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Polaron response dominated multiferroic property in 12R-type hexagonal Ba(Ti$_{1/3}$Mn$_{2/3}$)O$_3$-$\delta$ ceramics

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We report the multiferroic properties of 12R-type hexagonal Ba(Ti$_{1/3}$Mn$_{2/3}$)O$_3$-$\delta$ found in Mn-doped BaTiO$_3$ series samples. Hysteresis measurements reveal the coexistence of weak ferromagnetism and ferroelectricity at room temperature. Furthermore, frequency-driven dynamic ferroelectric phase transition is disclosed around a critical frequency of 220 Hz. Analyses on the dielectric relaxation, leakage current, crystal structure, and magnetic susceptibility lead us to conclude that the response of polarons dominates the observed physical properties, and the dynamic phase transition may ascribe to the response mode changes of the localized electrons. More importantly, we figure out the crucial factors leading to difference of the ferroelectric and magnetic properties of the 12R-type Ba(Ti$_{1/3}$Mn$_{2/3}$)O$_3$-$\delta$ samples from that of the 6H-type Ba(Ti$_{1-x}$M$_x$)O$_3$-$\delta$ (M = Fe, Mn) samples. © 2015 AIP Publishing LLC. [http://dx.doi.org/10.1063/1.4928180]

I. INTRODUCTION

High-temperature multiferroics and strong magnetoelectric effects are two key points in the research field of multiferroic materials. Concerning these two aspects, ferromagnetic/ferroelectric thin films and composites were found to possess excellent performances.$^{1,2}$ For example, in Co/PMN-PT layered film systems, the magnetic order was demonstrated to be manipulated by an electric field at room temperature.$^3$ Single-phase bulk multiferroics are generally confined by the following headaches, e.g., weak ferromagnetism in PbFe$_{1/2}$Nb$_{1/2}$O$_3$, weak coupling effects in BiFeO$_3$, low magnetic transition temperature in TbMnO$_3$, and large leakage current in LuFe$_2$O$_4$. However, single-phase thin films are found to have potential applications, recent exciting findings include Cu-doped ZnO with mutual ferromagnetic-ferroelectric manipulation,$^8$ multiferroic Ge$_{1-x}$Mn$_x$Te semiconductor with magnetic-field induced polarization reversal$^9$ and tuning of multiferroic orders by oxygen stoichiometry in Fe$_3$O$_4$ thin films.$^{10}$

Towards searching for high-temperature multiferroics, transition-metal doped ferroelectrics and paraelectrics have been widely investigated in recent years. For typical ferroelectrics,$^{11-13}$ 5 mol% Fe doping into perovskite BaTiO$_3$ introduces the high-temperature ferromagnetic order with $T_C$ = 680 K, which coexists with the ferroelectric order at room temperature.$^{12}$ In 50 mol% Mn-doped PbTiO$_3$, magnetic-field control of electric polarization was reported at ambient temperature.$^{13}$ For doped paraelectrics,$^{14-16}$ especially Fe-doped hexagonal BaTiO$_3$, oxygen-vacancy ordering induced cross-controlled magnetoelectric effects were observed at room temperature.$^{14}$ Moreover, the origin mechanism of high-temperature ferromagnetism was investigated with particular emphasis.$^{14,16-20}$ Nevertheless, in transition-metal doped SrTiO$_3$ and KTaO$_3$, it was clarified that there is no magnetoelectric coupling effect between spin and dipolar glass states.

Our previous study reported that the crystal structures of transition-metal doped BaTiO$_3$ are strongly dependent on the sample preparation conditions.$^{23}$ For Ba(Ti$_{1-x}$M$_x$)O$_3$ samples, the crystal structure evolves from tetragonal to 6H-type hexagonal structure with the increase in doping concentration. As the doping content further increases to $x > 0.50$, it is found that the 6H-type hexagonal phase transforms into a 12R-type hexagonal phase. In this paper, the dielectric, ferroelectric, and magnetic properties of 12R-type hexagonal Ba(Ti$_{1/3}$Mn$_{2/3}$)O$_3$-$\delta$ are investigated. In addition to the coexistence of weak ferromagnetism and ferroelectricity, frequency-driven dynamic ferroelectric phase transition is revealed at room temperature. From structure point of view, the crucial factors, leading to such weak ferroelectricity and ferromagnetism in the 12R type samples, are clarified with respect to that in the 6H-type transition-metal doped BaTiO$_3$.

II. EXPERIMENT

BaCO$_3$, TiO$_2$, and Mn$_3$O$_4$ powders were used to synthesize the 12R-type hexagonal Ba(Ti$_{1/3}$Mn$_{2/3}$)O$_3$-$\delta$ samples with solid-state reaction. After preliminary sintering at 1000°C in oxygen atmosphere for 20 h and 1300°C in air for 20 h, the sample was cut into two halves. The as-grown and post-annealed samples were sintered at 1300°C and 1100°C in air for 24 h, respectively. Thorough grinding and pelleting were performed before each sintering. The X-ray diffraction (XRD) data were collected on Philips X’Pert Pro powder diffractometer (Cu K$_{\alpha}$ $\lambda$ = 1.5406 Å) with a scan...
step of 0.02° and the profile was refined using FULLPROF software package. Temperature dependences of dielectric constant ($\varepsilon_r$) and loss tangent (tan\(\delta\)) were measured on a Hewlett-Packard 4192A gain phase analyzer. The ferroelectric hysteresis loops, switching current, and leakage current were measured on a TF 2000 FE analyzer at room temperature. Silver paste was painted on sample surface as electrode. DC magnetic measurements were performed on Quantum Design Physical Property Measurement System (PPMS). The susceptibility data was collected in the warming cycle both for the zero-field-cooled (ZFC) mode and the field-cooled (FC) mode.

III. RESULTS

A. Dielectric and ferroelectric properties

Figures 1(a) and 1(b) show the temperature dependences of dielectric constant and loss tangent of the as-grown 12R-type hexagonal Ba(Ti\(\frac{1}{3}\)Mn\(\frac{2}{3}\))O\(_3\)-sample. At temperatures above 300 K, we can clearly see dielectric dispersion, where the dielectric constant decreases and the loss tangent peaks shift to higher temperature with the increase in measurement frequency. When plotting the relationship between $f_r$ and temperature ($T$) extracted from the peaks of tan\(\delta\), see the inset in Fig. 1(b), we find that the linear relation can be best fitted by the Arrhenius relation

$$f_r = f_0 \exp(-E_a/k_BT),$$

wherein $k_B$ is the Boltzman constant. The relaxation frequency at an infinite temperature is $f_0 = 2.02 \times 10^9$ Hz (relaxation time $\tau_0 = 7.89 \times 10^{-11}$ s) and the activation energy for the relaxation is $E_a = 0.46$ eV. This order of magnitude suggests that the dielectric relaxation may possibly be attributed to excitation of electrons or polarons in the layered perovskite lattice.\(^{24}\)

Figure 2(a) presents the ferroelectric hysteresis loops for the as-grown sample measured at room temperature. It can clearly be seen that the maximum polarization, which is $\sim 140 \mu$C/m\(^2\) at $f = 10$ Hz, decreases greatly with the increase in measurement frequency. Meanwhile, the loop area reduces steeply as a function of frequency. This suggests a transition from a polar state at lower frequency to a nonpolar state at higher frequency. Although the characteristic switching current peaks in normal ferroelectrics\(^{25}\) cannot be well identified, a broadening of the switching current peak can still be seen in the $f = 10$ Hz curve, as illustrated in Fig. 2(b). This peak-broadening feature gradually disappears when the measurement frequency increases to $f = 1000$ Hz. In order to further explore the dynamic phase transition behavior, the polarization changes as a function of the applied electric field are monitored.

Figure 3(a) shows the remnant polarization ($P_r$) profiles as a function of the amplitude of the applied electric field ($E_0$), which are extracted from the ferroelectric loops measured at different frequencies. With the increase in $E_0$, the $P_r$ profiles measured at $f = 10$ Hz and 100 Hz exhibit nonlinear behaviors, which are found to be well fitted by the following formula:

$$P_r = c \ast (E_0)^n/\lg(f),$$

wherein the power exponent $n = 1/2$ and the coefficient $c$ is a constant with $c \approx 6.08$. The confidence level for the nonlinear fitting is 99.3% as $f = 10$ Hz and 98.6% as $f = 100$ Hz, respectively. However, as $f = 1000$ Hz, a linear fit with $n = 1$ gives the best fitting result, where $c = 0.009$ and the...
The observed in the post annealed, similar nonlinear to linear transition is also electric phase transition of our sample. When the sample is simultaneously, the power exponent $n$ scales the dynamic ferroelectric transition is probed. From Fig. 3(b), it can be seen that the loop area changes (traced by dashed lines) as a function of frequency measured under different $E_0$. The intersection points (dash-dot line) of the tangential directions (solid lines) extracted from traces of the low- and high-frequency regions are used to define the critical frequency for the dynamic phase transition.

The confidence level is 99.9%. Clearly, the $P_r$ vs $E_0$ behavior for $f = 1000$ Hz case deviates from the low frequency cases. Meanwhile, the power exponent $n$ scales the dynamic ferroelectric phase transition of our sample. When the sample is post annealed, similar nonlinear to linear transition is also observed in the $P_r$ vs $E_0$ profiles at the same measurement frequency. Therefore, our results demonstrate that frequency-driven dynamic ferroelectric-to-paraelectric phase transition takes place in the hexagonal Ba(Ti$_{1/3}$Mn$_{2/3}$)O$_3$-δ samples.

By plotting the loop area measured under different $E_0$ as a function of frequency, the critical frequency for the dynamic ferroelectric transition is probed. From Fig. 3(b), it can be seen that the loop area decays in an exponential way as a function of the measurement frequency, the dashed lines trace the changes. By extracting the tangential directions of the traces from the low- and high-frequency regions, the intersection points are regarded as the critical transition frequency. With increasing of $E_0$ from 39 V/cm to 194 V/cm, it was found that the critical frequency increases from $f_{cr} = 184$ Hz to 251 Hz. Therefore, the critical transition frequency essentially locates around $f_{cr} = 220$ Hz.

**B. dc conductivity and magnetic property**

In order to better understand the dielectric and ferroelectric properties, the dc conductivity was measured at room temperature. Figure 4 displays the leakage current as a function of the applied electric field. Within our measurement range, the leakage current changes by more than two orders of magnitude. The symmetric log $I$ vs $E$ profile illustrated in the inset of Fig. 4 rules out the interface-limited conduction. By fitting the linear log $I$ vs log $E$ profile, it is found that the slope of the relation is $\alpha = 1.17$, which reveals that the conduction in the Ba(Ti$_{1/3}$Mn$_{2/3}$)O$_3$-δ sample follows the trap-filled limit model. Considering the substitution of Ti$^{4+}$ ions by acceptor Mn$^{3+}$ ions and the accompanied oxygen vacancies, some impurity states created either below or above the Fermi level act as trap levels to capture excited electrons. For comparison, the leakage current in the annealed sample was also measured. As illustrated in Fig. 4, we find that the post-annealing treatment does not change the dc conductivity behavior in the Ba(Ti$_{1/3}$Mn$_{2/3}$)O$_3$-δ sample.

Considering the multiple valence states of Mn ions and their sensitivity to thermal treatment, the concentration determination for the Mn$^{3+}$ and Mn$^{4+}$ ions will be crucial for our understanding on the observed physical properties. Figure 5(a) shows the ZFC and FC magnetization curves of the as-grown Ba(Ti$_{1/3}$Mn$_{2/3}$)O$_3$-δ sample as a function of temperature. It is seen that magnetic anomaly takes place at $T_N = 44$ K, below which the convergent ZFC and FC curves separate into two branches at 35 K. When the sample is post annealed, the magnetism in the whole temperature range is enhanced with respect to the as-grown sample. It should be noted that the low-temperature magnetic transitions are probably not the intrinsic response of our Ba(Ti$_{1/3}$Mn$_{2/3}$)O$_3$-δ samples. On one hand, such magnetic anomaly was not found by Keith et al. in 12R-type Ba(Ti$_{1/3}$Mn$_{2/3}$)O$_3$ samples. On the other hand, the impurities, such as Mn$_2$O$_4$ impurity with $T_N = 43$ K (Ref. 28) and 4H-type BaMn$_2$O$_4$ with $T_C \approx 50$ K (Ref. 29), may account for the magnetic transitions observed in our samples. Due to the weak magnetism response of the hexagonal Ba(Ti$_{1/3}$Mn$_{2/3}$)O$_3$-δ sample, even tiny amounts of such impurities, which are indistinguishable by X-ray diffraction, can dominate the low-temperature magnetic response. However, since these impurities are paramagnetic above their transition temperatures, the weak magnetic hysteresis shown in the inset of Fig. 5(a) verifies that the Ba(Ti$_{1/3}$Mn$_{2/3}$)O$_3$-δ sample is intrinsically weak ferromagnetic at room temperature. This is consistent with the previous report on 12R-type...
hexagonal Ba(Ti$_{1/2}$Mn$_{1/2}$)O$_3$ ceramics.\textsuperscript{30} By fitting the linear parts of the magnetization curve in the hysteresis, from ±12.5 to ±40 kOe, respectively, the difference of magnetization $\Delta M = 8.5 \times 10^{-3} \text{emu/g}$ at $H = 0$ kOe (measurement error $\sim 5 \times 10^{-3} \text{emu/g}$) between the linear fittings evidences the non-paramagnetic behavior of our sample at room temperature.

Considering the very weak ferromagnetism, Curie-Weiss fit, $\chi = C/(T + \theta_p)$, to the magnetic susceptibility is performed to detect the concentration ratio of Mn ions with different valence states. As Fig. 5(b) shows, our fit ranging from 100 K to 300 K yields that the paramagnetic Curie temperature is $\theta_p = 280.6$ K and 388.09 K, and the effective paramagnetic moments are $\mu_{\text{eff}} = 3.69 \mu_B$ and 3.77 $\mu_B$ for the as-grown and post-annealed sample, respectively. Assuming the orbital moments are quenched, the spin moments are the effective moments for each element, i.e., $J = S$, $\mu_{\text{Mn}^{3+}} = 4.9 \mu_B$, $\mu_{\text{Mn}^{4+}} = 3.8 \mu_B$, and $\mu_{\text{Ti}^{3+}} = 1.8 \mu_B$ at high-spin state. Therefore, the concentration of Mn$^{3+}$, Mn$^{4+}$, and possible Ti$^{3+}$ ions can be calculated using the following equation:

$$\mu_{\text{eff}} = \sqrt{\mu_{\text{Mn}^{3+}}^2 + \mu_{\text{Mn}^{4+}}^2 + \mu_{\text{Ti}^{3+}}^2},$$ \hspace{1cm} (3)

with $x + y = 2/3$ due to the nominal composition ratio. By assuming all Mn ions are either trivalent or tetravalent state, the proper solutions to Eq. (3) can only be found as the Mn ions adopt high-spin arrangements. Supposing the concentration of Ti$^{3+}$ is zero ($z = 0$), the concentration of Mn$^{3+}$, Mn$^{4+}$ ions, and the content of oxygen vacancies in the as-grown sample are 62.1%, 37.9%, and $\delta = 0.207$, i.e., Ba(Ti$_{1/3}$Mn$_{2/3}$)O$_{2.793}$. For the post-annealed sample, the concentration of Mn$^{3+}$ ions increases to 72.3%, and that of Mn$^{4+}$ ions decreases to 27.7%. The corresponding oxygen vacancy content in the post-annealed sample is $\delta = 0.241$, i.e., Ba(Ti$_{1/3}$Mn$_{2/3}$)O$_{2.759}$.

IV. DISCUSSION

When reviewing the 12R-type Ba(Ti$_{1/3}$Mn$_{2/3}$)O$_{3-\delta}$ and the 6H-type Ba(Ti$_{1/3}$Mn$_{2/3}$)O$_{3-\delta}$ (M = Fe, Mn) samples,\textsuperscript{14–16} it is easy to find that both types of structures possess similar physical properties, from dielectric, ferroelectric to magnetic properties. However, both the ferroelectricity and the ferromagnetism in the 12R structure are weaker than that in the 6H structure.\textsuperscript{15,16} By means of structure investigation, we find out the important reasons for the differences.

In crystal structure, both the 6H- and 12R-type hexagonal structures are built up of the basic 3C and 2H structures, see Figs. 6(a) and 6(b),\textsuperscript{31} however, the stacking sequence of the closed-packed Ba$_3$O$_6$ layers is different. In the 6H structure, the (cch)$_2$ stacking sequence results in the face-sharing M$_2$O$_9$ dimers corner-connected by the isolated M$_1$O$_3$ octahedron, Fig. 6(c). While in the 12R structure, the (hhc)$_3$ stacking sequence leads to the face-sharing M$_2$O$_{12}$ trimers, which are corner-connected by the isolated M$_1$O$_3$ units, Fig. 6(d). To further distinguish their structural differences, as well as their decisive roles in explaining their physical properties, XRD refinements were performed.

As a representative, the refined XRD profile of the as-grown 12R-Ba(Ti$_{1/3}$Mn$_{2/3}$)O$_{3-\delta}$ sample using space group $R3m$ (Ref. 27) is presented in Fig. 7(a), the refined profile for the 6H-Ba(Ti$_{8/9}$Mn$_{1/9}$)O$_{2.79}$ sample using space group $P6_3/mmc$ is shown in Fig. 7(b). In our refinements, the transition metals are

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure6.png}
\caption{Perovskite crystal structure of (a) 3C-type viewed along [110] direction, (b) 2H-type, (c) 6H-type, and (d) 12R-type viewed along [100] direction, respectively. The Ba ions are omitted for clarity. The unit equivalent B-site and O-site atomic sites are indicated by different colors. The rectangles (dashed lines) outline their unit cells.}
\end{figure}
found to randomly distribute at the un-equivalent M-sites in the 12R and the 6H structures, and the important results are summarized in Table I. In the 12R structure, oxygen vacancies prefer to appear at O(2) site, the corner atoms linking the trimers with the isolated octahedron. The vacancy content qualitatively agrees with our results of magnetism analysis. However, in the 6H structure, oxygen vacancies prefer to appear at O(1) site,14,15 which transforms the face-sharing octahedra to edge-sharing pentahedra; the presence of O(2)-site vacancies is mainly attributed to connection of the octahedral units at the translational boundaries.32 When noting the M-O bond lengths, the difference of the shortest M(1)-O(1) bonds with the longest M(2)-O(2) bonds is ~12 pm in the 12R structure; while in the 6H structure, the difference is 8.52 pm in Ba(Ti_{1/3}Fe_{1/3})O_3·0.5 and 4.45 pm in the Ba(Ti_{8/9}Mn_{1/9})O_3·0.5. Clearly, such vacancy distribution and bond length variation reveal that long-range magnetic ordering is more favorably formed in the 6H structure rather than the 12R structure. Meanwhile, the presence of fractional Ti^{4+} ions, due to the low-spin arrangement of electrons, is also beneficial for the electron exchange interaction in the 6H structure. While the absence of Ti^{4+} ions, due to the high-spin arrangement of electrons, undoubtedly further decreases the probability of electron exchange in the 12R structure.

Constrained by the centrosymmetric space group structure, the oxygen vacancies can only break symmetry of some sub-structure units, e.g., the oxygen octahedra, which form the polarons together with the localized electrons. Therefore, on one hand, the ferroelectricity is contributed by such octahedral units with different oxygen coordinations. In the 6H structure, such distortion resides in M(2)-centered octahedra, and the bond-length difference between M(2)-O(1) and M(2)-O(2) is up to 8.52 pm in Fe-doped (x = 1/3) sample, which is 3.09 pm in Mn-doped (x = 1/9) sample. In the 12R structure, the bond length difference in the M(2)-centered octahedra is merely 0.26 pm. On the other hand, separation of the positive and the negative charge centers in the BaO_3 layers also contributes to the ferroelectricity owing to the random distribution of oxygen vacancies. In the 12R structure, the average separation in the as-grown sample is 15.5 pm, which increases to 17.7 pm after post annealing treatment. The difference of the separation is manifested in the polarization values, e.g., as the E_a ≈ 200 V/cm and f = 100 Hz, F_{Pmax} = 64 μC/m^2 in the as-grown sample, which increases to 77 μC/m^2 in the post-annealed sample. While in the 6H structure, the average separation is 10.5 pm or even smaller, see Table I. Thus, the ferroelectricity in the 6H structure is mainly attributed to the distorted octahedral units, e.g., the edge-sharing pentahedra, while in the 12R structure, the ferroelectric response mainly arises from the charge-center separation in the close-packed BaO_3 layers. In strongly disordered systems with localized charge-carrier states, a general form for d-dimensional conduction is expressed by ln(ρ) ∝ T^{−1/(d+1)};33 Similarly, the transition of the scaling power exponent n probably indicates the response mode changes of the localized electrons, i.e., either hopping among the nearest polarons (for n = 1/2) or complete binding by the distorted octahedra (for n = 1) due to the relaxation.

In the frequency range of 10^7 Hz ~ 10^6 Hz around room temperature, the activation energy for electron hopping is 0.338 eV for BiFeO_3 and 0.38 eV for Sr(Fe_{1/2}Nb_{1/2})O_3,34,35 which is much smaller in charge-ordered LuFe_2O_4, E_a = 0.29 eV.36 The activation energy of ~0.46 eV in our samples is very close to that in those materials. The slightly higher E_a in our samples may ascribe to the bigger bond length variations and the Ti^{4+} ions, which enhances the energy barrier for electron hopping. Thus, the dielectric

![FIG. 7. X-ray diffraction pattern (a) the as-grown 12R-type hexagonal Ba(Ti_{1/3}Mn_{1/3})O_3·0.5 and (b) post-annealed 6H-type hexagonal Ba(Ti_{8/9}Mn_{1/9})O_3·0.5.

| TABLE I. Structure parameter comparison between 12R-type and 6H-type Ba(Ti_{1-x}M_x)O_3·(M = Mn, Fe) samples refined by X-ray diffraction. AG and PA are short for “as-grown” and “post-annealed,” respectively. The occupation ratio of oxygen atoms in the 6H-type samples is cited from results of microstructure study.32 |
|----------------|----------------|----------------|
| Parameters     | 12R-type      | 6H-type        |
|                | Mn_{2/3}-AG   | Mn_{2/3}-PA    | Fe_{1/3}-PA | Mn_{1/3}-PA |
| α (Å)          | 5.68173       | 5.68023        | 5.714334    | 5.71213     |
| c (Å)          | 27.86502      | 27.85928       | 14.032117   | 13.94727    |
| O_{12R}/O_{vac} | 1.00000.996  | 1.00000.944    | 0.8890.891  | 0.9430.966  |
| M(1)-O(1)      | 1.8663 (×6)   | 1.8417 (×6)    | —           | —           |
| M(1)-O(2)      | —             | —              | 1.9916 (×6) | 1.9904 (×6) |
| M(2)-O(1)      | 1.9258 (×3)   | 1.9163 (×3)    | 2.0224 (×3) | 1.9768 (×3) |
| M(2)-O(2)      | 1.9515 (×3)   | 1.9422 (×3)    | 1.9372 (×3) | 1.9459 (×3) |
| M(3)-O(2)      | 1.9850 (×6)   | 1.9623 (×6)    | —           | —           |
| Δ_Ba(1)-O(2)   | —             | —              | 0.00        | 0.00        |
| Δ_Ba(2)-O(2)   | 19.44         | 22.37          | —           | —           |
| Δ_Ba(2)-O(2)   | 11.57         | 12.94          | 16.12       | 21.01       |
| R_p, R_s, %    | 12.3, 15.8    | 13.8, 12.5     | 14.4, 11.9  | 12.9, 12.5  |
| χ^2            | 1.62          | 1.82           | 1.22        | 1.39        |
relaxation in our Ba(Ti$_{1/3}$Mn$_{2/3}$)O$_3$ samples can be attributed to the electron hopping among the polaron. In addition, the grain boundary effect for the relaxation can essentially be ruled out. In CaCu$_3$Ti$_4$O$_{12}$, the activation energy for grain boundaries ranges from 0.60 eV to 0.76 eV,\textsuperscript{17,38} which locates in the range of 0.69 eV–0.77 eV for multiferroic BiFeO$_3$.\textsuperscript{34} When dielectric relaxation is dominated by oxygen vacancies, the activation energy is as high as 1.26 eV in Sr(Fe$_{1/2}$Nb$_{1/2}$)O$_3$ ceramics\textsuperscript{35} and 0.83 eV in Ba(Fe$_{1/2}$Nb$_{1/2}$)O$_3$ ceramics,\textsuperscript{39} and the response is well above room temperature.

V. CONCLUSIONS

In conclusion, we investigate the structure, electrical, and magnetic properties of 12R-type hexagonal Ba(Ti$_{1/3}$Mn$_{2/3}$)O$_3$ samples. Our results reveal that coexistence of the weak ferroelectricity and ferromagnetism at room temperature is mainly attributed to the response of polaron. Furthermore, owing to the response mode changes of the localized electrons, frequency-driven dynamic ferroelectric phase transition is observed around $f_c = 220$ Hz in the layered perovskite oxides. By comparing the structural details, we find out the fundamental reasons leading to difference of the physical properties between the 6H-type and 12R-type Ba(Ti$_{1/3}$Mn$_{2/3}$)O$_3$ samples. It is believed that our findings are significant in guiding the researchers towards searching for high-temperature multiferroics and exploring novel ferroelectrics based on the conventional ones.

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