such a difference between $\text{M} = \text{Cr}$ and $\text{M} = \text{Fe/Co}$ samples?

Note that the spin configurations of Ti^{3+} , Cr^{3+} , Fe^{3+} , and Co^{3+} are $3d^1$, $3d^3$, $3d^5$, and $3d^6$, respectively. Maybe the Fe and Co doping leads to a larger Hubbard U , which makes the system more localized than the Cr-doped samples. The Ti^{3+} in $\text{Ba}_{1-x-y}\text{La}_{x+y}\text{Ti}_{1-x}\text{M}_x\text{O}_3$ ($\text{M} = \text{Fe}$ and Co) should be considered as localized spins instead of charge carriers. This means that there are two kinds of magnetic Ti^{3+} and M^{3+} ions randomly distributed in the sample. Therefore, we suggest that the magnetism for $\text{Ba}_{1-x-y}\text{La}_{x+y}\text{Ti}_{1-x}\text{M}_x\text{O}_3$ ($\text{M} = \text{Fe}$ and Co) originates from the contributions of both superexchange interaction between the magnetic ions and the PM of isolated magnetic ions. For $\text{Ba}_{0.8}\text{La}_{0.2}\text{Ti}_{0.8}\text{Co}_{0.2}\text{O}_3$, the spin-glass behavior implies a short-range FM in this sample. With further increase of the La doping level, lattice shrinking and Ti^{3+} doping possibly change the environment of Co^{3+} , which in turn affects the spin state of Co^{3+} and suppresses FM while enhancing AFM interactions.

According to the analysis above, a long-range FM may appear in $\text{Ba}_{1-x-y}\text{La}_{x+y}\text{Ti}_{1-x}\text{M}_x\text{O}_3$ with a large y and an appropriate x . Unfortunately, if y is too large, a $\text{La}_2\text{Ti}_2\text{O}_7$ phase begins to occur. However, a larger y implies that there are more Ti^{3+} ions, which can easily reduce the M^{3+} ions to the simple substance M. Nevertheless, this still gives us an idea of how to design a functional material with a long range FM, in which the magnetism comes from the coupling

between charge and spin degree of freedom. The doping ions must be similar to the ions of the matrix to avoid a large Hubbard U , which can make the system localized. Moreover, the ions must have a stable oxide state to prevent reduction and oxidation.

V. CONCLUSION

In summary, we prepared a series of independent spin- and carrier-doped samples of $\text{Ba}_{1-x-y}\text{La}_{x+y}\text{Ti}_{1-x}\text{M}_x\text{O}_3$ ($\text{M} = \text{Cr}$, Fe and Co) and studied their structural, magnetic and transport properties. In $\text{Ba}_{1-x-y}\text{La}_{x+y}\text{Ti}_{1-x}\text{Cr}_x\text{O}_3$, a short-range FM appears upon charge-carrier doping. However, for $\text{Ba}_{1-x-y}\text{La}_{x+y}\text{Ti}_{1-x}\text{M}_x\text{O}_3$ ($\text{M} = \text{Fe}$ and Co), there is no obvious coupling between charge and spin degrees of freedom, perhaps because the samples are localized by the doping of Fe and Co ions, making charge carriers too localized to be the interaction media of magnetic ions.

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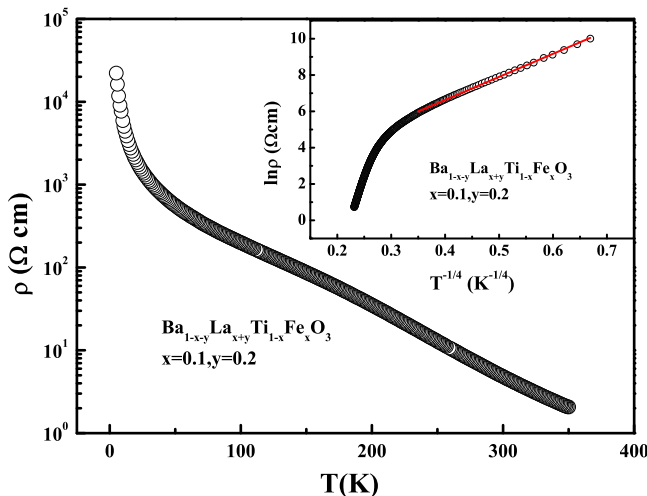


FIG. 8. Temperature dependence of resistivity for $\text{Ba}_{0.7}\text{La}_{0.3}\text{Ti}_{0.9}\text{Fe}_{0.1}\text{O}_3$ sample. The inset shows the 3D VRH fit.

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