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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.

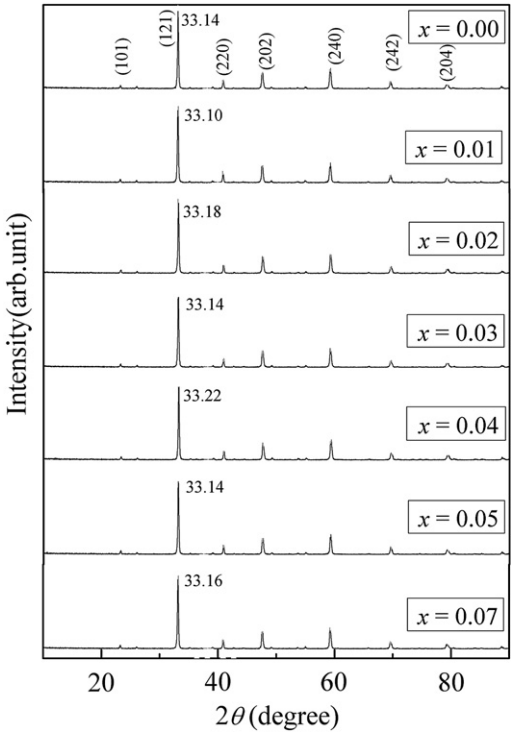

Fig. 1. Powder X-ray diffraction patterns measured at room temperature for $Pr_{0.5}Ca_{0.5}Mn_{1-x}Al_xO_3$ ($0 \le x \le 0.07$).

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

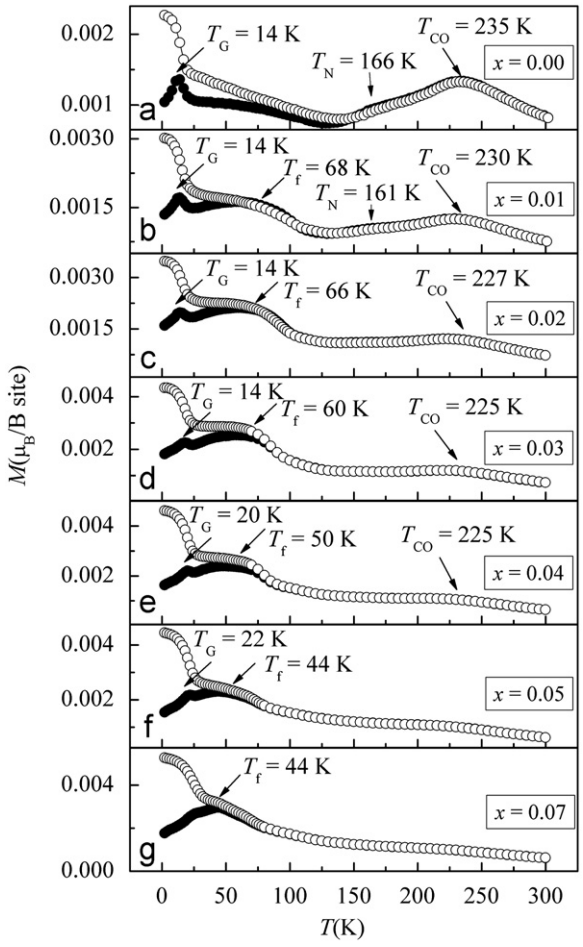

Fig. 2. Temperature dependence of ZFC (●) and FC (○) magnetization of $Pr_{0.5}Ca_{0.5}Mn_{1-x}Al_xO_3$, measured at 0.01 T field. (a), (b), (c), (d), (e), (f) and (g) for $x = 0$, 0.01, 0.02, 0.03, 0.04, 0.05 and 0.07, respectively.

almost superposes on the ZFC curve above the freezing temperature T_f. They keep linear increase as the temperature descends further, namely, no downturn is found in the FC curve at low temperatures, which indicates that there is no loss of magnetization at low temperatures (down to 2 K) even at low applied field [19]. The differences between FC and ZFC magnetization for $T < T_f$ exhibit the features of both the homogeneous spin glasses [1] and inhomogeneous clustered systems [20,21]. The irreversibility temperature between ZFC and FC magnetization curves measured at 0.01 T field can be clearly seen close to T_f. For the parent phase $Pr_{0.5}Ca_{0.5}MnO_3$, an additional peak is observed at ~14 K, the thermal blocking temperature of AFM spin cluster in a weakened COO system T_G, which is similar to Nair and Banerjee's report [2]. T_G increases from 14 K to 22 K with increase of Al^{3+} concentration. This indicates that the size of the AFM clusters in the samples changes with increase of Al^{3+} concentration [2].

Temperature dependence of real component χ' of the ac susceptibility for $Pr_{0.5}Ca_{0.5}Mn_{1-x}Al_xO_3$ measured in a field of 0.0005 T with different frequencies is shown in Fig. 3. The χ' value at low temperatures increases with increase of Al^{3+}

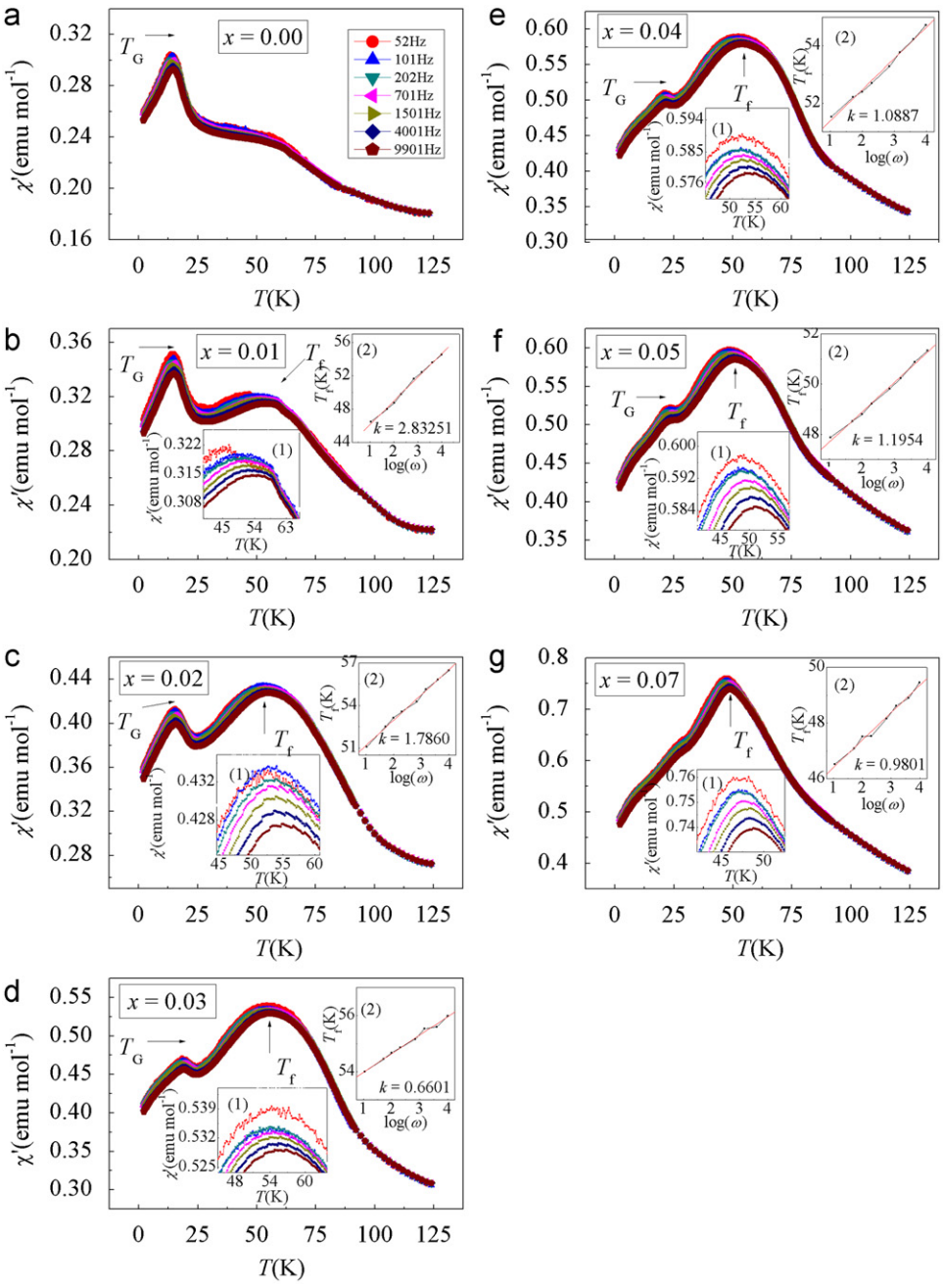

Fig. 3. Temperature dependence of real component (χ') of the ac susceptibility for $Pr_{0.5}Ca_{0.5}Mn_{1-x}Al_xO_3$ measured in a field of 0.0005 T with different frequencies. (a), (b), (c), (d), (e), (f) and (g) for x=0, 0.01, 0.02, 0.03, 0.04, 0.05 and 0.07, respectively. The inset (1) shows the magnification of the peaks, (2) shows the variation of the χ' peak temperature T_f with the frequency of the driving ac field. The matchups between frequencies and symbols in (b)–(g) are the same as (a). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

concentration, which is accordant with dc magnetic behavior shown in Fig. 2. The intensity of the main peak in $\chi'(T)$ decreases and shifts upwards in temperature with increase of frequency, which is qualitatively consistent with either a spin glass or a cluster system [20–22]. But it can be quantified through the frequency dependence of the freezing temperature as given by the peak position in $\chi'(T)$. As shown in the inset (2) of Fig. 3, T_f is linear with logarithm of frequency with a normalized slope $P=\Delta T_f/T_f\Delta\log_{10}\omega$. For $x=0$ sample, only an inflexion is detected at the freezing temperature. For other samples, P as shown in Table 1 is much lower than for canonical insulating spin glass systems ($0.06 \le P \le 0.08$). (Temperature dependence of resistivity of $Pr_{0.5}Ca_{0.5}Mn_{1-x}Al_xO_3$ indicating an insulating ground state below ~66 K, not shown here). This 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. Even the relative low P value of the sample (compared to typical superparamagnets) can be accounted for within the superparamagnetic framework by allowing a certain degree of interaction between the clusters [21]. The necessity of introducing such weak interactions is evidenced by the

Table 1
Value of $P=\Delta T_f/T_f\Delta\log_{10}\omega$ of $Pr_{0.5}Ca_{0.5}Mn_{1-x}Al_xO_3$ ($0 \le x \le 0.07$).

x	0.01	0.02	0.03	0.04	0.05	0.07
P	0.05316	0.0337	0.012	0.0356	0.0239	0.02

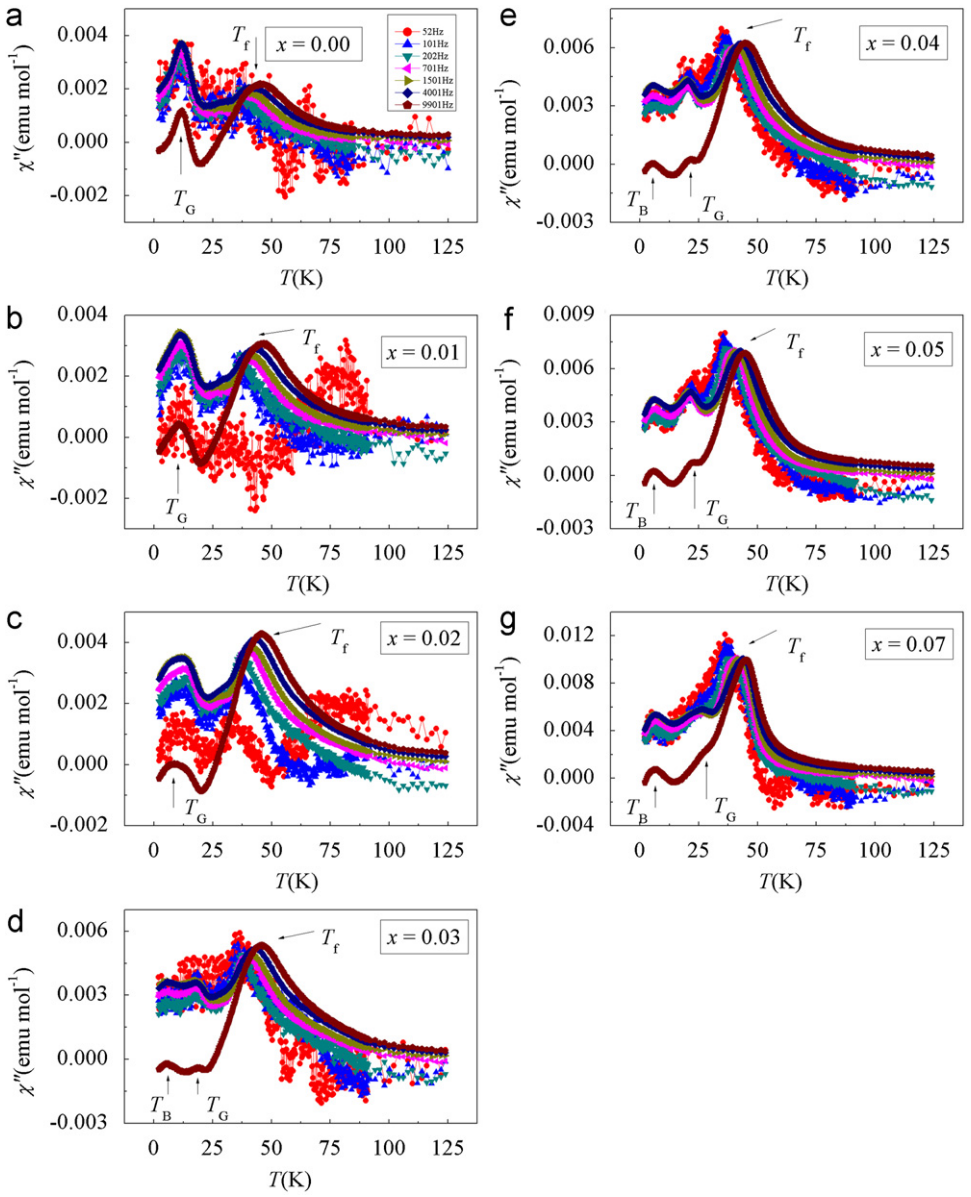

Fig. 4. Temperature dependence of imaginary component χ'' of the ac susceptibility for $Pr_{0.5}Ca_{0.5}Mn_{1-x}Al_xO_3$ measured in a field of 0.0005 T with different frequencies. (a), (b), (c), (d), (e), (f) and (g) for $x=0.00$, 0.01, 0.02, 0.03, 0.04, 0.05 and 0.07, respectively. The matchups between frequencies and symbols in (b)–(g) are the same as (a). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

inability of the Arrhenius law $\omega=\omega_0\exp(-E_a/k_BT_f)$ to describe the frequency dependence of T_f, where E_a is the energy barrier separating the up/down states in superparamagnet. The data $1/T_f$ is in inverse proportion to $\ln\omega$ for the whole sample series, not the linear relationship deduced from the Arrhenius law. From the frequency dependence, we can conclude that the whole sample series is not a conventional insulating spin glass and also probably not a simple superparamagnet. The thermal blocking temperature of the AFM spin clusters T_G as shown in Fig. 3 increases with increase of Al^{3+} doping, which is consistent with the variation trend in Fig. 2. The intensity at T_G decreases with increase of frequency for all the samples.

The temperature dependence of imaginary component χ'' of the ac susceptibility for $Pr_{0.5}Ca_{0.5}Mn_{1-x}Al_xO_3$ measured in a field of 0.0005 T with different frequencies are shown in Fig. 4. The peak at T_f increases with increase of frequency for $x=0$, 0.01, 0.02 samples. This is the features of both spin glass [1] and cluster glass [20,21]. Considering the data of χ', we can conclude that the ground states of $x=0$, 0.01, 0.02 samples are cluster glass. The peak decreases with increase of frequency for $x=0.05$, 0.07 samples. This is the feature of phase separation with ferromagnetic clusters embedded in charge-ordered antiferromagnetic matrix [1]. For $x=0.03$, 0.04 samples, χ'' shows an even more complicated behavior. The peak decreases with increase of frequency for $\omega\leq 701$ Hz and increases subsequently with further increase of frequency. The above data have good repeatability. A possible explanation is that the ferromagnetic clusters in the $x=0.03$, 0.04 samples have large size distribution. Large FM clusters in spin-glass matrix will act as phase separation ground state and induce the χ'' peak decrease with increase of frequency. Small FM clusters in spin-glass ground will act as cluster glass ground state and induce the χ'' peak decrease with increase of frequency. The competition between the two effects leads to the complicated χ'' variation trend. Perhaps the effect of large FM clusters is dominant for some frequency range and the effect of little FM clusters is dominant for other frequency range. 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. The peak at T_G is suppressed with increase of Al^{3+} doping and shifts to higher temperatures as shown in Fig. 4.

A small peak at $T_B\sim 5$ K in χ'' (T) is found as shown in Fig. 4. It could be related to the blocking of isolated spins between ferromagnetic clusters as has been suggested for similar features in traditional spin glass materials [23] and phase separated materials [1]. The peak intensity increases with increase of frequency for $\omega\leq 1501$ Hz and then decreases with further increase of frequency for the whole sample series.

4. Conclusions

The X-ray powder diffraction measurements show that the symmetry of the unit cell for the samples is orthorhombic. The differences between FC and ZFC magnetization exhibit the features of both the homogeneous spin glasses and inhomogeneous clustered systems. The real component χ' of $Pr_{0.5}Ca_{0.5}Mn_{1-x}Al_xO_3$ ($0\leq x\leq 0.07$) shows that freezing temperature T_f is linear function of logarithm of frequency with a normalized slope $P=\Delta T_f/T_f\Delta\log_{10}\omega$, which is much lower than canonical insulating spin glass systems ($0.06\leq P\leq 0.08$). The intensity of χ' at T_f are suppressed with the increase of frequency. The intensity of χ'' at T_f increases with increase of frequency for $x=0$, 0.01, 0.02 samples. The results of χ' and χ'' show that the $x=0$, 0.01, 0.02 samples have a cluster glass ground state. The peak of χ'' at T_f decreases with increase of frequency for the $x=0.05$, 0.07 samples. The results of χ' and χ'' show that the $x=0.05$, 0.07 samples have 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 $\omega\leq 701$ Hz and increases subsequently with further increase of frequency. The competition between large FM clusters and little FM clusters is responsible for this complex behavior. 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. The ZFC magnetization curve and the real component of ac susceptibility show that the AFM spin cluster thermal blocking temperature T_G increases with increase of Al^{3+} concentration indicating that the size of the AFM clusters in the samples changes with increase of Al^{3+} concentration.

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