Suppressed charge ordering and cluster glass behavior of Pr$_{0.75}$Na$_{0.25}$Mn$_{0.95}$Fe$_{0.05}$O$_3$

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Abstract. The cusps of charge ordering and the long range AFM order of the “pseudo”-CE type are suppressed with increasing Fe concentration in Pr$_{0.75}$Na$_{0.25}$Mn$_{1-x}$Fe$_x$O$_3$ (0 ≤ $x$ ≤ 0.30). Ac susceptibility at low temperatures of Pr$_{0.75}$Na$_{0.25}$Mn$_{0.95}$Fe$_{0.05}$O$_3$ was investigated. The real component ($\chi'$) shows that freezing temperature $T_f$ is linear in the logarithm of the frequency. The normalized slope $P = \Delta T_f / T_f \Delta \log_{10} \omega$, which is much lower than canonical insulating spin glass systems in which 0.06 ≤ $P$ ≤ 0.08. The $\chi'$ peak at $T_f$ are suppressed with the increasing frequency. The intensity of imaginary component ($\chi''$) at $T_f$ and spin blocking temperature $T_B ~ 10$ K shows a complicated variation trend with increasing frequency. The ground state of the sample is cluster glass with a coexistence of charge-ordered phase, correlated ferromagnetic clusters in spin glass matrix.

1. Introduction

Mixed valence manganates Ln$_{1-x}$A$_x$MnO$_3$ (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]. Those compounds of them 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]. 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 [6] or at Ln-A site [7]. 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 [8], 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 [9]. 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. On the other hand, the variation trend of imaginary component ($\chi''$) intensity of the ac susceptibility is a possible criterion for distinguishing a canonical spin glass from a phase separation material [10]. The ac susceptibility for Pr$_{0.75}$Na$_{0.25}$MnO$_3$ displays a cluster glass state [9]. Pr$_{0.75}$Na$_{0.25}$Mn$_{0.90}$Fe$_{0.10}$O$_3$ displays a Phase separation ground state [10]. In order to comprehend the frequency shift in $T_f$ and the variation trend of imaginary...
component ($\chi''$) peak with increasing frequency, investigate ac susceptibility of different Fe
dopant in Pr$_{0.75}$Na$_{0.25}$MnO$_3$ is important. In this paper, ac susceptibility at low temperatures
of Pr$_{0.75}$Na$_{0.25}$Mn$_{0.95}$Fe$_{0.05}$O$_3$ was investigated. The normalized slope $P=\Delta T_f / T_f \Delta \log_{10}\omega$ and the
variation trend of imaginary component ($\chi''$) of the ac susceptibility with increasing frequency
for Pr$_{0.75}$Na$_{0.25}$Mn$_{0.95}$Fe$_{0.05}$O$_3$ were investigated. Some complicated variation trends were
observed. The possible reason was presented. The ground state of the sample was presented.

2. Experimental
The single-phase polycrystalline perovskites Pr$_{0.75}$Na$_{0.25}$Mn$_{1-x}$Fe$_x$O$_3$ (0≤x≤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 all the magnetic measurements.

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$_x$O$_3$ is shown in Figure.1. The parent phase

![Figure 1](image1.png)

![Figure 2](image2.png)

Figure. 1 Field cooled (open symbols) and zero
field cooled (closed symbols) magnetizations of
Pr$_{0.75}$Na$_{0.25}$Mn$_{1-x}$Fe$_x$O$_3$ (0≤x≤0.30) as a function
of temperature, measured at 0.01 T.

Figure. 2 The temperature dependence of real
component ($\chi'$) of the ac susceptibility for
Pr$_{0.75}$Na$_{0.25}$Mn$_{0.95}$Fe$_{0.05}$O$_3$ measured in a field of
0.0005 T with different frequencies. The inset
of (1) shows the imaginary of the peaks, (2)
shows the variation of the $\chi'$ peak temperature
with the frequency of the driving ac field in the
range 11-9997 Hz.
Pr$_{0.75}$Na$_{0.25}$MnO$_3$ displays a behavior similar to that reported by Takuya Satoh [12] and J. Hejtmánek [13]. The broader anomaly at ~222 K and the small “hump” at ~181 K are associated with charge ordering (CO) and a long-range antiferromagnetic order of the “pseudo”-CE type, respectively. The branches of ZFC and FC bifurcate below ~41 K. The cusps of CO and the long range AFM order of the “pseudo”-CE type are suppressed with increasing Fe concentration. This sample series (except for the x = 0.02 sample) exhibit similar behavior to the parent phase sample at low temperatures. The x = 0.02 sample shows a more complicated behavior. The ZFC magnetization increases sharply below 140 K and cannot superpose on FC magnetization. The ZFC magnetization nearly levels off between 90 K and 50 K. Then the magnetization begins to decrease as the temperature is further lowered, which is similar to the ZFC magnetization of Pr$_{0.75}$Ca$_{0.5}$Mn$_{0.975}$Al$_{0.025}$O$_3$ [13].

The temperature dependence of real component of ac susceptibility of Pr$_{0.75}$Na$_{0.25}$Mn$_{0.95}$Fe$_{0.05}$O$_3$ for different frequencies is shown in Figure. 2. The intensity of the peak in $\chi'(T)$ decreases and shifts upwards in temperature with increasing frequency, which is also qualitatively consistent with either a spin glass [14-16] or a cluster system [17-20]. But it can be quantified through the frequency dependence of the freezing temperature ($T_f$) as given by the peak position in $\chi'(T)$. As shown in the inset (2) of Figure. 2, $T_f$ is linear in the logarithm of the frequency with a normalized slope $P=\Delta T_f/T_f \Delta \log_{10} \omega$. Normalized slope $P=0.01$ for this sample 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$_{0.95}$Fe$_{0.05}$O$_3$ has an insulating ground state below ~65 K [11]). Although the $P$ value for spin glass systems is $0.0045 \leq P \leq 0.08$ [14]. 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.

![Figure 2](image2.png)

The temperature dependence of Imaginary component ($\chi''$) of the ac susceptibility for Pr$_{0.75}$Na$_{0.25}$Mn$_{0.95}$Fe$_{0.05}$O$_3$ measured in a field of 0.0005 T with different frequencies. The inset shows the magnify of the peak.

![Figure 3](image3.png)

The temperature dependence of Imaginary component ($\chi''$) of the ac susceptibility for Pr$_{0.75}$Na$_{0.25}$Mn$_{0.95}$Fe$_{0.05}$O$_3$ measured in a field of 0.0005 T with different frequencies are
shown in Figure. 3. The inset shows the magnify of the peak. \( \chi'' \) at \( T_f \) shows an even more complicated behavior. The peak value decrease with increasing frequency for \( f \leq 52 \text{ Hz} \) and increase subsequently till 1501 Hz, and then decrease with further increasing frequency. The results of \( \chi'' \) give a stronger evidence that the low field ground state for the sample series does not behave as a conventional spin glass, nor a phase separation. Perhaps, the ground state of the sample is cluster glass with a coexistence of charge-ordered phase, correlated ferromagnetic clusters in spin glass matrix. The \( x = 0.05 \) ratio of the components for Fe doping induces the complicated ac susceptibility variation trend. The other factor affect the ac susceptibility perhaps is the difference of the size of the ferromagnetic clusters in the \( x = 0.05 \) sample from the \( x = 0 \) and \( x = 0.10 \) sample. The larger distribution in size of the ferromagnetic clusters induces the more complicated ac susceptibility variation trend. The peak at \( T_{\text{max}} \) of ZFC M-T curve measured at 0.01 T field for the \( x = 0.05 \) sample is more broad that suggests the magnetic clusters has a larger distribution in size in the field, and its ac susceptibility variation trend is more complicated.

A small maximum at \( \sim 10 \text{ K} \) in \( \chi'' \) (T) is found as shown in Figure. 3. It is corresponding to the inflexion in M (T) and \( \chi' \) (T) at the same temperature as shown in Figure. 1 and Figure. 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 [21] and phase-separated material [9]. The maximum at \( \sim 10 \text{ K} \) for the \( x=0.05 \) sample increase with increasing frequency when \( f \leq 4001 \text{ Hz} \) and then decrease with further increasing frequency. This is also different to the \( x = 0, 0.10 \) sample, which with a variation trend of the maximum at \( \sim 10 \text{ K} \) with increase frequency reverse to the variation trend of the maximum at \( T_f \).

4. Conclusions
The cusps of CO and the long range AFM order of the “pseudo”-CE type are suppressed with increasing Fe concentration in \( \text{Pr}_{0.75}\text{Na}_{0.25}\text{Mn}_{1-x}\text{Fe}_x\text{O}_3 (0 \leq x \leq 0.30) \). Ac susceptibility at low temperatures of \( \text{Pr}_{0.75}\text{Na}_{0.25}\text{Mn}_{0.95}\text{Fe}_{0.05}\text{O}_3 \) was investigated. The intensity of real component (\( \chi' \)) at \( T_f \) are suppressed with the increasing frequency and shows that freezing temperature \( T_f \) is linear in the logarithm of the frequency with a normalized slope \( P=\Delta T_f/\Delta \log_{10} \omega \), which is much lower than canonical insulating spin glass systems in which \( 0.06 \leq P \leq 0.08 \). The intensity of imaginary component (\( \chi'' \)) at \( T_f \) decrease with increasing frequency for \( f \leq 52 \text{ Hz} \) and increase subsequently till 1501 Hz, and then decrease with further increasing frequency. The maximum at \( \sim 10 \text{ K} \) in \( \chi'' \) (T) increase with increasing frequency when \( f \leq 4001 \text{ Hz} \) and then decrease with further increasing frequency. The ground state of the sample is cluster glass with a coexistence of charge-ordered phase, correlated ferromagnetic clusters in spin glass matrix.

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