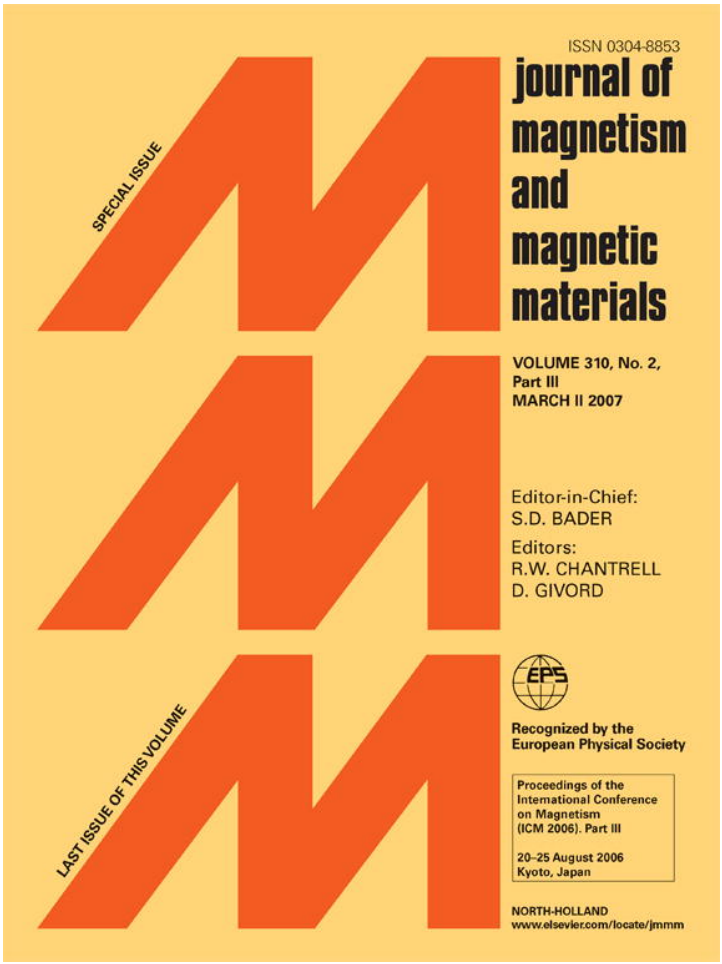

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Melting of the charge-ordering state by ruthenium doping in $Ca_{0.6}Pr_{0.4}Mn_{1-y}Ru_yO_3$ ($y = 0$, 0.03, 0.05, 0.07) perovskites

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Abstract

Single-phase perovskite compounds $Ca_{0.6}Pr_{0.4}Mn_{1-y}Ru_yO_3$ ($y = 0$, 0.03, 0.05, 0.07) were prepared by ceramic-technology method. Thermomagnetic plots, temperature dependence of resistivities, ac-susceptibilities of the produced samples were determined. The non-ruthenium doping ($y = 0$) sample presents charge-ordering phenomenon at $T_{CO} = 291$ K. The experiment results show that the ruthenium doping destroys the charge ordering state, enhances ferromagnetism tendency and conductivity.

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Keywords: Perovskite; Charge ordering

The calcium-praseodymium manganites $Ca_{1-x}Pr_xMnO_3$ systems exhibit charge-ordering (CO) phenomenon and complicate magnetic-phase diagram [1]. The good thermomagnetic properties of these compounds were examined in [2]. In this contribution, we investigate the destroying of CO state by doping of the ruthenium for manganese in antiferromagnetic $Ca_{0.6}Pr_{0.4}MnO_3$ perovskites. The $Ca_{0.6}Pr_{0.4}Mn_{1-y}Ru_yO_3$ ($y = 0$, 0.03, 0.05, 0.07) perovskites compounds were synthesized by solid-state reaction method described in [2]. Room temperature X-ray diffraction patterns recorded by a D5005 diffractometer showed that all samples were of single phase and had Pnma crystal structure. The lattice parameters of samples were given in the Table 1. The FC thermomagnetic measurements (Fig. 1) of the samples demonstrate that small Ru doping from $y = 0$ to 0.07 increases the maximum value of magnetization up to 100 times. Figs. 2 and 3 show the temperature dependence of real (χ') and imaginary (χ'') ac-susceptibilities for $y = 0$ and 0.07 samples. There were three anomalies in the susceptibilities curves for $y = 0$ sample: the first occurred at the charge-ordering temperature $T_{CO} = 291$ K and two other ones at the Neel temperatures. The strong Ru doping $y = 0.07$ sample had only one paramagnetic–ferromagnetic phase transition at $T_C = 210$ K (see Fig. 3). Characteristic temperatures for all samples were listed in Table 1. DC resistivity of the samples was measured and results were plotted in Fig. 4. One can see that Ru doping for Mn reduces resistivity in the region $T > 100$ K strongly. CO exhibits anomaly at the same temperature 291 K for $y = 0$ sample (see inset in Fig. 4) like that observed in Fig. 2. Ru ion may have valences varied from +4 to +8. Mn ions in our perovskites have valences +3 and +4. We suggest that strong damping of resistivity in doping samples may concern with pentavalent state of Ru ion differing from what of Mn ions. Raveau et al. [3] also supports this point of view. According to the Mott–Viret's variable range hopping (VRH) model [4], electrical carriers in magnetic perovskites are hopping between localized states due to random magnetic potential. Using the VRH law and the cell-volume value V given in Table 1, we obtained the characteristic temperature T_o, the localization length l of the sample's carriers in the temperature range

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Table 1
The lattice constants, volume of unit cell, characteristic temperatures and parameters of VRH conducting model of samples

Samples (y)	a (Å)	b (Å)	c (Å)	V (Å^3)	T_N (K)	T_C (K)	T_{CO} (K)	VRH: $\rho = \rho_o \exp(T_o/T)^{1/4}$		
								T_o (10^5 K)	l (nm)	R (nm)
0	5.41	5.36	7.58	219.82	137; 207	—	291	1.49	0.84	1.86
0.03	5.37	5.37	7.57	218.55	190	—	—	1.17	0.90	1.90
0.05	5.38	5.37	7.59	219.02	—	160	—	220.70	0.16	1.23
0.07	5.37	5.36	7.62	219.51	—	210	—	0.84	1.01	1.95

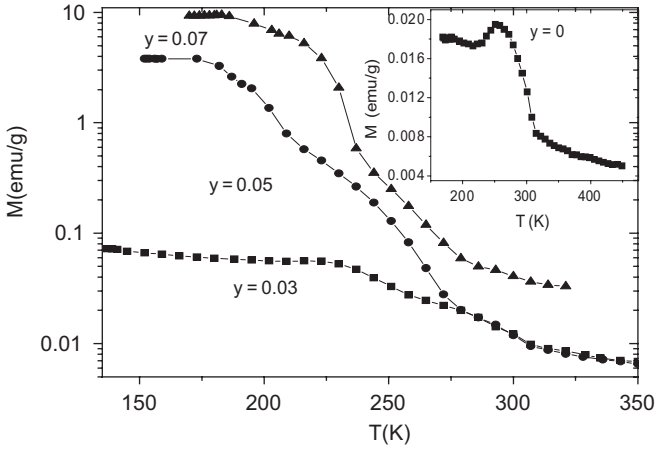

Fig. 1. FC $M(T)$ curves taken at 50 Oe for samples. The inset corresponds to $y = 0$ case.

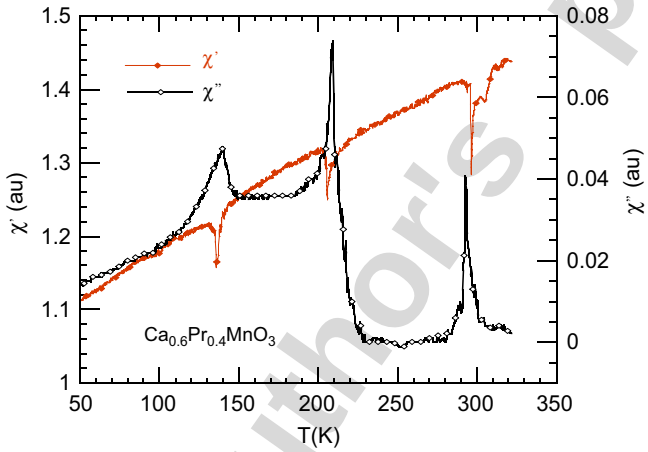

Fig. 2. Temperature dependence of real (χ'), imaginary (χ'') ac susceptibilities for $y = 0$ sample.

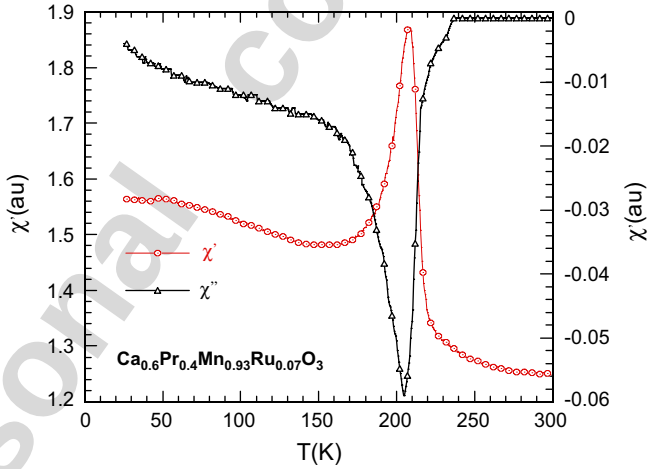

Fig. 3. Temperature dependence of real (χ'), imaginary (χ'') ac susceptibilities for $y = 0.07$ sample.

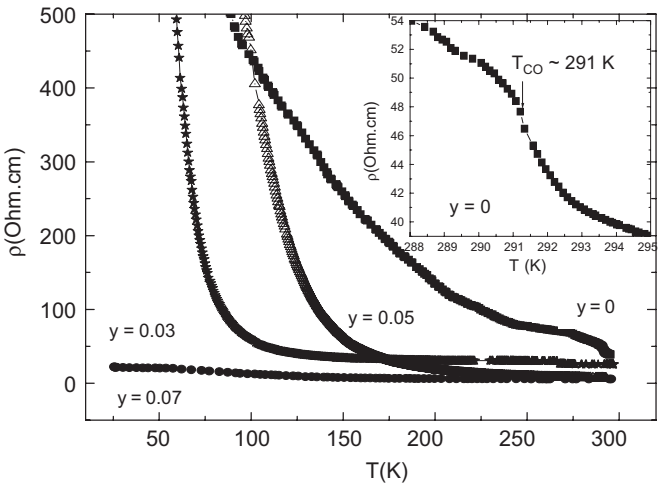

Fig. 4. DC resistivity vs. temperature for studied samples. The inset shows appearance of CO at 291 K ($y = 0$).

110 K < T < 150 K by fitting procedure for Fig. 4 curves (see also [5]). Based on the formula $R = 0.376\, l(T_o/T)^{1/4}$ we estimated the hopping distance of carriers in all samples at 120 K and result is shown in the last column of Table 1. The sample's carrier hopping distance is about several times of the lattice constant and generally has increasing tendency with increasing Ru content. In conclusion, the substitute Ru for Mn reduces the resistivity and enhances ferromagnetic tendency in $Ca_{0.6}Pr_{0.4}Mn_{1-y}Ru_yO_3$ perovskites essentially.

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