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Ferroelectricity in the Ferrimagnetic Phase of $Fe_{1-x}Mn_xV_2O_4$ *

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Ferroelectric and magnetic properties of $Fe_{1-x}Mn_xV_2O_4$ ($0 \le x \le 0.5$) spinels are investigated on the basis of dielectric, polarization, and susceptibility measurements. Ferroelectric polarization is discovered in collinear ferrimagnetic and Yafet–Kittel magnetic phases for $0.1 \le x \le 0.4$, which can be tuned by a magnetic field. As orbital-active Fe^{2+} is substituted with Mn^{2+}, ferroelectric polarization decreases for $0 \le x \le 0.4$ and disappears for x=0.5. We propose that the two polar components in ferroelectric polarization originate from the exchange striction mechanism and the spin-current model, respectively.

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Multiferroic materials have been extensively investigated for studying the fundamental properties and exploiting multifunctional device applications.[1,2] In the spinel oxide family, the magnetically driven ferroelectricity was first found in $CoCr_2O_4$ with spiral magnetic structure.[3] Further research demonstrated that the ferrimagnetic phase in $CoCr_2O_4$ and $FeCr_2O_4$ could also induce polarization, which is attributed to the complex magnetic interactions and is independent of the existence of Jahn–Teller ion at A-site.[4]

Vanadium spinel AV_2O_4, which has an orbital triplet degenerate on the V^{3+} site, has attracted considerable attention due to its complex magnetic structure and rich orbital ordering.[5–7] Recently, multiferroic behavior was also discovered in AV_2O_4 (A=Cd, Fe).[8,9] FeV_2O_4 is an extraordinary material that has orbital-active ions on both cation sites of the spinel.[9–11] The A-site Fe^{2+} ion has two-fold degeneracy in e orbital. FeV_2O_4 undergoes multiple structural and magnetic transitions at low temperatures.[11] At 140 K (T_{S1}), the structural transition from cubic to high-temperature (HT) tetragonal (tetra; $c < a$) phase is attributed to the cooperative Jahn–Teller effect of A-site Fe^{2+} ions. Collinear ferrimagnetic order emerges at 110 K (T_{N1}), and the crystal symmetry lowers from HT tetra ($c < a$) to orthorhombic (ortho) because of the spin–orbit interaction of Fe^{2+}. At 70 K (T_{S3}), the structure changes from ortho to low-temperature (LT) tetra ($c > a$), accompanied by the magnetic transition from the collinear to Yafet–Kittel (YK) magnetic structure ($T_{N2} = T_{S3}$). Zhang *et al.*[9] reported that the ferroelectric polarization develops below T_{N2} and suggested that polarization can be explained by the spin-current model.[12]

In the vanadium spinel family, MnV_2O_4 has two similar macroscopic magnetic transitions to FeV_2O_4. However, no spontaneous polarization was found in MnV_2O_4. More recently, the evolution of structural and magnetic properties of $Fe_{1-x}Mn_xV_2O_4$ ($0 \le x \le 1$) was investigated.[13–15] The substitution of Mn^{2+} for Fe^{2+} is regarded as the introduction of vacancies at A-site in terms of orbital degree of freedom. So far, the effect of the Mn doping on the ferroelectric polarization was not studied.

In this Letter, the evolution of ferroelectric properties of $Fe_{1-x}Mn_xV_2O_4$ is investigated by performing pyrocurrent and susceptibility measurements to clarify the effect of Mn-doping at A-site on polarization. We find that the electric polarization exists not only in the YK magnetic phase, but also in the collinear ferrimagnetic phase. Based on the structural and magnetic phase diagram, the origin of ferroelectricity is discussed.

Polycrystalline $Fe_{1-x}Mn_xV_2O_4$ samples were prepared by solid state reaction. Appropriate mixtures of FeO, MnO, and V_2O_3 were ground together, pressed into pellets, and then calcined in a sealed quartz tube at 1373 K for 20 h. Small pieces of polycrystalline were ground into fine powder for x-ray diffraction measurements, and all samples were identified as a single phase with a cubic spinel structure at room temperature. The lattice parameter of $Fe_{1-x}Mn_xV_2O_4$ was found to increase linearly with x, which is consistent with Vegard's law. The ac susceptibility measurements were performed at 10 kHz frequency with a driving field of 1 Oe. Dielectric measurements were carried out during warming by using QuadTech 1730 LCR meter with 1 V ac driving field under several frequencies (from

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1 kHz to 100 kHz). Electric polarization was calculated by integrating the pyrocurrent recorded with a Keithley 6517 A electrometer.[9,16] Polarization measurements included two procedures. One procedure was poling, in which a static electric field of 300 kV/m was applied at 80 K during cooling to align possible ferroelectric domains. At 6 K, the poling field was removed and the electrodes were shortened for 1 h to reduce the possible contribution from the detrapped charges. The other procedure was measurement, in which pyrocurrent was recorded during warming at a constant rate of 5 K/min in a zero electric field.

The temperature dependence of the real part χ' of ac susceptibility of $Fe_{1-x}Mn_xV_2O_4$ for $0 \le x \le 0.5$ is illustrated in Fig. 1. All the χ'–T curves show two anomalies, i.e., a sharp peak at a higher temperature (HT anomaly) and a small cusp at a lower temperature (LT anomaly). According to the previous results for $Fe_{1-x}Mn_xV_2O_4$,[13–15] the HT anomaly is assigned to the paramagnetic-ferrimagnetic transition at T_{N1}, and the LT anomaly is interpreted as the collinear-YK magnetic transition at T_{N2} for the solid solutions. As x increases, both T_{N1} and T_{N2} decrease for $0 \le x \le 0.5$. As suggested in Refs. [17,18], T_{N1} is mainly decided by V–V interaction and is inversely proportional to the V–V distance R_{V-V}. With increasing x, the successive increasing V–V distance leads to a monotonic decrease in T_{N1}. However, the magnetic phase transition at T_{N2} is driven by the cooperative interactions between the ordered orbitals of the A-site Fe^{2+} and B-site V^{3+} ions. As x increases, the long-range orbital interaction weakens due to the orbital dilution at A-sites, which induces a gradual decrease in T_{N2}.

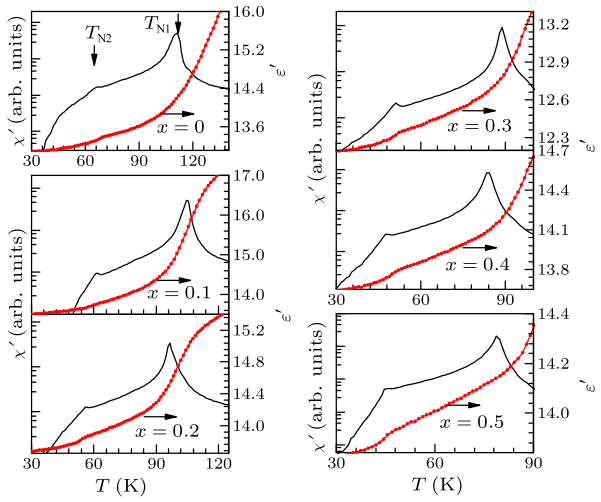

Fig. 1. Temperature dependence of the real part of ac susceptibility and dielectric permittivity for $Fe_{1-x}Mn_xV_2O_4$ ($0 \le x \le 0.5$). Dielectric permittivity was measured at 100 kHz frequency.

The temperature dependence of the real part ε' of dielectric permittivity at $f = 100$ kHz is also shown in Fig. 1. At the first glance, the dielectric constant increases with temperature at all doping levels. Near T_{N1}, the increase is sharp. A careful look found that a small kink appears at T_{N2}. To see it clearly, the temperature dependences of real part ε' and imaginary part ε'' of $Fe_{0.8}Mn_{0.2}V_2O_4$ at three frequencies are presented in Figs. 2(a) and 2(b), respectively. The temperature derivative of ε' is shown in the inset of Fig. 2(a). For comparison, the ac magnetic susceptibility is also re-plotted in the inset. Corresponding to the magnetic LT anomaly at T_{N2}, a frequency-independent peak of $d\varepsilon'/dT$ is obviously observed. This dielectric anomaly was reported in many magneto-dielectric materials, which is believed to arise from the strong spin-phonon coupling.[19,20] Near T_{N1} the peak in $d\varepsilon'/dT$, corresponding to the sharp increase in ε', was accompanied by a peak in ε'' (Fig. 2(b)). The ε'' peak shifts to lower temperature with decreasing frequency, indicating a thermally activated dielectric relaxation. A similar relaxation phenomenon was found in RMnO$_3$ (R=rare earth) and CdV_2O_4,[8,21] signaling the existence of the disordered or long-range ordered lattice dipoles.

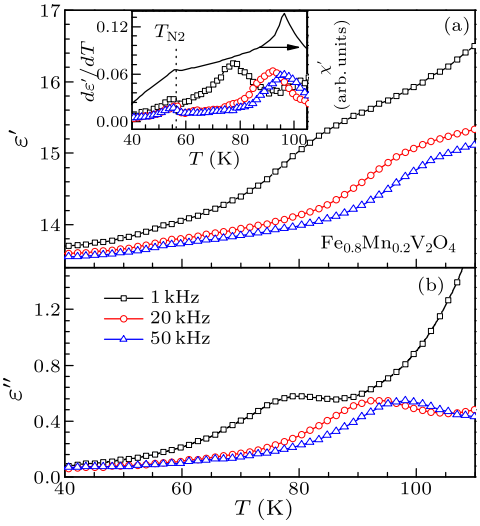

Fig. 2. Temperature dependence of the complex dielectric permittivity of $Fe_{0.8}Mn_{0.2}V_2O_4$ measured at various frequencies. The inset: $d\varepsilon'/dT$ versus T, showing the dielectric anomaly at the YK magnetic transition T_{N2}.

The measured pyrocurrent is shown in Fig. 3(a). According to the Bucci–Fieschi theory,[22] with single relaxation time assumption, all pyrocurrent curves can be fitted by two polarization components apart from $x = 0$, typically illustrated in the inset of Fig. 3(b) for $x = 0.2$. One component is peak-centered at a high temperature (polarization 1), and the other peak-centered at a low temperature (polarization 2). For $0.1 \le x \le 0.4$, each group of peaks has similar parameters: relaxation time τ_0 and activation energy E. Polarization 2 appears only in the YK magnetic phase, whereas polarization 1 extends into the collinear ferrimagnetic phase. Referring to the inset of Fig. 3(b), in

the temperature range of $T_1 < T < T_2$, both contributions from polarizations 1 and 2 coexist. When the poling field is applied during cooling within the temperature range of $6\,\mathrm{K} < T_{\mathrm{poling}} < T_1$, only LT peak appears upon subsequent warming. However, the pyrocurrent curve shows only the HT peak upon warming when poling is conducted within $T_2 < T_{\mathrm{poling}} < 80\,\mathrm{K}$ during cooling. These results indicate that the two polar peaks are induced through two polarization mechanisms that are uncorrelated. As shown in Fig. 3(a), the two polar peaks decrease and disappear simultaneously as x increases, suggesting that the substitution of Mn^{2+} for Fe^{2+} at A-site should influence both polarization mechanisms.

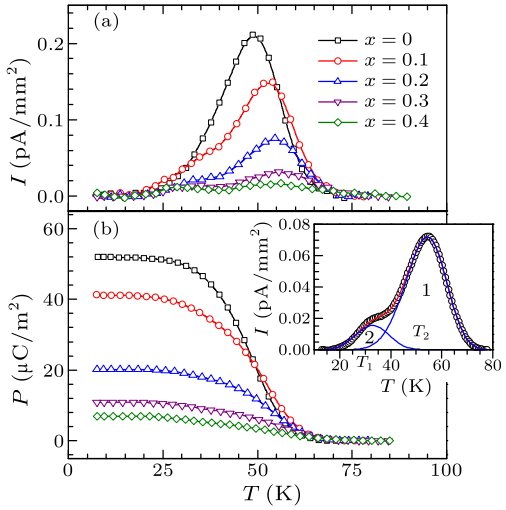

Fig. 3. Temperature dependence of pyrocurrent density and polarization for $Fe_{1-x}Mn_xV_2O_4$ ($0 \le x \le 0.4$). Inset: the pyrocurrent curve for $Fe_{0.8}Mn_{0.2}V_2O_4$ is fitted according to the Bucci–Fieschi theory.[22]

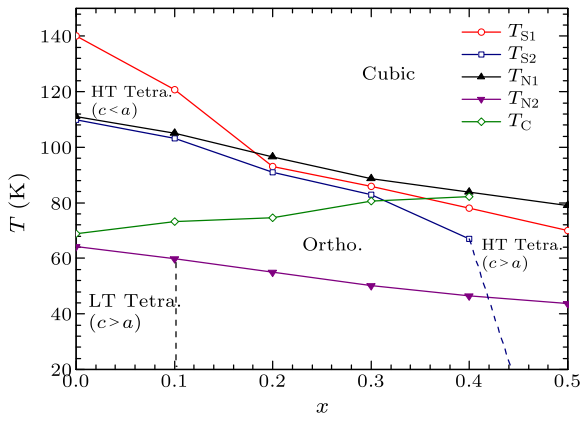

Fig. 4. Structural, magnetic, and ferroelectric phase diagram of $Fe_{1-x}Mn_xV_2O_4$ ($0 \le x \le 0.5$). The data of structural transitions T_{S1} and T_{S2} are taken from Ref. [15].

The calculated electric polarization P is displayed as a function of temperature in Fig. 3(b). The polarization decreases monotonically with doping for $0 \le x \le 0.4$ and disappears for $x = 0.5$. Reversing the poling field leads to a symmetric negative polarization for all components. The P–T curve and the saturated polarization ($53\,\mu\mathrm{C/m^2}$) for $x = 0$ agree with the results in the literature.[9] Zhang *et al.*[9] found that ferroelectric transition temperature T_C coincides with T_{N2} in FeV_2O_4. However, this correlation is absent in doped samples. We plot T_C for $0 \le x \le 0.4$ in phase diagram (Fig. 4). As x increases, T_C increases, approaching T_{N1}, and the divergence between T_C and T_{N2} increases. These results indicate the existence of polarization in ferrimagnetic phase, analogous to $FeCr_2O_4$ and $CoCr_2O_4$.[4]

The effect of magnetic field on polarization was studied to verify the correlation between polarization and magnetism, as typically shown in Fig. 5 for $x = 0.2$. For curve 1, no magnetic field was applied during the experiment. For curve 2, no magnetic field was applied in poling procedure during cooling, and the pyrocurrent was measured upon subsequent warming in a magnetic field of 10 T. For curve 3, a magnetic field of 10 T was applied at 120 K in poling procedure, and the same measurement procedure as curve 2 was used. In measurement, the magnetic and electric fields were perpendicular to each other. To avoid any effect of magnetic field history, the sample was heated up to 300 K before measuring each P–T curve. As seen from Fig. 5 the application of magnetic field in either poling process or in the following pyrocurrent measurement process enhances the polarization below T_C, consistent with the observation in $FeCr_2O_4$.[4] In addition, a difference exists between curves 2 and 3, suggesting that the magnetic field affects dipoles aligning in poling procedure.[23]

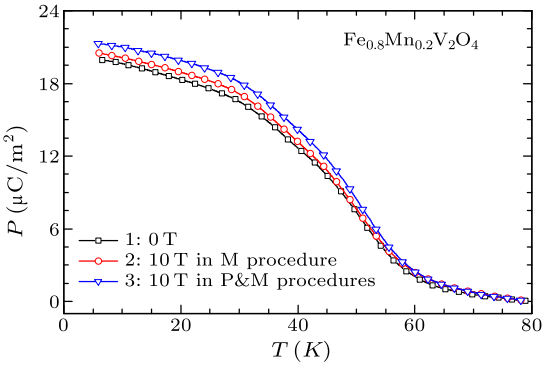

Fig. 5. Temperature dependence of the polarization in magnetic field for $Fe_{0.8}Mn_{0.2}V_2O_4$.

In the following, the origin of ferroelectricity is discussed based on structural and magnetic phase diagram. At T_{S1} and for $x < 0.2$, Fe^{2+} $3z^2 - r^2$ ferro-orbital order (F-OO) is formed with the cubic-HT tetra ($c < a$) structural transition, which does not induce ferroelectric polarization. In the temperature region of $T_{N2} < T < T_{N1}$, the tetragonal and orthorhombic phases are also induced by Fe^{2+} F-OO.[15] If considering the long-range orbital interactions only,

the crystal structure of tetragonal and orthorhombic phases are centrosymmetric and should not allow ferroelectricity. However, polarization 1 appears below T_{N1}, where the spin is in the collinear ferrimagnetic state. This result indicates that polarization 1 is mainly driven by the collinear ferrimagnetic order. It has been proposed that the collinear magnetic order could induce polarization through $\boldsymbol{S}_i \cdot \boldsymbol{S}_j$-type exchange striction mechanism.[8,24,25] In this scenario, the shifts of oxygens differ in the vicinity of ferromagnetic and antiferromagnetic bonds, which break the inversion symmetry and result in polarization. The appearance of polarization 1 below T_{N2} also supports exchange striction mechanism, due to the fact that the YK magnetic structure has a collinear magnetic component.

Below T_{N2} and for $0 \leq x \leq 0.4$, the magnetic structure changes to the non-collinear YK magnetic order. Polarization 2 emerges in LT tetra ($c > a$) and ortho phases. Despite the different space groups below T_{N2}, the P–T and ε'–T curves for $0 \leq x \leq 0.4$ exhibit similar properties emphasizing that polarization 2 is independent of structure and originates from the YK magnetic order. As proposed in Ref. [9] polarization 2 can be explained by the spin-current model, which predicts that the non-collinear spin order can give rise to an electric polarization.

We subsequently discuss the effect of A-site Fe^{2+} ion on polarization. According to Refs. [13–15], all $Fe_{1-x}Mn_xV_2O_4$ solid solutions have two similar macroscopic magnetic transitions. However, polarization disappears for $x \geq 0.5$, which implies that polarizations 1 and 2 are sensitive to the microscopic magnetic structure, even the macroscopic magnetic states are the same. The A-site doping has a subtle impact on the structure and magnetism, which ultimately affects polarization.

As reported in a previous work,[14] the average ionic radius of A-site increases with x, which would affect the magnetic interaction of V–V and A–V due to the fact that the magnetic interaction is functions of inter-atomic distances and angles. Meanwhile, the orbital configuration of A-site ion affects the magnetic interaction in AV_2O_4. The magnitude of magnetic exchange coupling J depends on the orbital occupancy and thereby on the shape and orientation of these orbitals. In FeV_2O_4, the anharmonic elastic and the spin–orbit interaction energy of e electron on Fe^{2+} ion favor $3z^2 - r^2$ and $y^2 - z^2$ orbitals, respectively. As x increases, the elastic energy decreases and then disappears at x=0.5, which exactly coincides with the variation of polarization with doping. We predict that in $Fe_{1-x}Mn_xV_2O_4$ the $3z^2 - r^2$ orbital of A-site Fe^{2+} ions may play an important role in some exchange pathways, leading to the centrosymmetry breaking required for developing polarization.

According to the above analysis, the polarization should exist in the collinear ferrimagnetic phase of FeV_2O_4. Why the polarization is not observed experimentally is unclear. One reason might be that FeV_2O_4 has a small gap and the finite conductivity of the sample in the collinear ferrimagnetic region may screen the polarization. As reported in Ref. [17] with decreasing the V–V distance, AV_2O_4 approaches the itinerant-electron limit. Therefore, with the decrease of the conductivity upon Mn doping, the screening effect weakens, and the polarization of $Fe_{1-x}Mn_xV_2O_4$ could be detected in ferrimagnetic phase. Obviously, more work is needed to justify the suggestion.

In summary, we have investigated the ferroelectricity and magnetism in $Fe_{1-x}Mn_xV_2O_4$ ($0 \leq x \leq 0.5$). For the first time, ferroelectric polarization is observed in the ferrimagnetic phase of spinel $Fe_{1-x}Mn_xV_2O_4$. Ferroelectric polarization decreases with increasing x, and disappears for $x \geq 0.5$. Magnetic field can enhance the polarization. Ferroelectric polarization includes two polar components arising from the exchange striction mechanism and the spin-current model.

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