Effects of Fe doping on ac susceptibility of $Pr_{0.75}Na_{0.25}MnO_3$*

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Ac susceptibility at low temperatures of $Pr_{0.75}Na_{0.25}Mn_{1-x}Fe_xO_3$ ($0 \leq x \leq 0.30$) is investigated. The peak value of the real component of ac susceptibility χ' at the freezing temperature T_f is suppressed with the increasing frequency. The peak value of χ' shows a linear relation between T_f and the logarithm of the frequency ω. The normalized slope $P = \Delta T_f/T_f\Delta\lg\omega$, which is much lower than canonical insulating spin glass systems in which $0.06 \leq P \leq 0.08$. The peak value of the imaginary component of the ac susceptibility χ'' at T_f for the $x = 0$, 0.02, 0.30 samples increases with increasing frequency, suggesting a cluster glass ground state with a coexistence of charge-ordered phase and correlated ferromagnetic clusters in spin glass matrix. The peak value of χ'' at T_f for the $x = 0.10$ sample decreases with increasing frequency, suggesting a phase separation ground state. The peak value of χ'' at T_f for the $x = 0.05$ sample decreases with increasing frequency for $\omega \leq 52$ Hz and increases subsequently till 701 Hz, and then decreases with further increasing frequency for $\omega \geq 1501$ Hz. This complex behaviour is ascribed to the competition between the effects of large and little ferromagnetic clusters in the sample. The ground state of $x = 0.05$ sample is a transition state from cluster glass to phase separation.

Keywords: magnetization, ac susceptibility, phase separation, cluster-glass

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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.[1−4] Among them, those compounds exhibiting charge order (CO) phenomena 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).[5−7] 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[8] or at Ln–A site.[9] Introducing impurity 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,[10] spin-glass and cluster glass.

The ac susceptibility for some single sample has been widely researched in order to decide the ground state of the sample.[11] The frequency shift in the freezing temperature T_f offers a possible criterion for distinguishing a canonical spin glass from a spin-glass-like material and from a superparamagnet. However, it does not allow a clear distinction in systems with intermediate frequency dependence. On the other hand, the variation trend of the peak value of the imaginary component of the ac susceptibility χ'' is a possible criterion for distinguishing a canonical spin glass from a phase separation material.[12] The ac susceptibility for $Pr_{0.75}Na_{0.25}MnO_3$ displays a cluster glass state.[11] $Pr_{0.75}Na_{0.25}Mn_{0.90}Fe_{0.10}O_3$ displays a phase separation ground state.[12] Investigating the ac susceptibility of the whole $Pr_{0.75}Na_{0.25}Mn_{1-x}Fe_xO_3$

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($0 \leq x \leq 0.30$) sample series is important to comprehend the ground state of the whole sample series and the peak value variations of the real and imaginary components of the ac susceptibility χ' and χ'' with frequency ω for different Fe dopings. In this paper, ac susceptibility at low temperatures of the whole sample series $Pr_{0.75}Na_{0.25}Mn_{1-x}Fe_xO_3$ ($0 \leq x \leq 0.30$) is investigated. The variations of the normalized slope $P = \Delta T_f/T_f \Delta \lg\omega$ with increasing Fe doping and the peak value of χ'' with increasing frequency are analysed. The ground states of the sample series are presented. The peak value of χ'' at T_f for the $x = 0.05$ sample shows a complicated variation trend with increasing frequency. A possible explanation is given.

2. Experimental

The single-phase polycrystalline perovskites $Pr_{0.75}Na_{0.25}Mn_{1-x}Fe_xO_3$ ($0 \leq x \leq 0.30$) were prepared by a sol-gel technique (see Ref. [11]). The room-temperature powder X-ray diffraction patterns show a single-phase orthorhombic structure for all the samples. A physical properties measurement system (PPMS, Quantum Design Inc.) was used for the ac susceptibility measurement.

3. Results and discussion

The temperature dependence of the zero-field cooled (ZFC) and field cooled (FC) magnetization at 0.01 T for $Pr_{0.75}Na_{0.25}Mn_{1-x}Fe_xO_3$ is shown in Fig. 1.[13] The parent phase $Pr_{0.75}Na_{0.25}MnO_3$ displays a behaviour similar to that reported by Satoh *et al.*[14] and Hejtmánek *et al.*[15] The broader anomaly at $\sim$ 222 K and the small "hump" at $\sim$ 181 K are associated with CO and a long-range antiferromagnetic order of the "pseudo"-CE type, respectively. The branches of ZFC and FC bifurcate below $\sim$ 41 K. The cusps of CO and the long range AFM order of the "pseudo"-CE type are suppressed with increasing Fe concentration.

The temperature dependence of χ' of $Pr_{0.75}Na_{0.25}Mn_{1-x}Fe_xO_3$ for different frequencies is shown in Fig. 2. The peak value of $\chi'(T)$ decreases and shifts upwards in temperature with increasing frequency, which is also qualitatively consistent with either a spin glass[16–18] or a cluster system.[18–21] However, it can be quantified through the frequency dependence of T_f as given by the peak position in $\chi'(T)$. As shown in the inset (b′) of Fig. 2, T_f is linear in the logarithm of the frequency with a normalized slope $P = \Delta T_f/T_f \Delta \lg\omega$. P increases with increasing Fe doping for $x \leq 0.02$ and decreases subsequently with further increasing Fe doping as shown in Fig. 3. The normalized slope P for the sample series is much lower than canonical insulating spin glass systems in which $0.06 \leq P \leq 0.08$ ($Pr_{0.75}Na_{0.25}Mn_{1-x}Fe_xO_3$ has an insulating ground state below $\sim$ 65 K[13]). $P \sim 0$ for the $x = 0$ sample suggests that FM cluster and AFM cluster coexist in this system, which is consistent with the results of Refs. [14] and [15]. 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. However, it does not allow a clear distinction in systems with intermediate frequency dependence. Even the relative low P value of the sample (compared with the typical superparamagnets) can be accounted for within the superparamagnetic framework by allowing a certain degree of interaction between the clusters.[21]

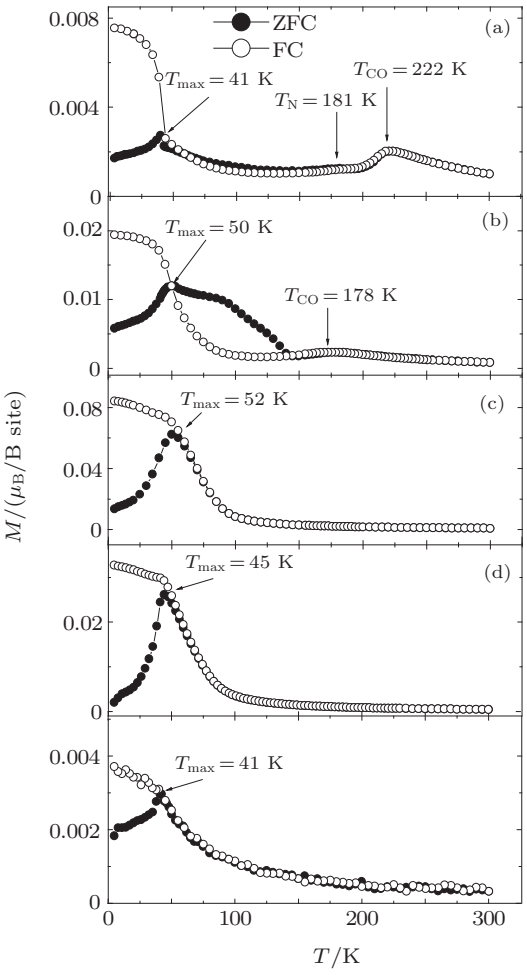


Fig. 1. Field cooled (open symbols) and zero field cooled (closed symbols) magnetizations M of $Pr_{0.75}Na_{0.25}Mn_{1-x}Fe_xO_3$ ($0 \leq x \leq 0.30$) as a function of temperature, measured at 0.01 T. Here, T_{CO} is the CO temperature, T_N is the AFM transition temperature, T_{max} is the maximum temperature of $M_{ZFC}(T)$. (a) $x = 0$, (b) $x = 0.02$, (c) $x = 0.05$, (d) $x = 0.10$, (e) $x = 0.30$.

The necessity of introducing such weak interparticle interactions is evidenced by the inability of the Arrhenius law $\omega = \omega_0 \exp(-E_a/k_B T_f)$ to describe the frequency dependence of T_f, where E_a is the energy barrier saparating the up/down states in superparamagnet. Since the data for the whole sample series yield similar unphysical large values for the parameters for Arrhenius law, only the result of $x = 0.05$ sample is presented here: $\omega_0 \sim 10^{103}$ Hz, $E_a/k_B \sim 13195$ K. The data for the whole sample series could be fitted to a Vogel–Fulcher law: $\omega/\omega_0 = \exp[-E_a/k_B\ (T_f - T_0)]$, which presumes correlations between spin clusters and the dynamic scaling relation $\omega = \omega_0\ (T_f/T_c - 1)^{z\nu}$, (where T_c corresponds to the dc (equilibrium) value of $T_f(\omega \to 0)$, $z\nu$ is valled the dynamical exponent), but the uncertainty in the fit parameters was too large to provide physical insight into the ground states of the sample series. We can thus conclude from the frequency dependence of T_f that the whole sample series is not a simple superparamagnet or a conventional insulating spin glass.

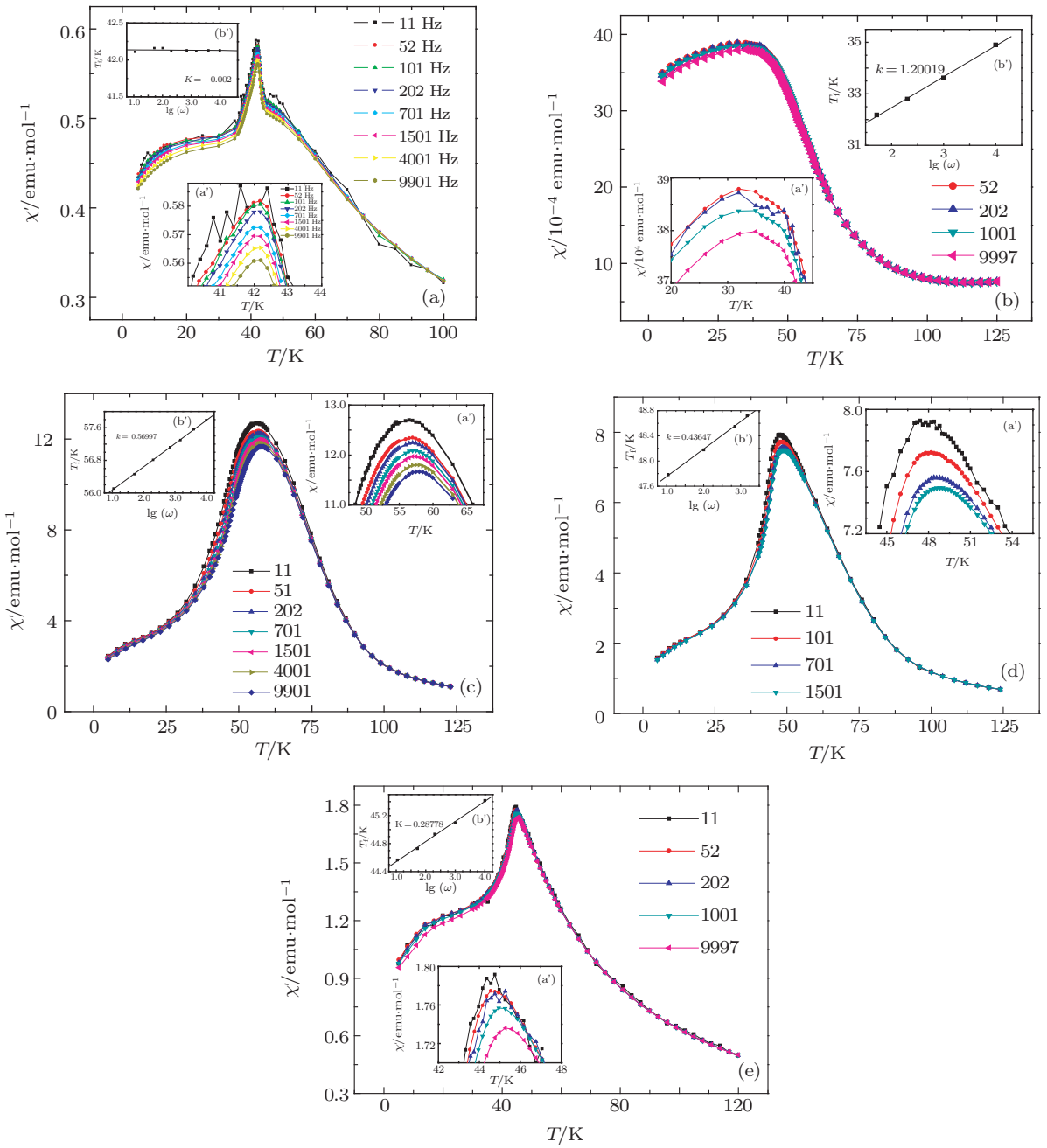


Fig. 2. (colour online) The temperature dependence of the peak value of χ' for $Pr_{0.75}Na_{0.25}Mn_{1-x}Fe_xO_3$ measured in a field of 0.0005 T with different frequencies. (a), (b), (c), (d), (e) are for $x = 0$, 0.02, 0.05, 0.10, 0.30, respectively. The inset of (a′) shows the magnification of the peaks, (b′) shows the variation of the χ' peak temperature with the frequency of the driving ac field, where k is the slope of the fitting straight line.

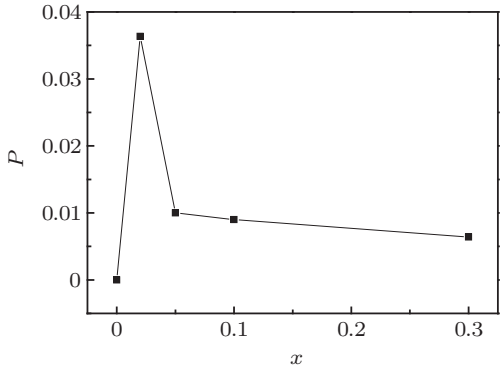


Fig. 3. The normalized slope $P = \Delta T_f/T_f \Delta \lg\omega$ versus Fe content for $Pr_{0.75}Na_{0.25}Mn_{1-x}Fe_xO_3$.

The temperature dependences of the peak vlaue of χ'' for $Pr_{0.75}Na_{0.25}Mn_{1-x}Fe_xO_3$ measured in a field of 0.0005 T with different frequencies are shown in Fig. 4. The inset shows the magnification of the peak. The peak increases with increasing frequency for $x = 0$, 0.02, 0.30 sample. The χ'' of 11 Hz for $x = 0$, 0.02, 0.30 sample is not shown since the large fluctuations. This is the feature of both spin-glass and cluster glass. The peak decreases with increasing frequency for $x = 0.10$ sample. This is the feature of phase separation with ferromagnetic clusters embedded in charge-ordered antiferromagnetic matrix.[11]

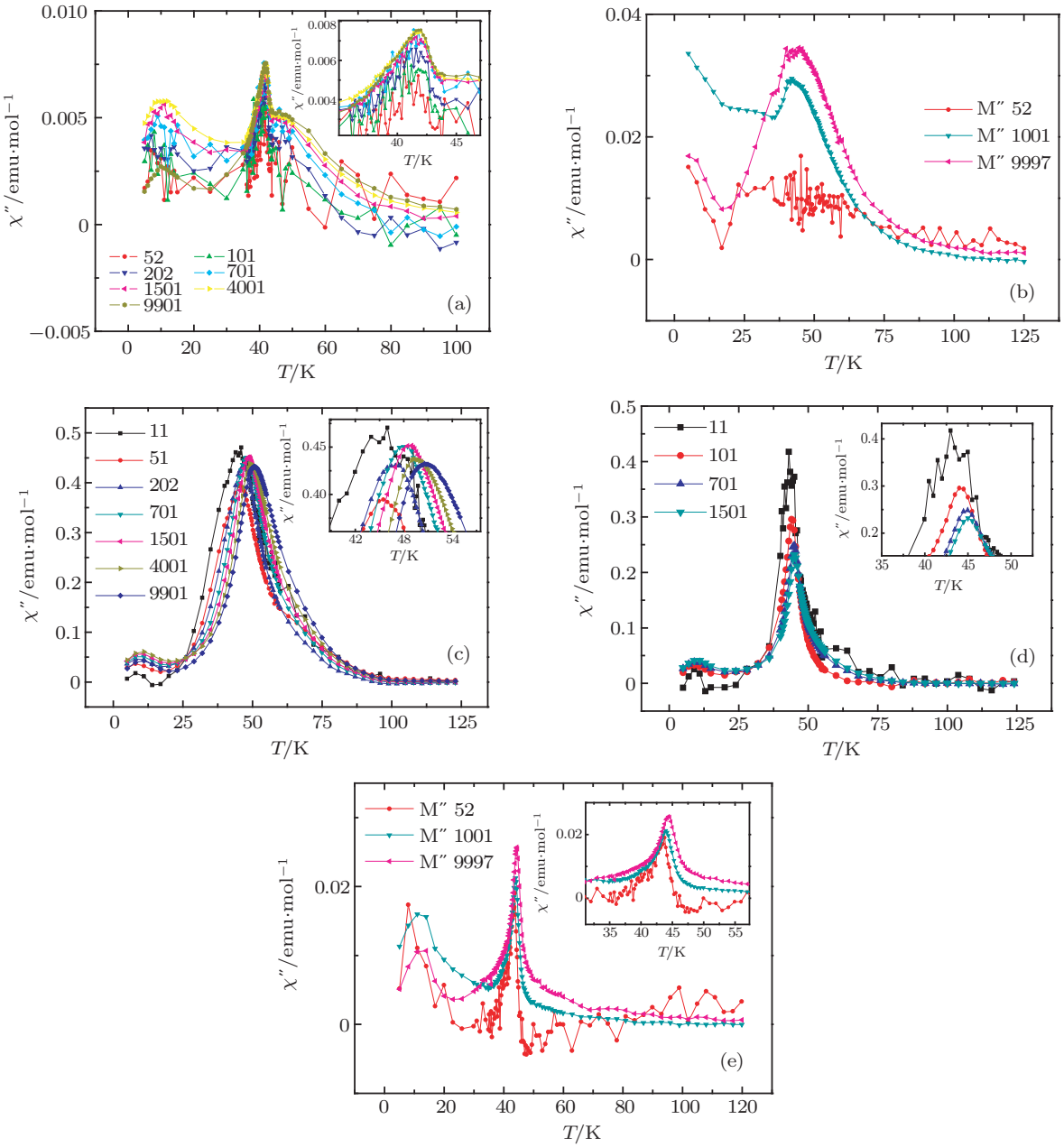


Fig. 4. (colour online) The temperature dependences of the peak value of χ'' for $Pr_{0.75}Na_{0.25}Mn_{1-x}Fe_xO_3$ measured in a field of 0.0005 T with different frequencies. (a), (b), (c), (d), (e) are for $x = 0$, 0.02, 0.05, 0.10, 0.30, respectively. The inset shows the magnification of the peaks.

The peak value of χ'' of $x = 0.05$ sample shows an even more complicated behaviour. The peak decreases with increasing frequency for $\omega \leq 52$ Hz and increases subsequently till 701 Hz and then decreases with further increasing frequency for $\omega \geq 1501$ Hz. The data was measured repeated using PPMS, Quantum Design Inc. The result suggested that the data have good repeatability. This complex behaviour can be ascribed to the larger spontaneous moment of FM component and the large size distribution of the ferromagnetic clusters in this sample. On the one hand, the spontaneous moment of FM component for the $x = 0.05$, 0.10 sample is larger than that for other samples in this sample series,[13] so the decrease of the peak value of χ'' with increasing frequency can be ascribe to the large FM cluster in the two sample. On the other hand, the size distribution of the ferromagnetic clusters in the $x = 0.05$ sample is large. The peak at $T_{\max}$ of ZFC M–T curve measured at 0.01 T field for the $x = 0.05$ sample is more broad,[13] which suggests that the magnetic clusters have a large distribution in size. Because little FM cluster in spin-glass ground will deduce cluster glass ground state and induce the peak value of χ'' decrease with increasing frequency just as the $x = 0$, 0.02, 0.30 sample. The two opposite effects originate from large and little FM cluster, respectively, inducing the complicated χ'' variation trend. Namely, the peak value of χ'' decreases with increasing frequency in some frequency ranges and increases with increasing frequency in other frequency ranges. The ground state of the $x = 0.05$ sample is the transition state from cluster glass for the $x = 0.02$ sample to phase separation for the $x = 0.10$ sample.

A small maximum at ~ 10 K in $\chi''(T)$ is found as shown in Fig. 4. It is corresponding to the inflexion in $M(T)$ and $\chi'(T)$ at the same temperature as shown in Figs. 1 and 2, respectively. 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[22] and phase-separated material.[11] The intensity increases with increase frequency for $\omega \leq 4001$ Hz and then decreases with further increasing frequency.

4. Conclusions

The peak value of χ' of $Pr_{0.75}Na_{0.25}Mn_{1-x}Fe_xO_3$ ($0 \leq x \leq 0.30$) shows that the freezing temperature T_f is linear in the logarithm of the frequency with a normalized slope $P = \Delta T_f / T_f \Delta \lg \omega$, which is much lower than canonical insulating spin glass systems in which $0.06 \leq P \leq 0.08$. The P increases with increasing Fe doping for $x \leq 0.02$ and decreases subsequently with further increasing Fe doping. The peak value of χ' at T_f are suppressed with the increasing frequency. The peak value of χ'' for the $x = 0$, 0.02, 0.30 samples increases with increasing frequency, decreases with increasing frequency, for the $x = 0.10$ sample. The results of χ' and χ'' show that the $x = 0$, 0.02, 0.30 samples have a cluster glass ground state with a coexistence of charge-ordered phase and correlated ferromagnetic clusters in spin glass matrix, the $x = 0.10$ sample with a phase separation ground state. The peak value of χ'' at T_f for the $x = 0.05$ sample decreases with increasing frequency for $\omega \leq 52$ Hz and increases subsequently till 701 Hz and then decreases with further increasing frequency for $\omega \geq 1501$ Hz. This complex behaviour is ascribed to the larger spontaneous moment of FM component and the large size distribution of the ferromagnetic clusters in this sample. Large FM clusters in spin-glass ground will act as phase separation ground state and induce the χ'' peak value with increasing frequency. Little FM cluster in spin-glass ground will act as cluster glass ground state and induce the decrease of the χ'' peak value with increasing frequency. The competition between the two effects leads to the complicated χ'' variation trend. Perhaps the large FM clusters effect is dominant for some frequency ranges and the little FM clusters action is dominant for other frequency ranges. The ground state of the $x = 0.05$ sample is the transition state from cluster glass for the $x = 0.02$ sample to phase separation for the $x = 0.10$ sample.

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