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Magnetic glassy behaviour in ferroelectric relaxor type solid solutions: Magnetoelectric relaxor

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Magnetic glassy behavior in ferroelectric relaxor type solid solutions: Magnetolectric relaxor

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Perovskite solid solution ceramics with compositions of $0.9\text{Pb}(\text{Fe}_{0.5}\text{Nb}_{0.5})\text{O}_3-0.1\text{PbTiO}_3$, $0.6\text{Pb}(\text{Ni}_{1/3}\text{Nb}_{2/3})\text{O}_3-0.4\text{PbTiO}_3$, and $0.6\text{Pb}(\text{Co}_{1/3}\text{Nb}_{2/3})\text{O}_3-0.4\text{PbTiO}_3$ were synthesized by the traditional solid state reaction method. Ferroelectric measurements revealed that these samples have well saturated polarization-electrical field loops. Dielectric measurements showed that abnormal dielectric peaks at their Curie temperature were frequency dependent. Both characteristics indicate that these samples are relaxor type ferroelectric materials. Field cooled and zero field cooled magnetization measurements revealed that the $0.6\text{Pb}(\text{Ni}_{1/3}\text{Nb}_{2/3})\text{O}_3-0.4\text{PbTiO}_3$ and $0.6\text{Pb}(\text{Co}_{1/3}\text{Nb}_{2/3})\text{O}_3-0.4\text{PbTiO}_3$ samples are paramagnetic down to 5 K, while the $0.9\text{Pb}(\text{Fe}_{0.5}\text{Nb}_{0.5})\text{O}_3-0.1\text{PbTiO}_3$ sample shows an antiferromagnetic-like ordering starting from around 40 K. Furthermore, a weak ferromagnetism is observed in the $0.9\text{Pb}(\text{Fe}_{0.5}\text{Nb}_{0.5})\text{O}_3-0.1\text{PbTiO}_3$ sample, as evidenced by the magnetic hysteresis loop measured at 10 K. The ac susceptibility measurement of this sample showed that the peak position around 40 K is strongly dependent on frequency, indicating a glassy or relaxor type behavior below that temperature. Therefore, relaxor type ferroelectric and magnetic $0.9\text{Pb}(\text{Fe}_{0.5}\text{Nb}_{0.5})\text{O}_3-0.1\text{PbTiO}_3$ is a magnetolectric relaxor. © 2009 American Institute of Physics. [DOI: 10.1063/1.3055266]

Magnetolectric materials (multiferroic), displaying simultaneous magnetic and dipolar electrical ordering, have recently stimulated much scientific and technological interest.¹ The coexistence of magnetic and electric subsystems endows materials with the “product” property, thus allowing an additional degree of freedom in the properties of actuators, sensors, and storage devices.^{2–7} However, the choice of single-phase materials exhibiting the coexistence of strong ferro-ferrimagnetism (FM) and ferroelectricity (FE) is quite limited.⁸ The available single-phase materials showing such multiferroic properties mainly include BiFeO_3 , ReFe_2O_4 , and ReMnO_3 (Re=rare earth element). BiFeO_3 is an antiferromagnetic and ferroelectric material at room temperature, with very weak ferromagnetism from the canted spin arrangement. This material, however, has a severe electrical leakage problem, which limits it for practical application, although considerable research has been done to solve this problem.^{9–11} ReFe_2O_4 (Re=Yb and Lu), in which the electric dipole is from charge ordering, and the spin frustrated system of ReMnO_3 (Re=Dy and Er, for example) are ferroelectric and antiferromagnetic at much lower temperatures, which limits their applications.^{3,12} Therefore, the exploration of new types of multiferroic materials is very necessary.

Relaxor type ferroelectric materials, for one typical example, $(1-y)\text{Pb}(\text{Tr}_x\text{Nb}_{1-x})\text{O}_3-y\text{PbTiO}_3$ (Tr=transition metal), solid solutions with a perovskite ABO_3 structure, are

famous piezoelectric materials. They show excellent ferroelectric properties as well and have realized practical applications as memory devices, actuators, and sensors.¹³ In this paper, $y\text{Pb}(\text{Tr}_x\text{Nb}_{1-x})\text{O}_3-(1-y)\text{PbTiO}_3$ solid solution doped with three transition metals, Fe, Ni, and Co, at the B sites was studied to examine the possibility of transforming these ferroelectric relaxor materials into magnetolectric materials.

The ceramic samples were prepared by the traditional solid state reaction method. The starting oxide materials, TiO_2 , Nb_2O_5 , Fe_2O_3 , NiO , Co_2O_3 , and PbO with 4N purity, were weighed and mixed according to three chemical formulas, $0.9\text{Pb}(\text{Fe}_{0.5}\text{Nb}_{0.5})\text{O}_3-0.1\text{PbTiO}_3$ (PFN-PT), $0.6\text{Pb}(\text{Ni}_{1/3}\text{Nb}_{2/3})\text{O}_3-0.4\text{PbTiO}_3$ (PNN-PT), and $0.6\text{Pb}(\text{Co}_{1/3}\text{Nb}_{2/3})\text{O}_3-0.4\text{PbTiO}_3$ (PCN-PT). These powders were pressed into pellets after grinding. After the first run of sintering at 1000 °C for 24 h in atmosphere, these pellets were ground, pressed into pellets 1 mm in thickness and 1 cm in diameter, and sintered at 1000 °C again for 24 h. The phases and structures of the obtained ceramic samples were examined by x-ray diffraction (XRD) with a JEOL-3500 diffractometer with $\text{Cu } K\alpha$ radiation. For the ferroelectric and dielectric measurements, electrodes were deposited on both sides of the pellets by coating with a layer of silver paste. The ferroelectric hysteresis loops were measured on an aixACCT TF analyzer 1000 ferroelectric tester with a Trek 609E-6 high voltage amplifier. The dielectric measurements were carried out on an HP4194A impedance analyzer. The magnetic measurements were carried out on a Quantum Design physical properties measurement system and a magnetic properties measurement system.

Figure 1 shows the XRD patterns of those three solid solution ceramic samples. $\text{Pb}(\text{Fe}_{0.5}\text{Nb}_{0.5})\text{O}_3$, without the in-

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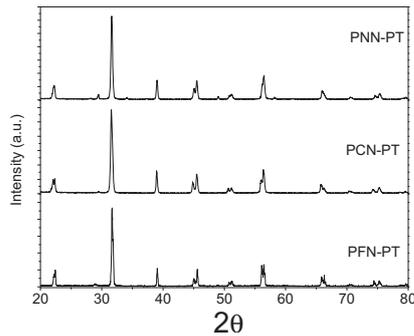


FIG. 1. XRD patterns of the $0.9\text{Pb}(\text{Fe}_{0.5}\text{Nb}_{0.5})\text{O}_3-0.1\text{PbTiO}_3$, $0.6\text{Pb}(\text{Ni}_{1/3}\text{Nb}_{2/3})\text{O}_3-0.4\text{PbTiO}_3$, and $0.6\text{Pb}(\text{Co}_{1/3}\text{Nb}_{2/3})\text{O}_3-0.4\text{PbTiO}_3$ ceramic samples measured at room temperature.

roduction of tetragonal PbTiO_3 , has a rhombohedral structure. After adding 10% PbTiO_3 , $0.9\text{Pb}(\text{Fe}_{0.5}\text{Nb}_{0.5})\text{O}_3-0.1\text{PbTiO}_3$ changes into a tetragonal structure. $\text{Pb}(\text{Ni}_{1/3}\text{Nb}_{2/3})\text{O}_3$ has a rhombohedral structure. After adding 40% PbTiO_3 , it becomes a tetragonal structure. Similarly, $0.6\text{Pb}(\text{Co}_{1/3}\text{Nb}_{2/3})\text{O}_3-0.4\text{PbTiO}_3$ also shows a tetragonal structure.

Ferroelectric hysteresis loops of the three samples measured at room temperature are shown in Fig. 2. The PNN-PT sample shows a well saturated loop with a remanent polarization (P_r) of $20 \mu\text{C}/\text{cm}^2$ and a coercive field of $7.73 \text{ kV}/\text{cm}$. Similarly, the PCN-PT sample shows a well saturated loop with a smaller P_r of $14 \mu\text{C}/\text{cm}^2$ and a coercive field of $10.8 \text{ kV}/\text{cm}$. However, the PFN-PT sample is quite different; in that it has an electrical leakage problem. A full polarization domain switched loop was not successfully obtained. From the composition of the samples, it is known that the concentration of the transition metal Fe in the PFN-PT is much higher than the concentration of transition metals in the other two samples. The multiple valences of the transition metals in the ferroelectric material will cause an increase in the conductivity. For example, it is well known that BiFeO_3 has a severe electrical leakage problem due to the multiple valence problem of the Fe.⁹

The temperature dependences of the real part and the imaginary parts of the dielectric constant of the PFN-PT and PNN-PT ceramic samples measured at frequencies of 1, 10, and 100 kHz are shown in Fig. 3. The abnormal behavior of the real part of the dielectric constant shows that the PFN-PT sample experiences a ferroelectric to paraelectric transition around 140°C . The peak position at this transition shows a

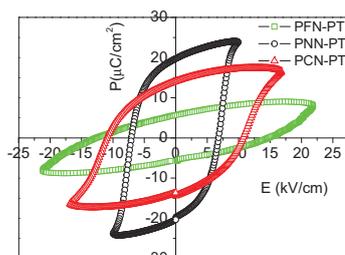


FIG. 2. (Color online) Polarization electrical hysteresis loops (P - E) of $0.9\text{Pb}(\text{Fe}_{0.5}\text{Nb}_{0.5})\text{O}_3-0.1\text{PbTiO}_3$, $0.6\text{Pb}(\text{Ni}_{1/3}\text{Nb}_{2/3})\text{O}_3-0.4\text{PbTiO}_3$, and $0.6\text{Pb}(\text{Co}_{1/3}\text{Nb}_{2/3})\text{O}_3-0.4\text{PbTiO}_3$ ceramic samples measured at 100 Hz and room temperature.

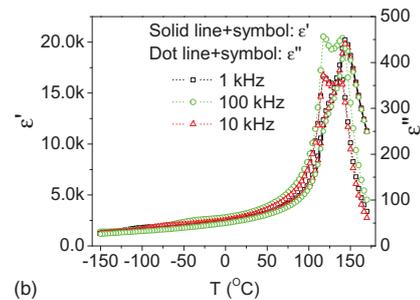
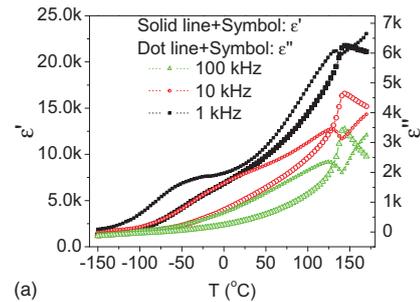


FIG. 3. (Color online) Temperature dependence of the real part and imaginary parts of the dielectric constant measured at 1, 10, and 100 kHz for the relaxor ferroelectric samples with the composition of (a) $0.9\text{Pb}(\text{Fe}_{0.5}\text{Nb}_{0.5})\text{O}_3-0.1\text{PbTiO}_3$ and (b) $0.6\text{Pb}(\text{Ni}_{1/3}\text{Nb}_{2/3})\text{O}_3-0.4\text{PbTiO}_3$.

dependence on the measured frequency. With increasing measurement frequency, the peak value of the real part of the dielectric constant decreases, and the peak position of the imaginary part of the dielectric constant shifts to higher temperature. A decrease in the peak value of the imaginary part with increasing frequency is observed as well. All of these characteristics are typical evidence of the phase transition of relaxor ferroelectric materials.¹⁴ Similarly, relaxor ferroelectric behavior is also observed in the temperature and frequency dependences of the real part and imaginary parts of the dielectric constant of the PNN-PT sample and the PCN-PT sample (not shown here).

Figure 4 shows the field cooled (FC) and zero field cooled (ZFC) magnetization curves of the three samples at the magnetic field of 1000 Oe in the temperature range of 10–300 K. The PFN-PT sample shows a bifurcation between the M_{ZFC} and M_{FC} curves starting from 30 K, which may indicate that the sample enters a spin glass state from this temperature. The inverse of the dc susceptibility χ_{dc} was calculated from the magnetization and plotted in a Curie–Weiss-like plot, as shown in the upper right inset of Fig. 4(a). It appears from the curve that, above the temperature corresponding to the meeting point of the FC and ZFC curves, two different fittings with Curie–Weiss-type linear behaviour are possible, corresponding to a high temperature part and a low temperature part, which result in two different Weiss temperatures. The fitting of the high temperature part results in a negative Weiss temperature, and the fitting of the low temperature part results in a positive Weiss temperature. This indicates that the system has an antiferromagnetic-like ground state and weak ferromagnetism appears at low temperature. The magnetic hysteresis loop measured at 10 K proves that the sample has a very weak ferromagnetic moment. ac magnetic susceptibility measurements show that the

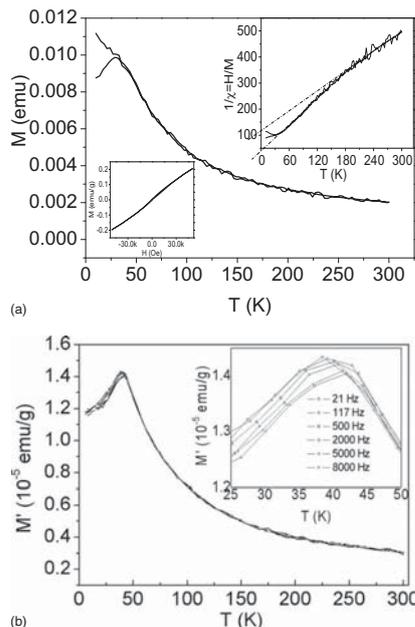


FIG. 4. (a) Temperature dependence of the FC and ZFC magnetization processes of PFN-PT. The upper right inset in (a) shows the temperature dependence of the inverse susceptibility with two Curie–Weiss fittings. The magnetic hysteresis loop in the lower left inset indicates a weak magnetic moment at 10 K. (b) Temperature dependence of the real part of the magnetic susceptibility at various frequencies, showing magnetic relaxor dispersion in PFN-PT. The inset is an enlargement of the peak area.

peak positions shift with the frequency of the ac magnetic field, which further indicates a glassy or relaxorlike behavior below 40 K. According to the above evidences, it is speculated that some ferromagnetic ordered nanoregions start to form below 40 K, while the main part of the sample remains antiferromagnetic ordering. The coexistence of the antiferromagnetic and ferromagnetic phases below 30 K is a cause for the observed glassy behavior.

The FC and ZFC curves of the PNN-PT and PCN-PT samples are much the same down to the lowest temperature measured (Fig. 5). The inverse of the dc susceptibility was calculated and plotted as a function of temperature, which indicates that these two samples have no detectable long-range magnetic ordering down to 10 K, and thus no magnetic hysteresis loop was measured at 10 K for either sample. It has been reported that $\text{Pb}(\text{Fe}_{0.5}\text{Nb}_{0.5})\text{O}_3$ (PFN) has an antiferromagneticlike phase transition in the temperature range of 143–170 K.¹⁵ Our experiment shows that this phase transition shifted to lower temperature after 10% PT was mixed into PFN, forming a solid solution. However, the 40% PT doping into $\text{Pb}(\text{Ni}_{1/3}\text{Nb}_{2/3})\text{O}_3$ and $\text{Pb}(\text{Co}_{1/3}\text{Nb}_{2/3})\text{O}_3$ caused the magnetic ordering to vanish in the measured temperature range. Considering that an exchange interaction (J) in a simple model is given by $J \propto t^2/U$ (where t is the electron transfer and U is the Coulomb repulsion), the magnetic interaction becomes weaker with lengthening of the distance between the magnetic ions in PCN-PT and PNN-PT with more diluted magnetic ions since the electron transfer is reduced by the lengthening.

In summary, the PFN-PT sample shows both a frequency dependent ferroelectric transition and a frequency dependent magnetic transition. Both transitions are classified as relaxor

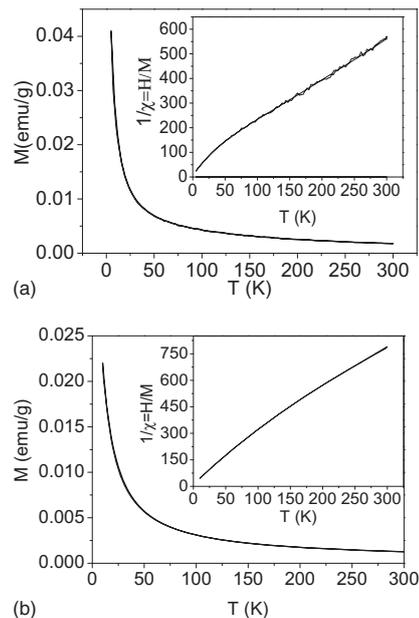


FIG. 5. Temperature dependence of the FC and ZFC magnetization processes of the (a) PCN-PT and (b) PNN-PT samples. The insets show the corresponding inverse susceptibilities as a function of temperature. The overlapping of the FC-ZFC curves of the PCN-PT and PNN-PT samples indicates that no magnetic interaction occurred in these two samples in the measured temperature range.

type. Therefore, with simultaneous ferroelectric behavior and weak ferromagnetism at low temperature, PFN-PT is a magnetoelectric relaxor, while the PNN-PT and PCN-PT samples show no magnetic ordering within the measured temperature range. Further exploration of the magnetoelectric coupling effect in the PFN-PT sample will be carried out in the future.

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