Effect of Cr-doping on charge ordering stability in $Bi_{1-x}Sr_xMn_{1-y}Cr_yO_3$

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Abstract

The effect of Cr-doping on electrical and magnetic properties of high-temperature charge-ordered manganites ($Bi_{1-x}Sr_xMn_{1-y}Cr_yO_3$, where $x = 0.25, 0.3, 0.4$; $0 \leqslant y \leqslant 0.1$) was investigated. Without Cr-doping, a charge disorder-to-order transition (T_{co}) and antiferromagnetic phase transition (T_N) were observed near 500 and 150 K, respectively. The charge-order phase transition broadened, but did not disappear upon Cr-doping up to $y = 0.1$. The antiferromagnetic phase disappeared upon 10% Cr-doping, transforming into a paramagnetic phase, rather than into a double exchange ferromagnetic metal, in contrast to the case of $Pr_{1-x}Ca_xMn_{1-y}Cr_yO_3$.
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Since the discovery of colossal negative magnetoresistance (CMR) [1–4], a family of perovskite manganese oxides $RE_{1-x}AE_xMnO_3$ (where RE is a trivalent rare earth and AE a divalent alkaline earth) have attracted much attention because of their novel physical properties and possible applications to magnetic devices. The charge ordering phase transition temperature (~ 600 K) of $Bi_{1-x}Sr_xMnO_3$ is much higher than that of other perovskite manganese oxides [5,6]. The strong localization of e_g electrons is presumably caused by the highly polarizable $6s^2$ lone pair of Bi^{3+} ions. From the standpoint of applications, such a high charge ordering transition temperature could lead to high-temperature CMR, which is caused by the melting of charge ordering in a magnetic field. Frontera et al., however, reported that no metal-insulator transition was observed in $Bi_{1-x}Sr_xMnO_3$ under an applied magnetic field of up to 40 T at 4 K [7]. It is necessary to suppress the charge ordering stability to achieve CMR in $Bi_{1-x}Sr_xMnO_3$.

Generally, charge ordering stability is suppressed by a deviation of the composition from $x = 0.5$. In the case of $Bi_{1-x}Sr_xMnO_3$, however, charge ordering stability is enhanced, rather than suppressed, near $x = 0.25$ [8]. Cr-doping at Mn sites is another way to suppress charge ordering stability [9]. Cr is doped at Mn sites as a trivalent ion that tends to make the neighboring Mn ions tetravalent. In addition, the unoccupied e_g orbital of the Cr^{3+} ion should weaken the orbital ordering network. Thus, one would expect the long-range charge and orbital ordering to collapse as a result of a small amount of Cr substitution for Mn. Indeed, Katsufuji et al. reported that the charge ordering state of $Pr_{1-x}Ca_xMnO_3$ ($0.35 \leqslant x \leqslant 0.55$) is suppressed and that a transformation into the ferromagnetic metallic phase occurs upon 3% Cr-doping of the Mn sites [10]. If one can successfully suppress the stability of charge ordering in this manner, one would expect to see the CMR effect at room temperature. In order to investigate the effect of Cr-doping in $Bi_{1-x}Sr_xMnO_3$, we measured the resistivity and magnetic susceptibility of $Bi_{1-x}Sr_xMn_{1-y}Cr_yO_3$.

$Bi_{1-x}Sr_xMn_yCr_{1-y}O_3$ samples were prepared by standard solid-state reaction. Bi_2O_3, $SrCO_3$, Cr_2O_3 and Mn_3O_4 powders with a purity of 99.9% were mixed, ground, and calcined at 900 °C for 12 h. The resultant powders were pressed into a pellet and sintered at 1100 °C for 24 h with

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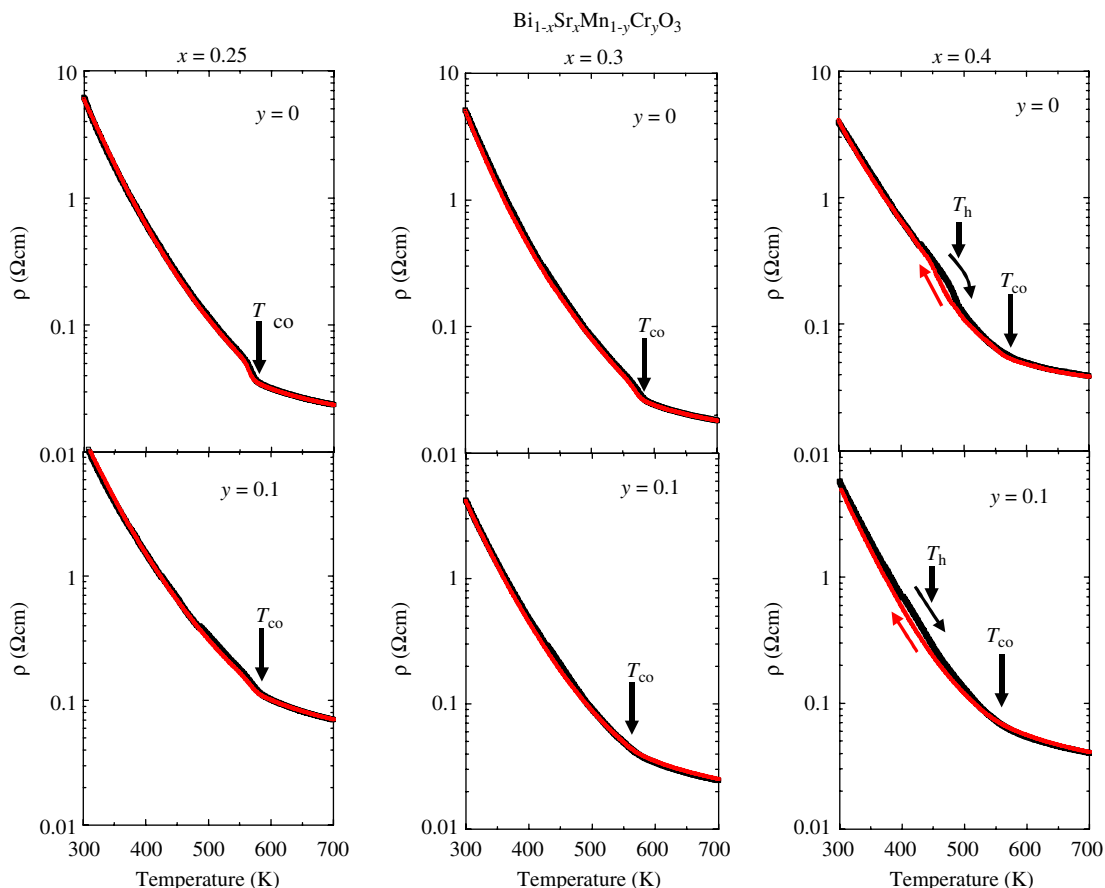*E-mail address:* shigeki@yokohama-cu.ac.jp (S. Yamada).

$Bi_{1-x}Sr_xMn_{1-y}Cr_yO_3$

Fig. 1. (Color online) Temperature dependence of the resistivity of $Bi_{1-x}Sr_xMn_{1-y}Cr_yO_3$ ($x = 0.25, 0.3, 0.4$: $y = 0, 0.1$). T_{co} is charge ordering transition temperature.

intermediate re-grinding. The samples obtained were confirmed to be of a single phase by X-ray powder diffraction. Magnetization was measured using a commercial superconducting quantum interference device magnetometer (Quantum Design Co., Ltd. MPMS-XL).

Fig. 1 shows the temperature dependence of resistivity of $Bi_{1-x}Sr_xMn_{1-y}Cr_yO_3$ above 300 K. For $y = 0$, an anomaly is observed at approximately 574–577 K, almost independently of the Sr concentration. This should be assigned to the charge disorder-to-order transition temperature T_{co}. For $x = 0.4$, the temperature dependence of resistivity shows a kink at $T_{co} \simeq 550$ K and another anomaly accompanied with a hysteresis at $T_h \simeq 500$ K. A similar successive phase transition was first reported by Hejtmánek et al. [11] for $x = 0.5$. They assigned T_{co}, which they named T_{crit}, to a structural transition temperature from cubic $Pm\bar{3}m$ to orthorhombic $Ibmm$ and T_h to the charge disorder-to-order transition temperature. On the other hand, our synchrotron X-ray diffraction study evidences that T_{co} is the charge disorder-to-order transition temperature [12]. One has to perform some diffraction study for various x to know which of T_{co} or T_h is the charge ordering transition temperature. With Cr-doping, both the kink at T_{co} and the hysteresis loop around T_h become broadened, but do not disappear up to $y = 0.1$. With 10%

Cr-doping in the $x = 0.4$ compound, T_{co} decreases from 574 to 556 K. For $x = 0.25$, however, the dependence of T_{co} on Cr-doping is much weaker. In other words, the effect of Cr-doping on charge ordering stability increases with increasing x toward $x = 0.5$. Table 1 shows the activation energy E_A, which is obtained from the best fit of resistivity $\rho \propto \exp(E_A/(k_B T))$. The activated-type temperature dependence is presumably dominated by the change in mobility, that is, the activation energy could be connected to the binding energy of a polaron [13]. Without Cr-doping, the activation energy above T_{co} is 0.07–0.10 eV, and decreases slightly with increasing x. The x-dependence should be correlated with the increase in the number of hole-type charge carriers with x in this temperature range. The activation energy increases slightly with Cr-doping. This indicates that Cr-doping mainly influences the mobility term of carrier motion. The activation energy below T_{co} (0.19–0.27 eV) is approximately twice as large as that above T_{co}. This abrupt change in E_A is universally observed at the charge disorder-to-order transition of all manganese oxides. The activation energy in the charge ordered phase for $x = 0.4$ is smaller than that for $x = 0.25$ and 0.3. This implies that the charge ordering state for $x = 0.25$ is more stable than that for $x = 0.4$, in contrast to other manganese oxide systems, where the stability of the

Table 1
T_{co}: Charge disorder-to-order temperature; E_A: activation energy of resistivity; θ: Weiss temperature; μ_{eff}: effective Bohr magneton

	$x = 0.25$		$x = 0.3$		$x = 0.4$	
	$y = 0$	$y = 0.1$	$y = 0$	$y = 0.1$	$y = 0$	$y = 0.1$
T_{co} (K)	577	581	578	564	574	556
E_A (eV) ($T > T_{co}$)	0.10(1)	0.12(1)	0.09(1)	0.11(1)	0.07(1)	0.10(1)
θ (K) ($T > T_{co}$)	240(10)	200(20)	250(20)	260(40)	290(10)	260(40)
μ_{eff} (μ_B/f.u.) ($T > T_{co}$)	4.8(1)	5.0(2)	5.0(2)	4.6(3)	4.7(1)	4.7(3)
E_A (eV) (300 K)	0.26(3)	0.24(3)	0.27(3)	0.25(2)	0.19(1)	0.21(1)
θ (K) (300 K)	100(20)	70(20)	100(20)	70(20)	70(20)	50(20)
μ_{eff} (μ_B/f.u.) (300 K)	5.6(2)	5.7(2)	5.8(2)	5.7(2)	5.9(2)	5.6(6)

The activated values of the effective moment $\langle 2\sqrt{S(S+1)} \rangle$ are 4.64 ($x = 0.25$), 4.59 ($x = 0.3$) and 4.49 ($x = 0.4$), respectively.

charge ordering state is suppressed by deviation of the hole concentration from $x = 0.5$. The activation energy in the charge order phase in $Bi_{1-x}Sr_xMnO_3$ does not depend on Cr-doping, which indicates that Cr-doping does not influence carrier motion for even charge ordering phase.

Fig. 2 shows the temperature dependence of inverse magnetic susceptibility of $Bi_{1-x}Sr_xMn_{1-y}Cr_yO_3$ above 300 K. Anomalies at around T_{co}, and T_h are observed in these $1/\chi - T$ curves as well. Once again, these anomalies become broadened, but do not disappear, upon Cr-doping up to $y = 0.1$. The temperature dependence of $1/\chi$ both above and below T_{co} seems to follow the Curie–Weiss law. Table 1 shows the Weiss temperature (θ) and effective Bohr magneton (μ_{eff}) obtained by the fit to the Curie–Weiss law, $\chi = C/(T - \theta)$, where C is Curie's constant. For all of the samples, θ is positive, which suggests ferromagnetic interaction between Mn spin moments in $Bi_{1-x}Sr_xMn_{1-y}Cr_yO_3$. θ is 240–290 K and increases with increasing x above T_{co}. This x dependence is reasonable if the double exchange interaction is taken into account. The value of θ does not increase upon Cr-doping. The ferromagnetic interaction is not enhanced by Cr-doping. The μ_{eff} value obtained above T_{co} is approximately consistent with the average of $2\sqrt{S(S+1)}$. Here, S is the spin angular momentum, whose value is 3/2 for Mn^{4+} and Cr^{3+}, and 2 for Mn^{3+}. In the charge ordering phase, θ is much reduced, down to 70–100 K, and does not depend on x. $BiMnO_3$, an end material of $Bi_{1-x}Sr_xMnO_3$, has a ferromagnetic phase below 100 K [14]. Santos et al. reported that the ferromagnetic interaction is due to the three-dimensional network of $(3x^2 - r^2/3x^2 - r^2/3x^2 - r^2)$-type orbitals [15]. Thus, the ferromagnetic interaction in the charge ordering phase of $Bi_{1-x}Sr_xMn_{1-y}Cr_yO_3$ could be due to the three-dimensional orbital network, because this temperature is near the Curie temperature of $BiMnO_3$. The value of θ for the charge ordering phase would increase if the charge ordering stability were suppressed by Cr-doping. However, θ does not increase, but rather, decrease slightly, upon Cr doping. Consequently, the charge ordering stability is not suppressed by Cr-doping. Below T_{co}, μ_{eff} is slightly larger than $2\sqrt{S(S+1)}$. This

could be the effect of interactions between the spins at (Mn,Cr) sites.

Fig. 3 shows the temperature dependence of magnetization in a magnetic field of 5 kOe. For $x = 0.3$ and 0.4, a kink ascribable to the antiferromagnetic phase transition (T_N) is observed near 145–160 K, while no such kink is observed for $x = 0.25$. Below 40 K, differences in magnetization are observed between the warming and cooling processes. These results are in good agreement with the report by Mantytskaya et al. [16]. Cr-doping suppresses the antiferromagnetic state for $x \geqslant 0.3$. For $x = 0.25$, the magnetization curve does not change appreciably with Cr concentration. For $x = 0.3$, the magnetization for $y = 0.1$ is smaller than that for $y = 0.05$. This indicates that the antiferromagnetic phase completely disappears at $y = 0.05$, and Cr doping with $y > 0.05$ only decreases the average spin moments in the (Mn,Cr)-sites. For $x = 0.4$, T_N slightly decreases with 3% Cr-doping. The magnetization in the antiferromagnetic phase increases with Cr-doping up to 10% and the kink at T_N disappears for $y = 0.1$. Thus, the degree of suppression of the antiferromagnetic state by Cr-doping decreases with increasing x. This indicates that the antiferromagnetic phase becomes more stable as x approaches 0.5, like the antiferromagnetic state of other perovskite manganese oxides. Regardless of x, the antiferromagnetic phase transforms into a paramagnetic phase, rather than a ferromagnetic phase, upon Cr-doping. This indicates that a magnetic long range ordering disappears due to the competition between the antiferromagnetic and ferromagnetic interaction. Therefore Cr-doping does not influence charge ordering stability even in the low temperature range. The charge ordering in the present case differs from that in $Pr_{1-x}Ca_xMn_{1-y}Cr_yO_3$, which melts and transforms into a ferromagnetic phase upon 3% Cr-doping [9,10]. The melting of charge ordering and appearance of the ferromagnetic phase in $Pr_{1-x}Ca_xMn_{1-y}Cr_yO_3$ is caused by the competition between ferromagnetic double-exchange interaction and Coulomb interaction between carriers, which is the origin of the charge ordering state. Generally, the charge ordering that occurs in real space is more amenable to spatial disorder than a ferromagnetic ordering, which can be regarded as a kind
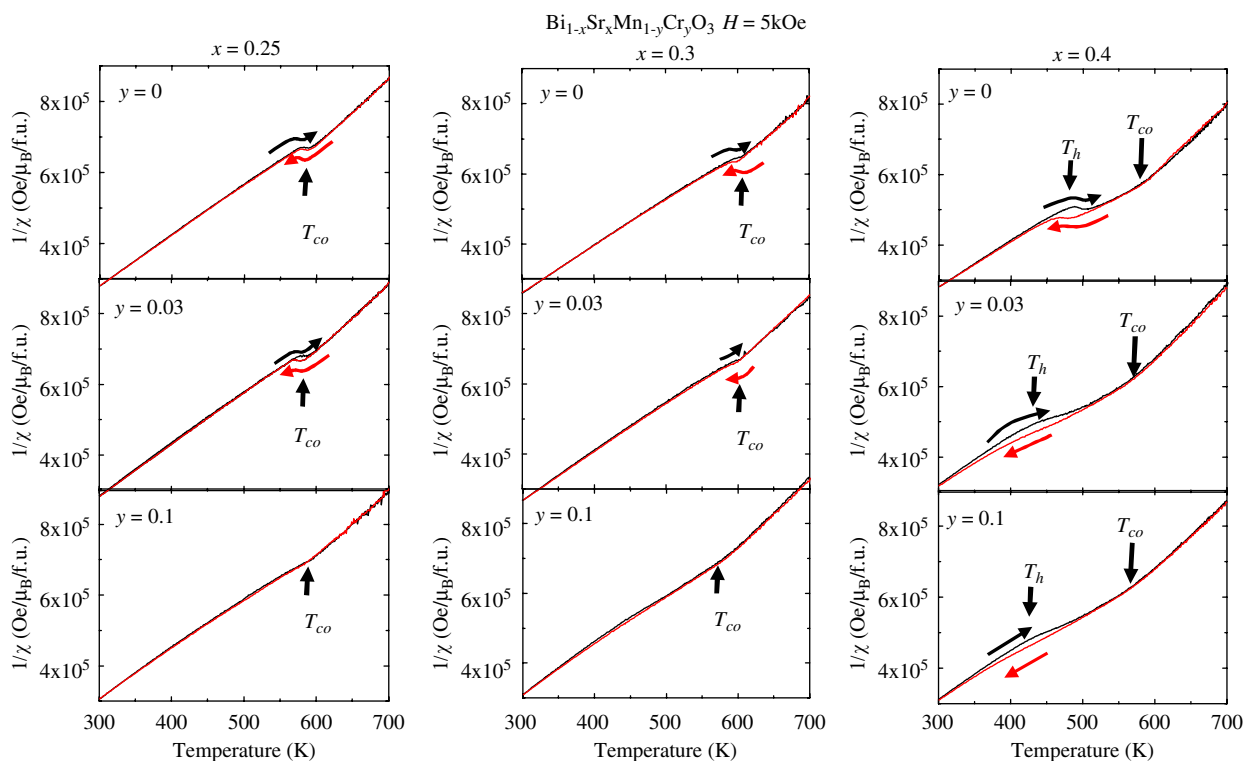
Fig. 2. (Color online) Temperature dependence of inverse magnetic susceptibility of $Bi_{1-x}Sr_xMn_{1-y}Cr_yO_3$ ($x = 0.25, 0.3, 0.4$: $y = 0, 0.03, 0.1$). The abbreviation 'f.u.' denotes the formula unit. Arrows indicate kinks or anomalies that involve hysteresis.
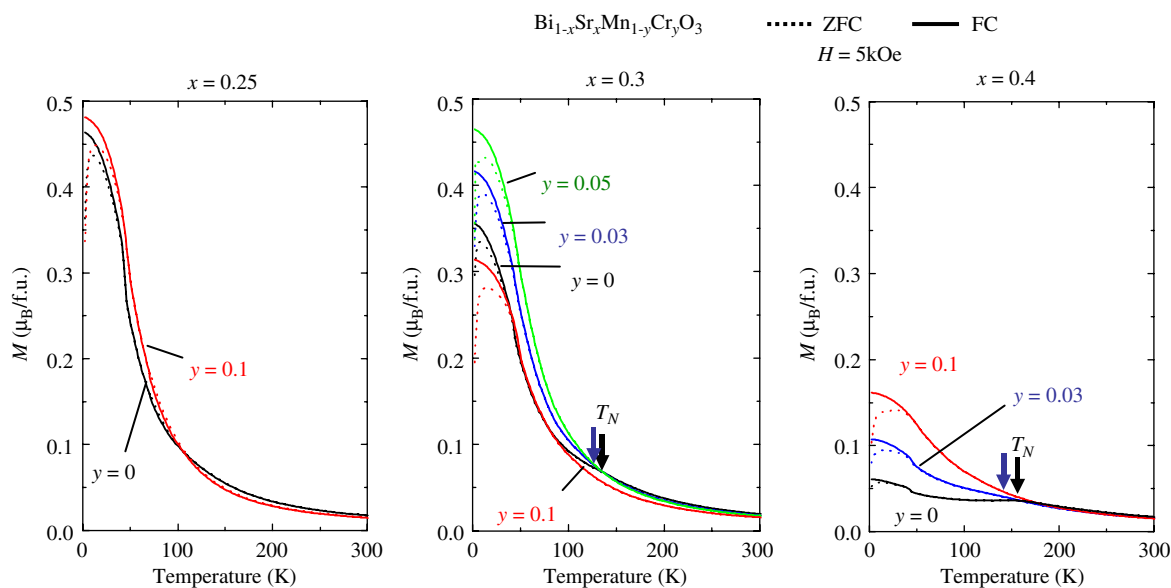

Fig. 3. (Color online) Temperature dependence of magnetic susceptibility of $Bi_{1-x}Sr_xMn_{1-y}Cr_yO_3$ ($x = 0.25, 0.3, 0.4$: $y = 0$–0.1) below 400 K. Solid and dotted lines show the data measured in the zero-field-cooling and field-cooling processes, respectively. T_N is Néel temperature. The abbreviation 'f.u.' denotes the formula unit.

of k-space ordering. Thus, in $Pr_{1-x}Ca_xMnO_3$, the double exchange ferromagnetic phase appears as a result of the suppression of charge ordering stability by Cr-doping. The stable charge ordering state in Cr-doped $Bi_{1-x}Sr_xMnO_3$ strongly suggests that the Bi^{3+} ion has an enhancing effect on the localization of d-electrons at Mn ions.

Cr-doping of Mn sites broadens the charge ordering phase transition of $Bi_{1-x}Sr_xMnO_3$, but it does not cause the transition temperature to disappear completely. The antiferromagnetic phase does disappear upon Cr-doping, transforming into a paramagnetic, rather than ferromagnetic, phase. This is in sharp contrast to the case of

$Pr_{1-x}Ca_xMn_{1-y}Cr_yO_3$, which transforms into a double-exchange ferromagnetic phase for a comparatively light doping of $y = 0.03$.

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