

Effect of B-site Al-doping on electric polarization in DyMnO₃

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We investigate the effect of Al-doping on the multiferroicity of DyMn_{1-x}Al_xO₃. It is indicated that a slight doping ($0.005 \leq x \leq 0.01$) can significantly enhance the electric polarization which will be suppressed as $x > 0.03$. The possible mechanism for the polarization enhancement is the rearrangement of the Mn spiral spin order upon the Al-doping. Our work demonstrates that the ferroelectricity of DyMnO₃ is sensitive to the B-site nonmagnetic doping, allowing an unusual enhancement of the electric polarization. © 2010 American Institute of Physics.

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Multiferroics are a class of materials exhibiting both spin and ferroelectric (FE) orders in a certain temperature (T) range.^{1,2} The two orders and gigantic magnetoelectric coupling have been observed in certain rare-earth manganites RMnO₃ ($R = \text{Eu, Gd, Tb, and Dy}$).³⁻⁸ Generally, it is believed⁹⁻¹⁵ that the noncollinear Mn spiral spin order (SSO) is an essential ingredient for the onset of polarization (P) and the possible microscopic mechanism is the inverse Dzyaloshinski-Moriya interaction or spin current scenario.^{10,16,17} In fact, the long-range SSO is not very robust against intrinsic/external fluctuations. Therefore, a technical roadmap to manipulate the ferroelectricity by either intrinsic doping or external modulation becomes attractive.

Among these manganites, DyMnO₃ exhibits the largest $P \sim 0.2 \mu\text{C}/\text{cm}^2$.¹⁸ It has the distorted orthorhombic perovskite structure (space group $Pbnm$) at low temperature (T) and shows the SSO below $T_{\text{lock}} \sim 18 \text{ K}$.³ Moreover, the strongly anisotropic Dy spin affects the FE state, evidenced by the suppressed P at the Dy-spin order point $T_{\text{Dy}} \sim 7 \text{ K}$, leading to a peaked dependence of P on T . The Mn-induced Dy spin ordering also contributes to P , as long as the Dy spins are not ordered independently.^{18,19} The significant enhancement of P in the intermediate H -range at low T features the possible reoccurrence of the induced Dy spin order with the same propagation vector as the Mn spin order.²⁰ Here, very interesting is that DyMnO₃ lies closely to the edge boundary between the SSO region and the E-type antiferromagnetically ordered one, which allows us to argue that the spin structure and ferroelectricity may be sensitive to intrinsic/external fluctuations.

In this work, we demonstrate that very tiny nonmagnetic Al-doping can enhance the P of DyMnO₃, an unusual effect. This suggests that DyMnO₃ is indeed an edge system in terms of ferroelectricity manipulation. In our experiment, polycrystalline DyMn_{1-x}Al_xO₃ ($x \leq 0.1$) was prepared by conventional solid-state reaction. The highly purified powders of Dy-, Mn-, and Al-oxides were mixed in stoichiometric ratios, followed by ground and fired at 1200 °C for

24 h in air. The resultant powders were pelletized and then sintered at 1400 °C for 24 h in air with intermediate grindings. The x-ray diffraction (XRD) with Cu $K\alpha$ radiation on these samples was performed at room temperature to identify the crystallinity. For magnetic measurements, the T -dependence of magnetization (M) was obtained using the superconducting quantum interference device magnetometer (Quantum Design). The zero-field-cooled (ZFC) and field-cooled (FC) measurements were conducted under a field $H \sim 100 \text{ Oe}$. With the gold pastes deposited on the sample surfaces as electrodes, the dielectric constant ϵ and P were measured by the Physical Properties Measurement System (PPMS-7, Quantum Design). The P was obtained by integrating the pyroelectric current measured using the Keithley 6514A in the warming process without any electric bias, while the samples were poled under an electric field $E \sim 10 \text{ kV/cm}$ during the cooling process. The details of the measurement can be found in earlier report,²¹ noting that those contributions other than the pyroelectric current can be excluded safely.

Figure 1(a) presents the measured θ - 2θ XRD patterns for the samples with $x = 0$ to 0.1, indicating that they have the single-phase orthorhombic structure and no detectable impurity phase is available. In order to identify details of the structural distortion, we perform high-precision Rietveld refining of the XRD data. As an example, the refinement details are shown in Fig. 1(b) for $x = 0.5\%$. The difference between the measured spectrum and refined one is very small. The refinement reliability is ensured by the refinement parameter $R_{\text{wp}} = 10.56\%$, with lattice parameters $a = 5.27107 \text{ \AA}$, $b = 5.8149 \text{ \AA}$, and $c = 7.38260 \text{ \AA}$. For the other samples, the obtained R_{wp} is in the similar level. Furthermore, one can evaluate the Mn-O-Mn bond angle from the structure refinement data, and the evaluated x -dependences of the Mn-O₁-Mn bond angle and lattice volume are presented in Fig. 1(c). It is identified that both the angle and lattice unit volume decrease with increasing x . This fact is crucial for understanding the doping induced change in P , to be presented below.

We pay attention to the spin ordering sequence and polarization in response to variations in T and H . For $x = 0$, the measured M - T curves in the ZFC and FC cycles are

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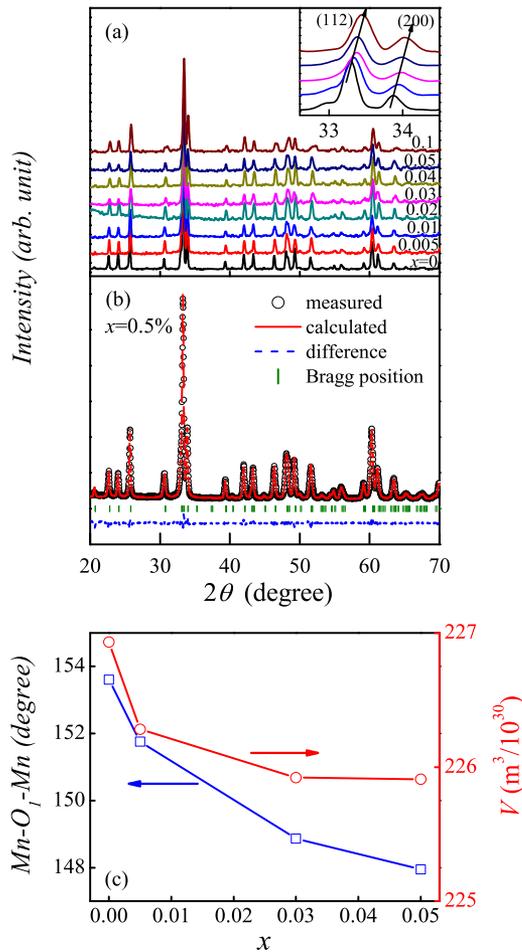


FIG. 1. (Color online) (a) Measured XRD θ - 2θ spectra for polycrystalline $\text{DyMn}_{1-x}\text{Al}_x\text{O}_3$ ($0 \leq x \leq 0.10$). (b) The Rietveld refinement for sample $x=0.5\%$. (c) Evaluated Mn-O₁-Mn bond angle and lattice volume V as a function of x .

presented in Fig. 2(a). The ZFC data exhibits a peak at $T \sim 7$ K, roughly corresponding to the Dy spin ordering point in competing with the Mn spin ordering, while no clear signature of the SSO sequence and incommensurate *lock-in* transition is observed, due to the subtle nature of the transition in polycrystalline samples. The M - T curves in the ZFC cycle for several samples are presented in Fig. 2(b). One

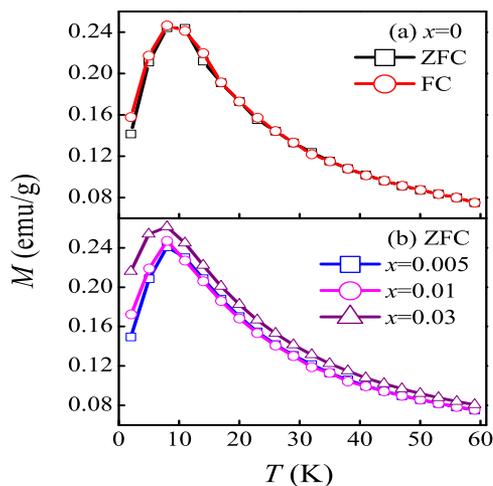


FIG. 2. (Color online) Measured M - T relations under (a) the ZFC and FC conditions for $x=0$ and (b) the ZFC condition for $x=0.005$, 0.01 and 0.03 . $H=100$ Oe.

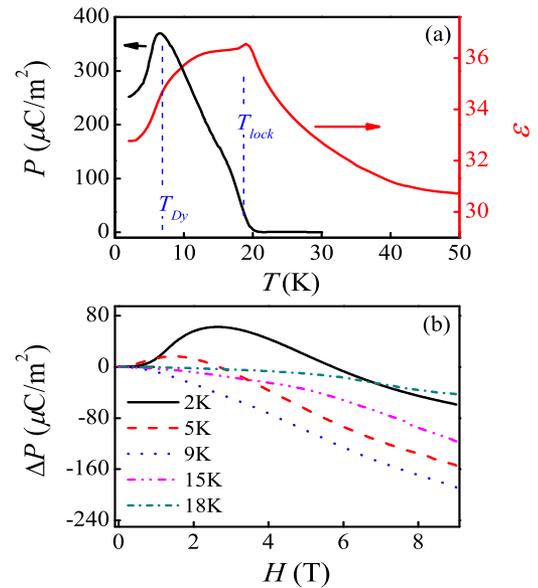


FIG. 3. (Color online) Measured ε - T and P - T relations at $H=0$ (a) and P - H relations at fixed T (b) for DyMnO_3 .

notes that the doping does not change the spin order substantially, evidenced with negligible change in the M - T curves in spite of small enhancement in M at $x=0.03$, probably attributed to the slightly suppressed antiferromagnetic Dy spin order. In general, all the samples have the similar M - T behaviors.²² Surely, these M - T data alone cannot reveal the possible subtle fluctuations of the spin configuration because of the relatively poor sensitivity.

We then show in Fig. 3(a) the measured P - T and ε - T curves at $H=0$ and in Fig. 3(b) the measured P - H curves at several fixed T for sample $x=0$ as a reference. Despite no expected anomalies in the M - T curves at $T \sim T_N$ and T_{lock} are observed, anomalies in the ε - T and P - T curves at $T \sim T_{\text{lock}}$ and T_{Dy} are identified, as revealed by earlier report.³ The anomaly at $T_{\text{lock}} \sim 18$ K features the development of noncollinear SSO with a T -independent wave vector, at which the polarization is generated and accompanied with a sharp peak in the ε - T curve. Upon further cooling down to $T_{\text{Dy}} \sim 7$ K, a second anomaly in the P - T curve associated with the long-range ordering of Dy^{3+} moments can be identified. In Fig. 3(b), the measured P is enhanced in the intermediate H -range and then suppressed when H is high enough at low T (2 and 5 K). In contrast, at $T=9$, 15, and 18 K, the observed P is suppressed by H . These observations confirm earlier hypothesis that for DyMnO_3 the P -enhancement by applying H at low T is mainly from the induced Dy spin ordering.¹⁸

Now, we look at the effect of Al-doping on $P(T)$ and $\varepsilon(T)$, as displayed in Figs. 4(a) and 4(b), with the inset presenting the evaluated $P(x)$ data at $T=2$ and 9 K. The slight Al-doping modulates P and ε significantly. P is enhanced in the low level by doubling the peaked value from $370 \mu\text{C}/\text{m}^2$ ($x=0$) up to $680 \mu\text{C}/\text{m}^2$ at $x \sim 0.005$. A remarkable suppression of P is identified as $x > 0.03$ and no identifiable polarization is measurable at $x > 0.05$. In addition, the independent Dy ordering (i.e., irrelevant with Mn-spin induced sequence) is melted gradually and eventually disappears at $x \sim 0.03$, because the dielectric peak at $T_{\text{lock}} \sim 18$ K observed for $x=0$ becomes broader and merged with increasing x , while the anomaly at T_{Dy} also disappears

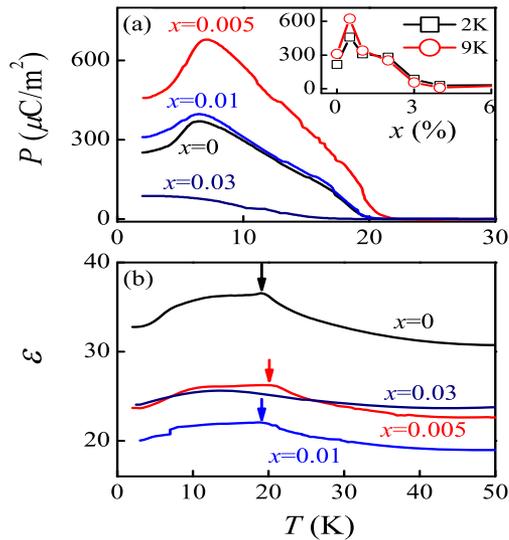


FIG. 4. (Color online) Measured T -dependences of P (a) and ϵ (b) under $H=0$ for $x=0, 0.005, 0.01,$ and 0.03 . The inset shows the P - x dependence at $T=2$ and 9 K.

at $x \sim 0.03$. It seems that a proper Al-doping can damage the Dy spin ordering and enhance the P .

At this stage, one can understand qualitatively the effect of Al-doping on P . Our XRD data already identified the lattice contraction and the reduction in the Mn–O–Mn bond angle with increasing x , as shown in Fig. 1(c). According to Arima *et al.*,²³ neutron scattering experiment on $\text{Tb}_{1-x}\text{Dy}_x\text{MnO}_3$ demonstrated that the slight decreasing of the lattice parameters induces bending of the Mn–O–Mn bond angle, favoring a canted spin arrangement. This effect will shorten the period of the Mn SSO, and thus enhance polarization P , given an appropriate doping level. The underlying mechanism is $P \sim e_{ij} \times (S_i \times S_j)$, with S_i and S_j the two neighboring spins and e_{ij} the spatial vector connecting them. From our refinement results, we believe that the Al doping also shortens the period of the Mn SSO because of the bended Mn–O–Mn bond angle and lattice contraction, thus enhances polarization P . A qualitative sketch of the original and rearranged Mn SSO upon the doping is shown in Fig. 5. However, this long range SSO plus the Mn-induced Dy spin order seems to be seriously disturbed when the doping exceeds $x=0.01$, ultimately leading to the decay of P . In addition, it is believed that the suppression of the independent Dy spin order is also beneficial to the P -enhancement. Our experiments show that the independent Dy order is not completely suppressed even at the optimized doping in terms of polarization P [Fig. 4(a)], in contrast to the effect of H .²⁰ Surely, further direct evidence by neutron scattering would allow more details of the spin structure in response to the Al-doping, such as why a low doping ($x > 0.01$) can break the long-range SSO in DyMnO_3 . Nevertheless, our experiments do show that DyMnO_3 is sensitive to the Al-doping, allowing a possibility for easy manipulation of the spin structure and polarization.

In conclusion, we have shown that a slight Al-doping at the B-site of DyMnO_3 can enhance significantly the electric polarization, characterized by the rearrangement of the Mn SSO upon the low level doping ($x \leq 0.01$). A doping over 0.03 will suppress the polarization, probably due to the breaking of the long range Mn SSO and the associated Dy

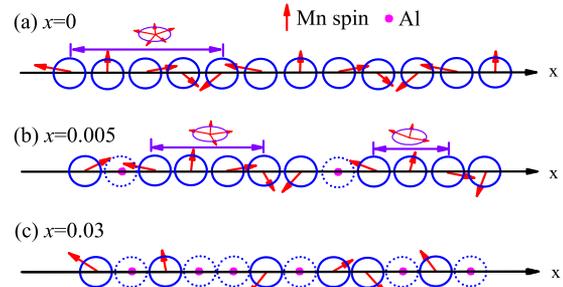


FIG. 5. (Color online) A qualitative sketch of the Mn SSO for $x=0$ (a), $x=0.005$ (b), and $x=0.03$ (c) below $T=18$ K. The open circle represents the contrast of the Mn spin, and the double head arrow indicates the period of the Mn SSO.

spin order. Our experiment reveals that DyMnO_3 is an edge multiferroic in terms of multiferroicity manipulation upon the intrinsic fluctuations.

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