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Effects of Al doping upon ac susceptibility of $Pr_{0.5}Ca_{0.5}MnO_3$

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Abstract

$Pr_{0.5}Ca_{0.5}Mn_{1-x}Al_xO_3$ ($0 \le x \le 0.07$) compounds were prepared by standard solid-state reaction. The ac susceptibility of the samples at low temperatures was investigated. The real component χ' peak at the freezing temperature T_f is suppressed with increasing the frequency. χ' shows a linear relation between T_f and the logarithm of the frequency. The normalized slope $P=\Delta T_f/T_f\Delta \log_{10}\omega$ is much lower than for canonical insulating spin glass systems ($0.06 \le P \le 0.08$). The intensity of imaginary component χ'' at T_f for the $x=0$, 0.01, 0.02 samples increases with increasing frequency. The results of χ' and χ'' suggest that the $x=0$, 0.01, 0.02 samples have a cluster glass ground state. The intensity of χ'' at T_f for the $x=0.05$, 0.07 samples decreases with increasing frequency, suggesting a phase separation ground state. The intensity of χ'' at T_f for the $x=0.03$, 0.04 samples decreases with increasing frequency for $\omega \le 701$ Hz and increases with further increase of frequency. This complex behavior is ascribed to the competition between the effects of large and small ferromagnetic clusters in the sample. The ground state of the $x=0.03$, 0.04 samples is the transition state from cluster glass (for the $x=0.02$ sample) to phase separation (for the $x=0.05$ sample). AFM cluster blocking and the spin blocking were observed in the same sample.

Keywords: Ac susceptibility; Ferromagnetic cluster; Cluster-glass; AFM cluster blocking

1. Introduction

Mixed valence manganates $Ln_{1-x}A_xMnO_3$ (where Ln is a lanthanide and A is an alkaline earth ion or alkaline ion) have been widely researched because of their variety of properties [1–7]. Among them, those compounds exhibiting charge order (CO) phenomena have become the focus of intense studies because the percolative paths of coexisting ferromagnetic (FM) metallic phase are suspected to be responsible for the colossal magnetoresistance (CMR) [8–11]. The low temperature ordering of Mn^{3+} and Mn^{4+} can be destroyed by the cation disorder resulting from the substitution, either at Mn site [12–15] or at Ln-A site [16]. Introducing doping into Mn site results in insulator-to-metal as well as antiferromagnetic-to-ferromagnetic transitions and induces the electronic phase separation of CO antiferromagnetic domain and charge-disordered FM domain [17].

The doping at Mn site can affect the Mn^{4+}/Mn^{3+} ratio and destroy the order of Mn^{3+} and Mn^{4+}, and affect the ground state of the sample at low temperatures. The ac susceptibility of single sample has been widely researched in order to decide the ground state of the sample [2,18]. The frequency shift in T_f offers a possible criterion for distinguishing a canonical spin glass from a spin-glass-like material, and from a superparamagnet. Nevertheless it does not allow a clear distinction in systems with intermediate frequency dependence. Investigation of ac susceptibility of the whole $Pr_{0.5}Ca_{0.5}Mn_{1-x}Al_xO_3$ ($0 \le x \le 0.07$) sample series is necessary in order to comprehend the ground state of the whole sample series as well as the variation of χ' and χ'' with frequency for different Al doping. In this paper, ac susceptibility of the whole sample

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series $Pr_{0.5}Ca_{0.5}Mn_{1-x}Al_xO_3$ ($0 \le x \le 0.07$) was investigated. The variation of the normalized slope $P = \Delta T_f / T_f \Delta \log_{10}\omega$ and the imaginary component χ'' of the ac susceptibility with increase of frequency were analyzed. The intensity of imaginary component χ'' at T_f for the $x = 0.03$ and 0.04 samples shows a complicated variation trend with increase of frequency. A possible explanation is given. The thermal blocking of AFM spin cluster is observed as Nair and Banerjee reported [2].

2. Experimental

The $Pr_{0.5}Ca_{0.5}Mn_{1-x}Al_xO_3$ compounds were prepared by standard solid-state reaction. Stoichiometric proportions of Pr_6O_{11}, CaO, MnO_2, and Al_2O_3 with purities more than 99.9% were mixed and heated in air at 1100 °C for 24 h. After grinding, they were pressed into disks of 13 mm diameter/1–2 mm thickness. The disks were sintered in air at 1300 °C for 24 h three times with intermediate grinding. The crystalline phases of sintered samples were identified by powder x-ray diffraction (XRD) using Cu Ka radiation (Rigaku D/max 2550 PC, Rigaku Co., Tokyo, Japan). Physical properties measurement system (PPMS) of quantum design was used for all magnetic measurements. Zero-field-cooled (ZFC) and field-cooled (FC) magnetization curves were measured in the temperature range from 2 to 300 K at 0.01 T. Ac susceptibility at different frequencies was measured in the temperature range from 2 to 125 K with the amplitude of the ac field being 0.0005 T.

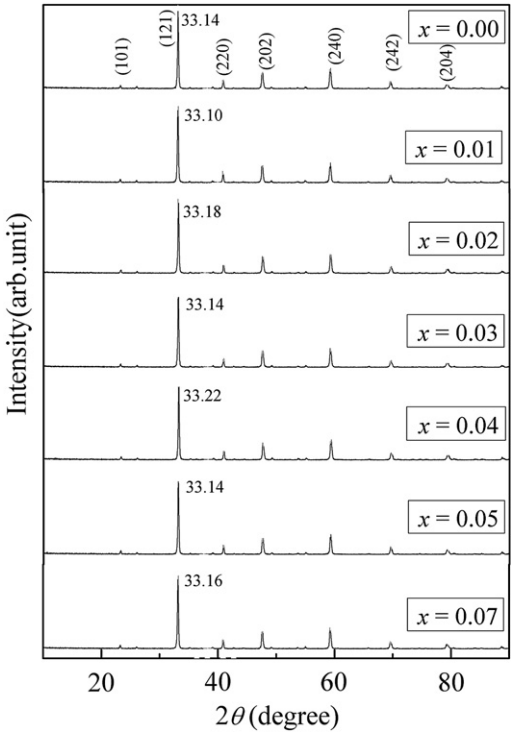

Fig. 1. Powder X-ray diffraction patterns measured at room temperature for $Pr_{0.5}Ca_{0.5}Mn_{1-x}Al_xO_3$ ($0 \le x \le 0.07$).

3. Results and discussion

The X-ray powder diffraction patterns of $Pr_{0.5}Ca_{0.5}Mn_{1-x}Al_xO_3$ as shown in Fig. 1 show a single-phase orthorhombic structure. The positions of the main peaks as marked in Fig. 1 have no obvious shift with increase of Al^{3+} concentration.

Temperature dependence of ZFC (zero field cooled) and FC (field cooled) magnetization of $Pr_{0.5}Ca_{0.5}Mn_{1-x}Al_xO_3$ is shown in Fig. 2. The broader anomaly at ~240 K and the small "hump" at ~175 K of the parent phase $Pr_{0.5}Ca_{0.5}MnO_3$ are associated with charge ordering (CO) and a long range AFM order of the "pseudo"-CE type, respectively. With increasing Al^{3+} concentration, the cusps of CO and the long range AFM order of the "pseudo"-CE type are suppressed strongly. The Jahn–Teller (JT) distortion of the Mn^{3+} can be counterbalanced by the doping of Al^{3+} on a microscopic level and the local structure can be more symmetric [12]. Accordingly, the orbital and charge ordered structure cannot be set and ferromagnetic fraction is reinforced at the expense of COOAF in spite of lack of magnetic interactions (Al^{3+} acts as nonmagnetic cation). The FC magnetization curve

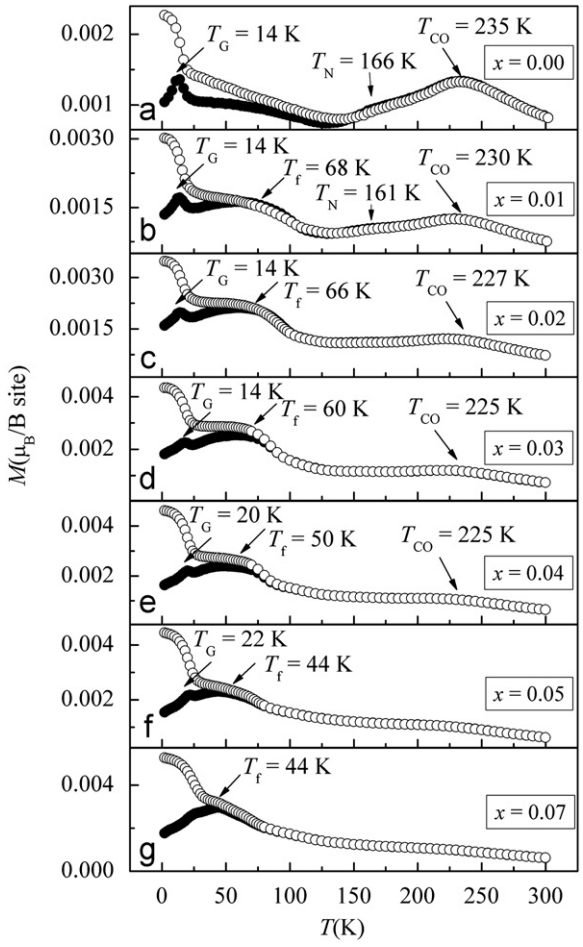

Fig. 2. Temperature dependence of ZFC (●) and FC (○) magnetization of $Pr_{0.5}Ca_{0.5}Mn_{1-x}Al_xO_3$, measured at 0.01 T field. (a), (b), (c), (d), (e), (f) and (g) for $x = 0$, 0.01, 0.02, 0.03, 0.04, 0.05 and 0.07, respectively.