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Cation, dipole, and spin order in $\text{Pb}(\text{Fe}_{2/3}\text{W}_{1/3})\text{O}_3$ -based magnetoelectric multiferroic compounds

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Long range 1:1 cation order was developed in $\text{Pb}(\text{Fe}_{2(1-x)/3}\text{Sc}_{2x/3}\text{W}_{1/3})\text{O}_3$ solid solution compounds by high temperature solid state reaction. It is found that the degree of cation order directly influences the saturation magnetization in these single phase compounds. A high saturation magnetization ($\sim 0.61\mu_B/\text{f.u.}$) was observed for $x=0.15$ at 10 K under 5 T. A ferrimagnetic structure was suggested to take into account for the observed magnetic behavior. These compounds also display a saturated electrical polarization of $\sim 15\mu\text{C}/\text{cm}^2$ at 40 kV/cm at 120 K. © 2007 American Institute of Physics. [DOI: 10.1063/1.2748098]

Magnetoelectric multiferroic compounds, combining a spontaneous electrical polarization with a net magnetization, have attracted worldwide interest recently due to their great potentials for fundamental research and practical applications.¹⁻³ However, all the known magnetic ferroelectric oxides either have a low transition temperature or display an extremely small polarization/magnetization. Among these multiferroic compounds, those with the ABO_3 perovskite structure show the highest magnetic transition temperatures and the largest electrical polarizations.³ Considering the fact that most magnetic perovskite oxides have an antiferromagnetic order due to a superexchange coupling between magnetic ions on the B site,⁴ Baettig and Spaldin⁵ and Baettig *et al.*⁶ proposed to introduce spontaneous magnetization via *ferrimagnetism* and predicted that $\text{Bi}(\text{Fe}_{1/2}\text{Cr}_{1/2})\text{O}_3$ would display an electrical polarization of $80\mu\text{C}/\text{cm}^2$ and a saturation magnetization of $1\mu_B/\text{ABO}_3$ f.u. if Fe^{3+} and Cr^{3+} occupy separate B sublattices (B' and B'') to form a double perovskite structure. The Neel temperature was calculated to be low (<100 K), though. However, such a double perovskite structure with long range B -site cation order is not likely to form since Fe^{3+} and Cr^{3+} have the same charge and close ionic sizes. $\text{Bi}(\text{Fe}_{1/2}\text{Cr}_{1/2})\text{O}_3$ is, thus, expected to adopt a simple perovskite structure with random occupancy of Fe^{3+} and Cr^{3+} on B site. Recent experimental work confirmed that the $\text{Bi}(\text{Fe}_{1/2}\text{Cr}_{1/2})\text{O}_3$ epitaxial thin film is isostructural to BiFeO_3 with a rhombohedral distortion.⁷ A saturation magnetization of only $0.26\mu_B/\text{f.u.}$ was measured at room temperature due to the absence of long range cation order. In addition, the film was found to be very leaky with an induced polarization of only $2.8\mu\text{C}/\text{cm}^2$ at 82 kV/cm. In the bulk form, $\text{Bi}(\text{Fe}_{1/2}\text{Cr}_{1/2})\text{O}_3$ shows neither B -site cation order nor any ferri—or ferromagnetic order down to 2 K.⁸

In contrast, a few ferroelectric Pb-based complex perovskite oxides have been reported to display long range 1:1 B -site cation order, such as $\text{Pb}(\text{Sc}_{1/2}\text{Ta}_{1/2})\text{O}_3$,⁹ La-doped $\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3$,^{10,11} and $\text{Pb}(\text{Sc}_{2/3}\text{W}_{1/3})\text{O}_3$.¹² The multifer-

roic $\text{Pb}(\text{Fe}_{2/3}\text{W}_{1/3})\text{O}_3$ compound also shows 1:1 cation order, however, the chemical order is very weak and the cation ordered domains are limited to the nanometer scale (<5 nm).¹³⁻¹⁵ Developing long range cation order in $\text{Pb}(\text{Fe}_{2/3}\text{W}_{1/3})\text{O}_3$ for large saturation magnetization has been experimentally attempted previously with Mg^{2+} doping¹⁶ and Co^{2+} doping.¹⁷ The present work aims to enhance cation order in $\text{Pb}(\text{Fe}_{2/3}\text{W}_{1/3})\text{O}_3$ through solid solution with $\text{Pb}(\text{Sc}_{2/3}\text{W}_{1/3})\text{O}_3$, both of which have a B -cation ratio of 2:1. Magnetic as well as ferroelectric properties are assessed as a function of the degree of B -site cation order.

Ceramics in the solid solution ($1-x$) $\text{Pb}(\text{Fe}_{2/3}\text{W}_{1/3})\text{O}_3-x\text{Pb}(\text{Sc}_{2/3}\text{W}_{1/3})\text{O}_3$ ($x=0.09, 0.15, 0.21$), or $\text{Pb}(\text{Fe}_{2(1-x)/3}\text{Sc}_{2x/3}\text{W}_{1/3})\text{O}_3$, were prepared via a solid state reaction method with high purity powders (better than 99.9%). Proportional amount of Fe_2O_3 , WO_3 , and Sc_2O_3 powders were mixed and calcined at 900 °C for 24 h. Then appropriate amount of PbO powder was mixed and a second calcination was carried out at 850 °C for 2 h. Ceramic pellets were formed by sintering at 890 °C for 2 h followed by a slow cooling procedure at 9 °C/h to 800 °C. The surface layers of the sintered disks were removed before x-ray diffraction experiments. Dielectric characterization was performed with a LCR meter (HP-4284A, Hewlett-Packard) in conjunction with an environmental chamber (9023, Delta Design). A heating rate of 3 °C/min was used during measurement. The polarization hysteresis measurement was carried out with a standardized ferroelectric test system (RT-66A, Radiant technologies). A Quantum Design 5T MPMS was used for magnetic characterization.

X-ray diffraction indicates that the as-sintered ceramics are phase pure and display a pseudocubic perovskite structure, as shown in Fig. 1. The lattice parameters increase with Sc^{3+} content and were determined to be 3.9760, 3.9837, and 4.0004 Å for ceramics of $x=0.09, 0.15$, and 0.21, respectively. This is consistent with the fact that Sc^{3+} has a larger ionic radius than both Fe^{3+} and W^{6+} . Furthermore, $(\frac{1}{2}\frac{1}{2}\frac{1}{2})$ -type superlattice peaks get strengthened as Sc^{3+} content increases, as revealed clearly by the inset in Fig. 1. In

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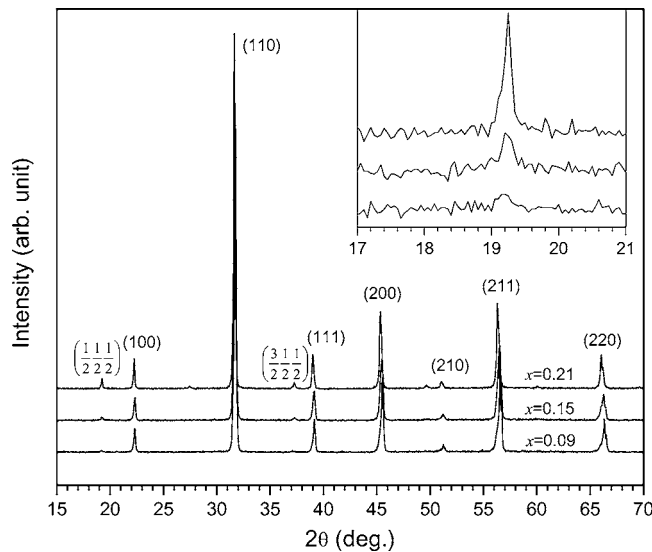
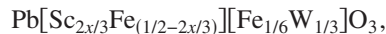


FIG. 1. X-ray diffraction pattern of the sintered $\text{Pb}(\text{Fe}_{2(1-x)/3}\text{Sc}_{2x/3}\text{W}_{1/3})\text{O}_3$ ceramics. Major peaks are indexed on the basis of a simple cubic perovskite structure. The $(\frac{1}{2}\frac{1}{2}\frac{1}{2})$ -type superlattice peaks due to B -site cation order are also indexed. The inset shows the close view of the $(\frac{1}{2}\frac{1}{2}\frac{1}{2})$ superlattice peak.

complex perovskite oxides, the presence of the $(\frac{1}{2}\frac{1}{2}\frac{1}{2})$ superlattice peak is an indication of the development of 1:1 B -site cation order and the intensity of this superlattice peak has been routinely used to calculate the ordering parameter S .^{10,11} This parameter ranges from 0 to 1, with 0 marking the complete disorder and 1 marking the complete order. The ordering parameters S are calculated to be 0.26, 0.55, and 0.81 for ceramics of $x=0.09$, 0.15, and 0.21, respectively. The double perovskite model,



was used for the calculation.

The dielectric response of these ceramic pellets was examined and the result is shown in Fig. 2. It is noted that broad peaks appear for all three compositions. At 100 kHz, the maximum relative permittivities ϵ_m were measured to be 5130 at 198 K, 5460 at 206 K, and 4160 at 198 K for ceramics of $x=0.09$, 0.15, and 0.21, respectively. It appears that the ceramic with $x=0.15$ behaves slightly abnormally. The

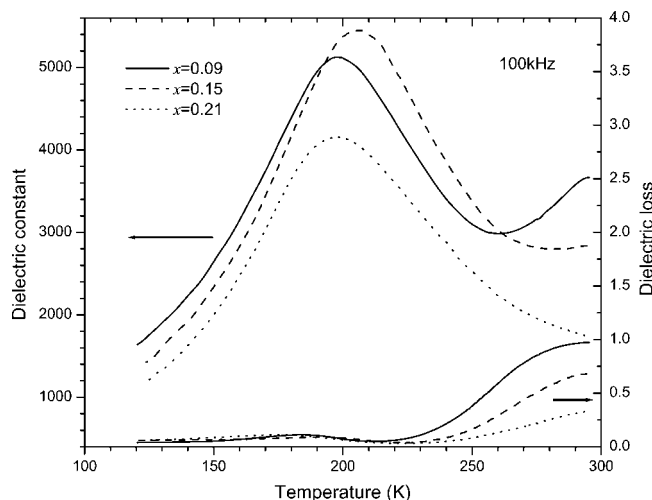


FIG. 2. Relative dielectric permittivity and dielectric loss of the $\text{Pb}(\text{Fe}_{2(1-x)/3}\text{Sc}_{2x/3}\text{W}_{1/3})\text{O}_3$ ceramics as a function of temperature at 100 kHz.

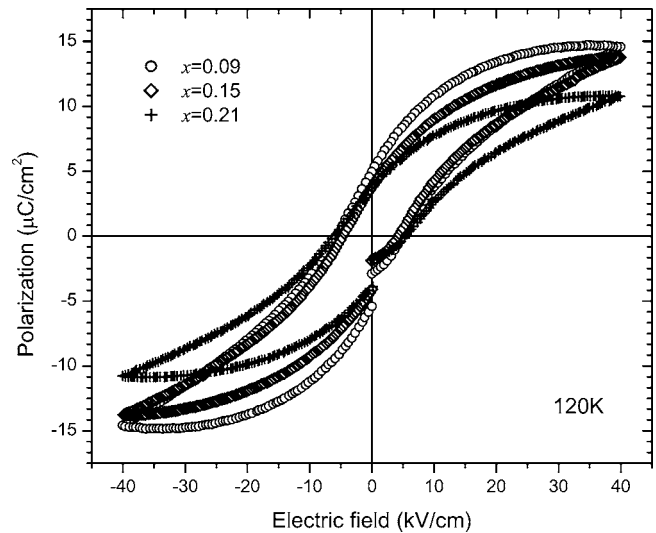


FIG. 3. Polarization vs electric field hysteresis loops measured at 4 Hz at 120 K in the $\text{Pb}(\text{Fe}_{2(1-x)/3}\text{Sc}_{2x/3}\text{W}_{1/3})\text{O}_3$ ceramics. Well defined saturated loops are observed.

dielectric loss is relatively low for all three ceramics, especially under 230 K. Compared to pure $\text{Pb}(\text{Fe}_{2/3}\text{W}_{1/3})\text{O}_3$ ($\epsilon_m=11\,700$ at $T_m=190$ K at 100 kHz),¹³ solid solution with $\text{Pb}(\text{Sc}_{2/3}\text{W}_{1/3})\text{O}_3$ leads to a slight higher T_m but a much lower ϵ_m value.

The low dielectric loss at low temperatures allows the electric field-induced polarization measurement under quasi-static fields. The electrical polarization versus electric field hysteresis loop was evaluated at 4 Hz at 120 K. As shown in Fig. 3, saturated loops were recorded for all three compositions. Saturation polarizations of 14.6, 13.8, and $10.9\ \mu\text{C}/\text{cm}^2$ for ceramics of $x=0.09$, 0.15, and 0.21, respectively, were measured at the peak electric field of 40 kV/cm at this temperature. Remanent polarizations of 5.2, 4.0, and $3.8\ \mu\text{C}/\text{cm}^2$ for $x=0.09$, 0.15, and 0.21, respectively, were recorded. The coercive fields were determined to be 5.5, 4.5, and 5.5 kV/cm for $x=0.09$, 0.15, and 0.21, respectively. Therefore, strong ferroelectricity with large electrical polarizations and low coercive fields is demonstrated in the $\text{Pb}(\text{Fe}_{2(1-x)/3}\text{Sc}_{2x/3}\text{W}_{1/3})\text{O}_3$ solid solution.

The magnetization under weak field indicates a clear transition from paramagnetic to ferrimagnetic at ~ 224 , ~ 245 , and ~ 222 K for the ceramics of $x=0.09$, 0.15, and 0.21, respectively. Compared to pure $\text{Pb}(\text{Fe}_{2/3}\text{W}_{1/3})\text{O}_3$ ($T_N=370$ K),¹³⁻¹⁵ incorporating Sc decreases the transition temperature, which can be attributed to the dilution of the magnetic cations. The magnetization under a strong magnetic field of 5 T for the three ceramics is shown in Fig. 4. Interestingly, the ceramic of $x=0.15$ shows the highest magnetization. The saturation magnetizations at 10 K under 5 T were determined to be $0.22\ \mu_B/\text{ABO}_3$ f.u., $0.61\ \mu_B/\text{ABO}_3$ f.u., and $0.48\ \mu_B/\text{ABO}_3$ f.u. for $x=0.09$, 0.15, and 0.21, respectively. The saturation magnetizations observed in these ceramics are about one order of magnitude higher than disordered perovskite compounds^{3,15} and are even two times as high as single crystalline $\text{Bi}(\text{Fe}_{1/2}\text{Cr}_{1/2})\text{O}_3$ epitaxial thin films.⁷

We believe that the observed magnetic behavior is dictated by the B -site cation order in the ceramics. As mentioned previously, the solid solution can be expressed as a double perovskite compound $\text{Pb}[\text{Sc}_{2x/3}\text{Fe}_{(1/2-2x/3)}]$

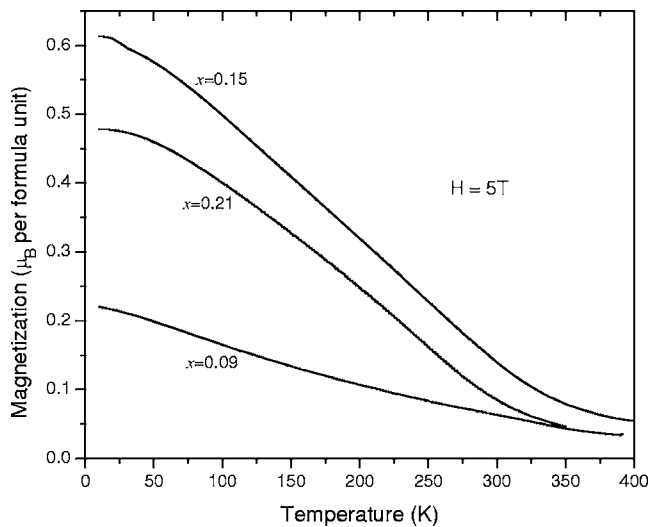


FIG. 4. Magnetization vs temperature during cooling under 5 T in the $\text{Pb}(\text{Fe}_{2(1-x)/3}\text{Sc}_{2x/3}\text{W}_{1/3})\text{O}_3$ ceramics.

$\times[\text{Fe}_{1/6}\text{W}_{1/3}]\text{O}_3$ when it is fully ordered. We denote the sublattice occupied by $[\text{Sc}_{2x/3}\text{Fe}_{(1/2-2x/3)}]$ as B' , while the one occupied by $[\text{Fe}_{1/6}\text{W}_{1/3}]$ as B'' . Due to the superexchange coupling between the Fe^{3+} cations, an antiferromagnetic order is developed on the magnetic moment of Fe^{3+} between the two B -site sublattices. Therefore, the measured magnetization depends on the partition of the Fe^{3+} cations on the two sublattices. For $0.00 \leq x \leq 0.50$, the double perovskite model $\text{Pb}[\text{Sc}_{2x/3}\text{Fe}_{(1/2-2x/3)}][\text{Fe}_{1/6}\text{W}_{1/3}]\text{O}_3$ indicates that the B' sublattice has more Fe^{3+} cations than the B'' sublattice and the difference is $(1-2x)/3 \text{ Fe}^{3+}$ ions/f.u. The magnetization data above T_c indicate that the magnetic moment for each Fe^{3+} in the paramagnetic state is roughly $3\mu_B$. Therefore, we estimate that in the ordered state, the saturation magnetization of our double perovskite model for the composition series will be $(1-2x)\mu_B/\text{f.u.}$ for a fully ordered structure. This is a straight line with respect to x and is plotted in Fig. 5.

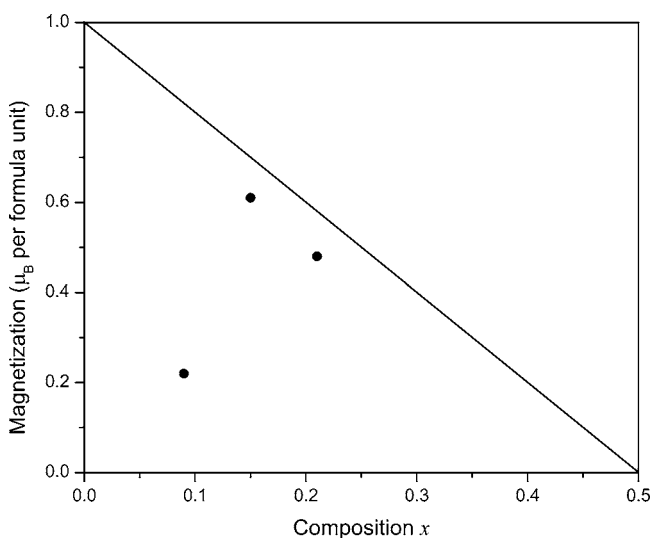


FIG. 5. Predicted linear relation between the saturation magnetization and the composition x in the $\text{Pb}(\text{Fe}_{2(1-x)/3}\text{Sc}_{2x/3}\text{W}_{1/3})\text{O}_3$ solid solution system based on the ferrimagnetic double perovskite model. The dark dots mark the measured saturation magnetizations.

The three dark dots in Fig. 5 are the measured saturation magnetization at 10 K under 5 T for the ceramics of $x=0.09$, 0.15, and 0.21, respectively. The experimental values of the saturation magnetization correspond to 27%, 87%, and 83% of the predicted values from the straight line for each composition, respectively. For the ceramics of $x=0.15$ and 0.21, it is clear that the experimental data match the ferrimagnetic double perovskite model quite well. The large discrepancy between the experimental data and the ferrimagnetic model for $x=0.09$ is due to the weak long range B -site cation order. As mentioned in the x-ray diffraction section, the cation ordering parameters S are 0.26, 0.55, and 0.81 for the ceramics of $x=0.09$, 0.15, and 0.21, respectively. It is interesting to note that the values of the chemical order parameter S are in good agreement with the percentage of the predicted saturation magnetization in these ceramics, especially for $x=0.09$ and $x=0.21$. Clearly there is a direct correlation between the degree of the long range cation order and the achieved saturation magnetization. The low saturation magnetization measured in the ceramic of $x=0.09$ is due to antisite occupancy of the B -site cations. For the ceramic of $x=0.15$, we believe that the ordering parameter S is under estimated due to the small size of cation ordered domains.

In summary, long range cation order is developed in ceramics of $\text{Pb}(\text{Fe}_{2(1-x)/3}\text{Sc}_{2x/3}\text{W}_{1/3})\text{O}_3$ solid solution prepared with a simple solid state reaction method. Saturated polarization versus electric field hysteresis loops were observed for all three ceramics under quasistatic electric fields. Large electrical polarizations ($14.6 \mu\text{C}/\text{cm}^2$ for $x=0.09$) were measured at 40 kV/cm at 120 K. Direct correlation between the measured saturation magnetization and the degree of B -site cation order is observed. Ultrahigh saturation magnetization ($0.61\mu_B/\text{ABO}_3$ f.u.) was measured in the ceramic of $x=0.15$.

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