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Peng Liu
*University of Wollongong, pl990@uowmail.edu.au*

Xiaolin Wang
*University of Wollongong, xiaolin@uow.edu.au*

Zhenxiang Cheng
*University of Wollongong, cheng@uow.edu.au*

Yi Du
*University of Wollongong, ydu@uow.edu.au*

Hideo Kimura
*National Institute For Materials Science*

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Peng Liu, Xiaolin Wang, Zhen-Xiang Cheng, Yi Du, and Hideo Kimura

Institute for Superconducting and Electronic Materials, Faculty of Engineering, University of Wollongong, South Wales 2500, Australia

Crystal Science and Technology Group, National Institute for Materials Science, 1-2-1 Sengen, Tsukuba, Ibaraki 305-0047, Japan

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The Er doping effects on the structural, dielectric, ferroelectric, magnetic, and thermal properties of the hexagonal Ho$_{1-x}$Er$_x$MnO$_3$ (0 $\leq$ x $\leq$ 1) compounds synthesized by the solid-state reaction method have been investigated by Rietveld refinement and by measurements of dielectric constant, ferroelectric hysteresis loops, magnetic susceptibility, and specific heat. The a lattice parameter decreases as the Er content increases, whereas the c lattice parameter nearly keeps constant with pretty minor fluctuations. Dielectric data and ferroelectric hysteresis loops show all the samples are not only ferroelectric materials with leaky nature, but also with dielectric relaxation related to oxygen vacancies. The magnetizations of these compounds gradually decrease with increasing Er content. The Mn$^{3+}$ ions in each sample remain stable in the high-spin state in the Mn-O$_5$ trigonal bipyramidal crystal field. Specific heat measurements show that the antiferromagnetic transition temperature continuously rises from 72 K for HoMnO$_3$ to 76 K for ErMnO$_3$. The Debye temperatures are 381 K for ErMnO$_3$ and 422 K for HoMnO$_3$.

I. INTRODUCTION

Rare-earth manganites, RMnO$_3$, possess two phases according to the ionic radii of the rare-earth elements.  The compounds with small atoms ($R$ = Ho to Lu, Y, and Sc) crystallize in the hexagonal structure, while the others with large-R atoms ($R$ = La to Dy) crystallize in the orthorhombic phase. Since ferroelectricity can only be observed in the hexagonal manganites with the noncentrosymmetric p6cm space group, these compounds have attracted great interest due to the coupling between ferroelectric and antiferromagnetic orderings. The strong coupling allows magnetization and electrical polarization to be mutually controlled in an external electrical field and an external magnetic field, respectively. The novel property makes such multiferroic compounds promising in potential applications, such as spintronics devices, multistate memory storage, transducers, actuators, and magnetoelectric sensors.

The hexagonal RMnO$_3$ compounds show ferroelectric transitions ($T_C$) at high temperatures in the range of 590–1000 K and antiferromagnetic transitions ($T_N$) at low temperatures from 70 to 130 K. Their crystal structures are constructed alternatively from two layers along the c axis. One layer consists of the corner-sharing Mn-O$_5$ trigonal bipyramids, where Mn$^{3+}$ ions are encompassed by three in-plane oxygen ions and two apical oxygen ions. The other layer comprises eightfold coordinated rare-earth ions with two symmetric sites. The hexagonal RMnO$_3$ compounds are characterized by the frustrated triangular magnetic structure of the Mn$^{3+}$ moments in the ab plane, with neighboring Mn spins rotated by 120$^\circ$. Mn$^{3+}$ ions are antiferromagnetically coupled below $T_N$ by Mn-O-Mn superexchange interactions through in-plane oxygen ions. The ferroelectric ordering along the c axis is attributed to two kinds of anti-parallel electric dipoles produced by the R-O displacements.

The hexagonal HoMnO$_3$ and ErMnO$_3$ individually have similar antiferromagnetic transitions at 72 and 76 K. However, their ferroelectric transition temperatures have a large difference, 875 K for HoMnO$_3$ and 525 K for ErMnO$_3$. The coupling between antiferromagnetic and ferroelectric orderings has been proved by magnetic field dependence of ferroelectric polarization below antiferromagnetic transition temperature. In addition, HoMnO$_3$ exhibits spin reorientation of Mn$^{3+}$ ions at 33 K and antiferromagnetic ordering of Ho$^{3+}$ ions below around 5 K. However, there is only one magnetic transition below 5 K in ErMnO$_3$ due to the ferrimagnetic ordering of Er$^{3+}$ spins. Despite the crystal structures of HoMnO$_3$ and ErMnO$_3$ are quite similar, the mutual doping in Ho$_{1-x}$Er$_x$MnO$_3$ provides a chance to investigate additional contributions to the doping effects. Especially, large differences in ferroelectric transitions make it significant to investigate how the ferroelectric and dielectric properties are modified through mutual doping between HoMnO$_3$ and ErMnO$_3$. Zhou et al. reported the magnetic phase diagram of the Ho$_{1-x}$Er$_x$MnO$_3$ system with a maximum doping level of $x$ = 0.4 by studying the specific heat and the dielectric constant at low temperatures. The aim of this work is to investigate how the mutual doping affects crystal structures, antiferromagnetic states, as well as the thermal and ferroelectric properties of the Ho$_{1-x}$Er$_x$MnO$_3$ system. The investigated doping levels of this system have been extended up to $x$ = 1. Moreover, the high temperature dielectric properties have been particularly examined. It is found that all the samples are ferroelectric materials that possess a dielectric relaxation process caused by oxygen vacancies.

II. EXPERIMENT

Polycrystalline samples of Ho$_{1-x}$Er$_x$MnO$_3$ (0 $\leq$ x $\leq$ 1) were synthesized by the conventional solid-state reaction method, using Ho$_2$O$_3$, Er$_2$O$_3$, and MnCO$_3$ with purity of 99.9% as starting materials. Stoichiometric mixtures of these compounds were ground thoroughly, hydrostatically pressed into a pellet, and annealed in air at 1000 °C for 16 h. After

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a second grinding, the resulting powder was compressed into a pellet again. The final sintering was carried out in air at 1200 °C for 24 h. The X-ray diffraction (XRD) patterns of all samples were obtained by a GBC-MMA diffractometer using Cu Kα radiation (λ = 1.54059 Å). Rietveld refinement of the XRD data was carried out using the Rietica program. The magnetic properties were examined on a physical properties measurement system (PPMS, Quantum Design), using a vibrating sample magnetometer. Magnetic susceptibility data were collected between 5 and 300 K at a magnetic field of 1000 Oe under both zero-field-cooled (ZFC) and field-cooled (FC) process. The specific heat capacity was obtained without magnetic fields by using the specific heat option in PPMS. The dielectric properties of pellets that were coated with gold as electrodes were measured from 350 to 800 K within the frequency range from 10 to 100 kHz by utilizing an HP 4284A LCR meter. Ferroelectric hysteresis loops were measured at room temperature with the frequency of 1 kHz using an aixACCT TF 2000 ferroelectric tester.

III. RESULTS AND DISCUSSION

The samples with the composition of \( x = 0.0-0.4 \) and \( 0.7-1 \) are all in single phase. As can be seen in Fig. 1, each XRD reflection peak can be indexed according to the hexagonal structure with the \( P6_3c/m \) space group, in agreement with previous reports.\(^{15,16} \) The diffraction peaks are quite distinct and shift to higher angles with increasing Er doping levels. The XRD peak splitting of the Ho\(_1-x\)Er\(_x\)MnO\(_3\) samples with \( x = 0.5 \) and 0.6 at 51.5° and 61.5° indicates the coexistence of ErMnO\(_3\) and HoMnO\(_3\) phases, which is also confirmed later by two transition peaks at 72 and 76 K in the specific heat data. Zhou et al.\(^{14} \) investigated the magnetic phase diagram of single-crystalline Ho\(_{1-x}\)Er\(_x\)MnO\(_3\) samples with a maximum doping level of only \( x = 0.4 \), greatly supporting our observations that the mixed-phase samples with \( x = 0.5 \) and 0.6 show distinctive chemical phase separation. The chemical immiscibility is likely despite of the small differences in the sizes between Ho\(^{3+}\) and Er\(^{3+}\) ions. The Rietveld refinement method was used to refine the XRD patterns of all single-phase compounds. The goodness of fit of Ho\(_{0.3}\)Er\(_{0.7}\)MnO\(_3\) is shown as a typical example in Fig. 2, illustrating that the calculated XRD pattern well matches the observed pattern. A summary of refinement results, including lattice parameters, atomic positions, and agreement factors, is given in Table I. The agreement factors of all the samples are no larger than \( R_p = 10\% \) and \( R_{wp} = 12.9\% \). Both calculated lattice parameters and structural data are in good line with another reported work.\(^{17} \)

Figure 3(a) presents the Er doping variations of the lattice parameters \( a \) and \( c \) of the single-phase Ho\(_{1-x}\)Er\(_x\)MnO\(_3\) compounds. The \( a \) lattice parameter decreases as the Er content increases, whereas the \( c \) lattice parameter, ranging from 11.39 to 11.42 Å, nearly keeps constant with pretty minor fluctuations. The decreases in the \( a \) lattice parameter is ascribed to the small ionic radius of Er\(^{3+}\) ions (103 pm) compared with that of Ho\(^{3+}\) ions (104.1 pm). The evolutions of \( ab\)-plane Mn-O3 and Mn-O4 bond lengths with the Er content are shown in Fig. 3(b). The Mn-O3 bond lengths show a general increasing trend from 1.96 Å for \( x = 0 \) to 2.22 Å for \( x = 1 \) with certain fluctuations. In contrast, the Mn-O4 bond lengths show a fluctuant decrease over a smaller range from 2.11 Å for \( x = 0 \) to 2.02 Å for \( x = 1 \). The Mn-O1 and Mn-O2 bond lengths along the \( c \) axis exhibit minor changes with doping, which are not shown here. In order to better understand variations of the crystal structure, the schematic illustrations of the crystal structure of RMnO\(_3\) and Mn-O\(_3\) trigonal bipyramids along the \( ab\) plane are shown in the inset of Fig. 2. In general, the Er doping does not notably affect the structure of the Mn-O\(_3\) polyhedron, in agreement with the weak changes of the trigonal bipyramidal crystal field, which is proved by the fact that the Mn\(^{3+}\) ions (3d\(^{6}\)) remain in the high-spin state (\( S = 2 \)) throughout the whole doping range.

FIG. 1. The room temperature XRD patterns of Ho\(_{1-x}\)Er\(_x\)MnO\(_3\) (\( x = 0, 0.2, 0.4, 0.6, 0.8, 1 \)) as representative samples.

FIG. 2. (Color online) Rietveld refinement results on the XRD pattern of the Ho\(_{0.3}\)Er\(_{0.7}\)MnO\(_3\) sample. The cross marks and red line are the experimental pattern and the calculated pattern, respectively. The blue vertical marks are the peak positions of Bragg diffraction. The green line at the bottom is the difference between the experimental pattern and the calculated pattern. \( R_p = 8.07\% \) and \( R_{wp} = 10.26\% \). Insets: schematic illustrations of the crystal structure (right) and the three-dimensional Mn-O\(_3\) trigonal bipyramids (left) of RMnO\(_3\) along the \( ab\) plane. Blue balls and red polyhedra represent the rare-earth atoms and Mn-O\(_3\) trigonal bipyramids, respectively.
Figure 4 shows the temperature dependence of the relative dielectric constant of Ho$_{1-x}$Er$_x$MnO$_3$ (x = 0, 0.1, 0.2, 0.4, 0.7, 0.8, 0.9, 1) at different frequencies of 40, 71, and 100 kHz. No previous data about high-temperature dielectric constant of the Ho$_{1-x}$Er$_x$MnO$_3$ system were ever reported except for ErMnO$_3$ measured at a fixed frequency, to which the dielectric constant value of our ErMnO$_3$ sample is comparable. In the $\varepsilon$-$T$ curve of HoMnO$_3$, the dielectric constant is independent of frequency and temperature, with a value of about 60 below 400 K. Once the temperature exceeds 400 K, the dielectric constants go up dramatically with strong dispersions, which are followed by a plateau with $\varepsilon \approx 310$ from 620 to 700 K. The drop-off temperature ($T_m$), where the dielectric constant on the plateau begins to reduce with decreasing temperatures, shifts towards higher temperatures as frequencies increase, indicating dielectric relaxation behavior in this compound. Above 750 K, the dielectric constants display a second sharp increase at higher temperatures. This is caused by enhanced current leakage, since grain boundaries have large conductivity and oxygen loss at high temperatures. Thus, large oxygen loss is responsible for the absence of high-temperature ferroelectric transitions in the temperature dependence of the dielectric constants, which occur in all as-prepared samples. ErMnO$_3$ shows similar relaxation behavior below 550 K. The plateau, with $\varepsilon \approx 270$, is extended over a temperature range from 550 to 700 K. The increase in the dielectric constants above 750 K is not so sharp as in HoMnO$_3$, indicative of different oxygen diffusion behavior at high temperatures. Regarding the other doped samples, strong relaxation behavior is also observed below $T = 480$ K. Thus, all single-phase Ho$_{1-x}$Er$_x$MnO$_3$ compounds possess a dielectric relaxation process. However, the temperature dependent dielectric constants of the doped samples have two differences from those of the two undoped samples. Firstly, the dielectric constant values of doped samples have two differences from those of the two undoped samples, except with $x = 0.4$, are much smaller than those of the HoMnO$_3$ and ErMnO$_3$ samples. Moreover, broad peaks appear instead of steplike decreases over a wide temperature range from 350 to 650 K. The dielectric relaxation processes mentioned above are also confirmed by corresponding frequency-dependent dielectric steps or
FIG. 3. (a) Evolutions of lattice parameters $a$ and $c$ of Ho$_{1-x}$Er$_x$MnO$_3$ ($x = 0, 0.1, 0.2, 0.4, 0.7, 0.8, 0.9, 1$) compounds with Er concentration. (b) The Er doping variations of the Mn-O3 and Mn-O4 bond lengths.

FIG. 4. (Color online) The temperature dependence of dielectric constant of Ho$_{1-x}$Er$_x$MnO$_3$ ($x = 0, 0.1, 0.2, 0.4, 0.7, 0.8, 0.9, 1$) at different frequencies.

broad peaks in the temperature dependence of the imaginary part of dielectric constant, which are shown in Fig. 5 with Ho$_{1-x}$Er$_x$MnO$_3$ ($x = 0, 0.4, 0.7, 1$) as representative samples. The variations of drop-off temperatures ($T_m$) with frequencies are fitted with Arrhenius law $f = f_0 \exp(-E_0/K_BT_m)$, where $E_0$ is activation energy, $K_B$ is the Boltzman parameter, and $f_0$ is the characteristic relaxation frequency at infinite temperature. As can be seen in the insets of Fig. 5, measured frequencies well obey the Arrhenius law with fitting parameters $f_0 = 2.91 \times 10^{15}$ Hz and $E_0 = 1.27$ eV for HoMnO$_3$, $f_0 = 6.20 \times 10^{14}$ Hz and $E_0 = 0.65$ eV for Ho$_{0.8}$Er$_{0.2}$MnO$_3$, $f_0 = 9.60 \times 10^{13}$ Hz and $E_0 = 0.62$ eV for Ho$_{0.3}$Er$_{0.7}$MnO$_3$, and $f_0 = 1.60 \times 10^{11}$ Hz and $E_0 = 0.64$ eV for ErMnO$_3$. These activation energy are reasonable compared with 0.98 eV for Bi$_{0.8}$Ba$_{0.2}$Fe$_{0.8}$Mn$_{0.2}$O$_3$,18 0.59 eV for BaTiO$_3$,19 They are close to typical 1 eV of the oxygen vacancies mobility activation energy, suggesting the observed dielectric relaxation of the Ho$_{1-x}$Er$_x$MnO$_3$ system is induced by oxygen vacancies.

Ferroelectric hysteresis loops of Ho$_{1-x}$Er$_x$MnO$_3$ ($x = 0, 0.2, 0.7, 1$) compounds collected at the frequency of 1 kHz at room temperature are shown in Fig. 6. We did not observe saturation in these loops due to the leaky nature of ceramic samples. HoMnO$_3$ and ErMnO$_3$ are much leakier compared with Ho$_{0.8}$Er$_{0.2}$MnO$_3$ and Ho$_{0.3}$Er$_{0.7}$MnO$_3$. The remnant polarizations for Ho$_{1-x}$Er$_x$MnO$_3$ ($x = 0, 0.2, 0.7, 1$) compounds are 0.01, 0.004, 0.01, and 0.05 $\mu$C/cm$^2$, respectively, and the corresponding coercive fields are 7.10, 3.97, 6.45, and 8.45 kV/cm in sequence. The ferroelectric polarization values of as-prepared samples are small in contrast with thin films and those synthesized by pyrophoric reaction process.9,20 Even though the hysteresis loops are small, they are still significant enough to definitely confirm the ferroelectricity of the Ho$_{1-x}$Er$_x$MnO$_3$ compounds.

Figure 7 presents the FC (field-cooled) $\chi$-$T$ curves of Ho$_{1-x}$Er$_x$MnO$_3$ ($x = 0, 0.2, 0.4, 0.8, 1$) under a magnetic field of 1000 Oe. These $\chi$-$T$ curves all show a paramagnetic-like behavior. The FC and zero-field cooled (ZFC) curves overlap over the whole temperature range, and no clear magnetic transition peaks are observed, similar to previous reports.21 This is because the paramagnetism originating from the Ho$^{3+}$ and Er$^{3+}$ ions masks the antiferromagnetic moments from the
Mn-Mn ordering. The inverse magnetic susceptibility data exhibit linear behavior above 100 K, as shown in Fig. 7. The Curie-Weiss temperatures ($\theta_{cw}$) and effective magnetic moments were calculated based on linear parts according to the Curie-Weiss fitting. For example, the respective $\theta_{cw}$ values are $-23$ K for ErMnO$_3$ and $-21$ K for HoMnO$_3$, implying the existence of antiferromagnetic ordering below the Néel temperature ($T_N$). The experimental effective magnetic moments of the Ho$_{1-x}$Er$_x$MnO$_3$ ($x = 0, 0.2, 0.4, 0.8$, and $1$) samples are $11.3, 11.1, 11.7, 10.5$, and $10.4$ $\mu_B$, respectively, with $\mu_B$ the Bohr magneton, which are well consistent with the theoretical magnetic moments calculated from $10.6\,\mu_B$ for Ho$^{3+}$ ($S = 2, J = 8$), $9.6\,\mu_B$ for Er$^{3+}$ ($S = 3/2, J = 15/2$), and $4.9\,\mu_B$ for Mn$^{3+}$ ($S = 2$). Thus Mn$^{3+}$ ions ($3d^4$) in single-phase samples remain stable in the high-spin state. As the Mn$^{3+}$ ions possess three energy levels in the trigonal bipyramidal crystal field, the $d_{x^2}$ orbitals of the high-spin Mn$^{3+}$ ions are not occupied by any electrons. The Er doping at the Ho sites does not affect the crystal field of the Mn-O$_5$ polyhedron significantly, responsible for stability of the spin state of the Mn$^{3+}$ ion.

The isothermal magnetization (M-H) curves of Ho$_{1-x}$Er$_x$MnO$_3$ ($x = 0, 0.2, 0.4, 0.8, 1$) measured at 10 K are shown in Fig. 8. The magnetizations of these samples increase linearly with increasing magnetic field below 20 kOe and do not saturate up to 50 kOe. As for HoMnO$_3$ and ErMnO$_3$, the magnetization at 50 kOe is 5.6 $\mu_B$ and 3.7 $\mu_B$, respectively, which is much smaller than the corresponding theoretical saturated values of 8 $\mu_B$ and 7 $\mu_B$. Moreover, the magnetizations of these samples decrease according to the increasing erbium concentration, as a result of the smaller effective magnetic moment of Er$^{3+}$ (9.6 $\mu_B$) compared to Ho$^{3+}$ (10.6 $\mu_B$).

The temperature dependence of the specific heat ($C_P$) for the Ho$_{1-x}$Er$_x$MnO$_3$ ($x = 0, 0.3, 0.5, 0.8, 1$) samples was measured from 2 to 100 K without magnetic fields, as shown in Fig. 9. Our specific heat data is in good line with previous reports. The characteristic $\lambda$-shape anomalies observed in all the samples are caused by the phase transition from a conventional second-order paramagnetic phase to an antiferromagnetic phase. As the Er content increases, the $C_P$ anomaly peak position gradually shifts from 72 K for HoMnO$_3$...
to 76 K for ErMnO$_3$, indicating that the increasing Er content enhances the antiferromagnetic transition temperature. It is noteworthy that two transition peaks at 72 and 76 K were observed in the sample with $x = 0.5$ due to the coexistence of ErMnO$_3$ and HoMnO$_3$ phases, supporting the analysis of XRD patterns. A small peak observed in HoMnO$_3$ at very low temperature ($\sim$12 K) is possibly ascribed to the antiferromagnetic ordering of the Ho$^{3+}$ ions. In order to study the excess magnetic heat capacity ($\Delta C_P$), smooth backgrounds of lattice contribution to specific heat were extracted using a third-order polynomial fitting exclusive of the regions around $T_N$ from the $C_P$-$T$ data of HoMnO$_3$ and ErMnO$_3$, as illustrated in Fig. 10. In the upper left insets of Fig. 10, the magnetic entropy changes ($\Delta S_{\text{Mag}}$) near $T_N$, corresponding to the variation of disordering around the transition from a paramagnetic state to an antiferromagnetic state, can be calculated from $\Delta S_{\text{Mag}} = \int_{T_1}^{T_2} \frac{\Delta C_P}{T} dT$, where $T_1$ and $T_2$ define a temperature range around $T_N$, e.g., $T_N \pm 25$ K. The calculated $\Delta S_{\text{Mag}}$ are 0.745 J/mol K for ErMnO$_3$ and 0.728 J/mol K for HoMnO$_3$, respectively. These $\Delta S_{\text{Mag}}$ values are comparable to 1.3 J/mol K for ScMnO$_3$ and 0.67 J/mol K for La$_{0.5}$Ca$_{0.5}$MnO$_3$. The theoretical value of $\Delta S_{\text{Mag}}$, known as the magnetic entropy changes for the transition from a paramagnetic state to a perfectly ordered state, is obtained through the equation of $\Delta S_{\text{theo}} = R \ln(2S + 1)$, where $S$ is the spin number of Mn$^{3+}$ ions in these samples and $R$ is the molar gas constant. Thus, the calculated values are much smaller than the theoretical values of $R \ln 5 = 13.38$ J/mol K. The deviations are possibly as a result that either a larger proportion of the spin entropy is “located” at low temperature or short-range magnetic correlations persist to temperatures much higher than $T_N$. The lower right insets show the curves in the low-temperature region ($2 < T < 30$ K), which are fitted by $C_P(T) = \gamma T + \beta T^3$, where the $\gamma T$ term describes the electronic contribution to specific heat due to free charges and the $\beta T^3$ term describes the lattice contribution arising from lattice vibration. The Sommerfeld coefficient $\gamma$ to identify the electronic linear term is given in a free-electron model by $\gamma = \frac{\pi^2 k_B^2 N(E_F)}{3}$, where $N(E_F)$ is the density of states at the Fermi level. The coefficient $\beta$ of lattice contri-
temperature that represents the effective cutoff phonon energy of materials. ErMnO$_3$ has $\gamma = 6 \times 10^{-6}$ J/mol K$^2$ and $\beta = 3.5 \times 10^{-5}$ J/mol K$^2$, while HoMnO$_3$ has $\gamma = 0.038$ J/mol K$^2$ and $\beta = 1.29 \times 10^{-4}$ J/mol K$^2$. As the density of charge carriers is proportional to the value of $\gamma$, the current leakage of HoMnO$_3$ is larger than that of ErMnO$_3$, consistent with observations from ferroelectric hysteresis loops. It is also proven that the HoMnO$_3$ and ErMnO$_3$ samples synthesized by solid-state reaction method are dielectric materials with distinct current leaky nature. The Debye temperatures $\Theta_D$ are 381 K for ErMnO$_3$ and 422 K for HoMnO$_3$. These calculated values agree well with other reported work.$^{24}$

IV. CONCLUSIONS

Single-phase Ho$_{1-x}$Er$_x$MnO$_3$ ($0 \leq x \leq 0.4$ and $0.7 \leq x \leq 1$) compounds were synthesized by the solid-state reaction method. The decreases in the $a$ lattice parameter with increasing Er content are caused by the small ionic radius of the Er$^{3+}$ ions. All the samples are ferroelectric materials not only with a current leaky nature, but also with dielectric relaxation related to oxygen vacancies. Nevertheless, the high oxygen loss at high temperature prevents the appearance of high-temperature ferroelectric transition peaks in the dielectric constant data. The weakening magnetizations of the samples with the higher Er doping levels are due to smaller magnetic moments of the Er$^{3+}$ ions compared to those of the Ho$^{3+}$ ions; meanwhile the Mn$^{3+}$ ions remain stable in the high-spin state. The antiferromagnetic transitions, which cannot be observed in the magnetic susceptibility data, are confirmed in the specific heat measurements, where the $T_N$ gradually shifts from 72 K for HoMnO$_3$ to 76 K for ErMnO$_3$.

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