Low temperature magnetic behaviour of PZT-PFW bulk multiferroic ceramics

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Abstract.
Combining the ferroelectric and magnetic components into the solid solution, it is expected to obtain the magneto-electric multiferroic material. Novel bulk ceramic compounds \(x\)PZT+(1−\(x\))PFW, where PZT = \(\text{Pb(Zr}_{0.575}\text{Ti}_{0.425})\text{O}_3\) and PFW = \(\text{Pb(Fe}_{2/3}\text{W}_{1/3})\text{O}_3\), for \(x\) = 0.15, 0.20, 0.25, 0.50, 0.70, 0.80 were synthesized and their magnetic investigation was performed, including the measurement of zero-field cooled (ZFC) and field-cooled (FC) magnetization curves, magnetic hysteresis loops and AC susceptibility.

In the low temperature region (below 20 K) splitting between the ZFC and FC curves together with the frequency dependent peaks in AC susceptibility point to the glassy freezing/blocking of magnetic moments and magnetic relaxor-like behaviour.

1. Introduction
Multiferroics are of great interest in solid state physics [1] because of coexistence of the magnetic and ferroelectric order and their coupling [2, 3]. One of the most known classes of multiferroics are the perovskite oxides [4], where the spin-spiral order is of crucial importance for the multiferroicity. Combining the ferroelectric and magnetic materials into single compound/structure, one hopes to achieve the coupling between the two orders and formation of the magneto-electric multiferroic.

Therefore, we prepared and investigated the PZT-PFW compounds, where PZT = \(\text{Pb(Zr}_{0.575}\text{Ti}_{0.425})\text{O}_3\) and PFW = \(\text{Pb(Fe}_{2/3}\text{W}_{1/3})\text{O}_3\). PZT is known as a tetragonal ferroelectric below 500-750 K depending on the PbTiO\(_3\) concentration [5], whereas PFW is known as a weak ferromagnet below 20 K and antiferromagnet below 350 K [6].

The magneto-electric coupling was already observed in the PZT/PFW layered nanostructure [7]. The aim of present research was to elucidate some open questions in the interpretation of magnetic properties in this class of compounds, which are smearing over ferrimagnetism, weak (anti)ferromagnetism, spin glass, short range order, frustration, etc. We performed magnetic

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studies on ceramic PZT-PFW solid solutions with different concentrations, with emphasis on the low temperature magnetic behaviour.

2. Experimental

Novel bulk solid solution ceramics between the PZT and PFW were synthesized using the same method as for the similar $0.65 \text{Pb(Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3-0.35 \text{PbTiO}_3$ system [8]. The compounds $x\text{PZT}+(1-x)\text{PFW} \ (x = 0.15, 0.20, 0.25, 0.50, 0.70 \text{ and } 0.80)$ were prepared by the solid-state mechano-chemical synthesis, including the high energy milling of the metallic oxides for 4 hours in isopropanol and sintering at 850 °C for 2 h in oxygen atmosphere. The single phase polycrystalline perovskite structure was obtained, as confirmed by the X-ray diffraction [9].

Measurements of magnetization were mostly performed at low temperature using the QD MPMS-XL-5 SQUID magnetometer. The temperature dependence of magnetization $M(T)$ was measured in applied magnetic field $H$ after zero field cooling (ZFC) and after field cooling (FC). The magnetic hysteresis loops $M(H)$ were measured with maximum field of 5T. AC magnetic susceptibility $\chi(T)$ was measured in a broad frequency range (0.1 Hz – 1500 Hz) with the excitation field of 6.5 Oe.

Other measurements are still in progress, including the heat capacity, electrical (magneto)resistivity and dielectric susceptibility.

3. Results

The temperature dependence of magnetization $M(T)$ measured in field of 100 Oe for all compounds is presented in Fig.1. Splitting between the ZFC and FC $M(T)$ curves points to the blocking/freezing of magnetic moments. Similar behaviour of the FC curves was reported in another solid solution $\text{PbFe}_{2/3}\text{W}_{1/3}\text{O}_3-\text{PbTiO}_3$ ceramic [6]. Appearance of the magnetic hysteresis, presented in Fig.2, below the splitting temperature is in accordance with such kind of irreversibility.

AC in phase susceptibilities $\chi'(T)$ of $x\text{PZT}+(1-x)\text{PFW}$ systems exhibit the peaks in the low temperature region, depending on $x$ as shown in Fig.3. The shift of the peaks toward higher

![Figure 1](https://example.com/image1.png)

**Figure 1.** The temperature dependence of PZT-PFW magnetization $M(T)$ in magnetic field of 100 Oe after the zero-field cooling (ZFC) and field cooling (FC). Inset: The same data extended up to room temperature.
Figure 2. Magnetic hysteresis $M(H)$ loops of PZT-PFW at 5 K temperature. Inset: Enlarged region around the origin.

Figure 3. Low temperature in phase AC susceptibilities $\chi'(T)$ of $x$PZT+(1−$x$)PFW at different frequencies $f$.

temperature with increase of the frequency is clearly observable. The out of phase components $\chi''(T)$ for corresponding $x$ (not shown here) have similar shapes, and their maxima also move to higher temperatures with increase of the frequency. Peaks of $\chi''(T)$ are at temperatures slightly below the peaks of $\chi'(T)$, while the values of $\chi''$ are considerably smaller than the values of corresponding $\chi'$. The $\chi'(T)$ at higher temperatures follow the same profile as the FC curve for corresponding $x$.

4. Discussion

The dispersion of the AC susceptibility peaks with frequency is characteristic of several different magnetic systems, and is a sign of the thermal activation of magnetic moments, or unfreezing of
the short range ordered magnetic regions, as well as the spin glass disorder unfreezing. Certainly, the long range magnetic order can be excluded, because it does not exhibit such shift at so low frequencies [10]. The dispersion of peaks is ordinarily accompanied by the observed ZFC-FC splitting.

In our case, the relative shift of the temperature of peak, $T_m$, over decade of the frequency $f$, expressed as $\Delta T_m/(T_m \Delta \log f)$, amounts 0.068, 0.051, 0.042, 0.017 and 0.023, for $x = 0.15, 0.20, 0.25, 0.50$ and 0.70, respectively. These values are one order of magnitude bigger than in most of spin glasses, but also fit well within the values for some rare earth compounds and those with non metallic ingredients, both accepted as the spin glasses [10]. However, the obtained values are somewhat smaller than in the pure superparamagnets, excluding thus the thermal activation of independent single domain magnetic entities.

The frequency dependence of the peak temperature $T_m(f)$ is described very well with the Vogel-Fulcher type of activation $f = f_0 \exp(E_a/(T_m - T_f))$, where $E_a$ is the activation energy, $T_f$ the freezing temperature, and $f_0$ the microscopic reversal attempt frequency [10]. The agreement between this model and the experimental data is presented in Fig.4. From the least square fitting procedure it is obtained $E_a = 53$ K, 98 K, 132 K, 58 K and 22 K, for $x = 0.15, 0.20, 0.25, 0.50$ and 0.70, respectively. Parameter $f_0$ stays around $10^{10} - 10^{11}$ Hz order of magnitude, and $T_f$ is consistently lower than the ZFC-FC splitting temperature of corresponding compound. The same model was used for the interpretation of dielectric (and magnetic) susceptibility for slightly different system where polar (and magnetic) nano-regions were found to be responsible for the relaxor behaviour [11, 12]. Therefore, the observed magnetic behaviour could be understood within the activation of magnetic moments of short range ordered regions that possibly interact. Similar magnetic fluctuations of the short range ordered regions were found in other compounds and experiments, as is the electron spin resonance in Pb(Fe$_{1/2}$Nb$_{1/2}$)O$_3$ [13]. Additional analysis of $T_m(f)$ using the Arrhenius activation law gave the unphysical values for the parameters, especially $f_0$, that supports the exclusion of pure superparamagnetic blocking.

Furthermore, from Fig.1 it can be seen that higher magnetization is attained for smaller concentration of magnetic PFW component at low temperature, as confirmed by the $M(H)$ loops in Fig.2. Oppositely appears at room temperature, as can be observed in the inset of Fig.1. Based on the above AC analysis, this behaviour could be explained with development/coexistence of the superparamagnetic regions and weak/canted antiferromagnetic order. Smaller concentration

![Figure 4. Vogel-Fulcher type plots of $x$PZT+$(1-x)$PFW. Lines are the fitting curves.](image-url)
x of PZT gives more place for the long range magnetic ordering of PFW, which is basically antiferromagnetic, and therefore reducing the total magnetization. Higher concentration of PZT enhances the localized ordering of PFW into finite magnetic regions, having the magnetic moments that contribute appreciably to the total magnetization.

5. Conclusion
ZFC-FC DC magnetization curves and AC susceptibility indicate the magnetic moment blocking/freezing in $x$PZT+$(1−x)$PFW in low temperature region, that could also be the reason for magnetic hysteresis. Frequency dispersion of the AC susceptibility peaks is in favour of formation of the short range magnetically ordered regions responsible for the relaxor-like magnetic behaviour.

Vogel-Fulcher approach to the activation of magnetic moments describes very well the shift of AC susceptibility peaks with frequency, for all PZT-PFW, supporting thus the unfreezing of the locally ordered magnetic moments.

The magnetization reached at the low temperature for different PZT/PFW concentration ratio indicates the competition between the formation of magnetic regions and long range weak ferromagnetic ordering. This is evident from the magnetic hysteresis loops, as well as from ZFC-FC magnetization curves.

Presented results are of importance for design of the novel multiferroic materials in form of bulk solid solution ceramics, in particular with the relaxor-like behaviour [14].

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