Ferroelectricity of multiferroic hexagonal $TmMnO_3$ ceramics synthesized under high pressure

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Dense hexagonal $TmMnO_3$ ceramics were synthesized by solid-state reaction technique combined with high-pressure treatment which significantly increased the density of ceramic samples. The crystal structure of the hexagonal $TmMnO_3$ oxide was refined by using Rietveld analysis based on powder x-ray diffraction experiment. We observed obvious dielectric peaks through dielectric measurement on the specimen subjected to postannealing in oxygen atmosphere. A ferroelectric-paraelectric transition around 348 °C is identified. Polarization-electric field hysteresis (*P-E*) loop measurement proved the ferroelectricity of the sample at room temperature. © *2007 American Institute of Physics*. [DOI: 10.1063/1.2800816]

Rare earth manganates $RMnO_3$ with smaller rare earth atoms (R=Ho to Lu, Y, and Sc) have been found to exist in hexagonal structure (space group $P6_3\,cm$), while those with larger rare earth atoms (R=La to Dy) assume orthorhombic perovskite structure (space group $Pbnm$).[1] These compounds with the multiferroic properties (the coexistence of two or three of the properties: ferroelectricity, antiferromagnetism, and ferroelasticity) have been receiving intensive attention recently.[2–4] Because of the spontaneous electric polarization (magnetization), which can be switched by an applied electric field (magnetic field), and intrinsic coupling of ferroelectric and magnetic ordering, they have a wide range of applications including data storage, transducers, actuators,[5] nonvolatile memory,[6] and gate ferroelectrics in field-effect transistors.[7]

The hexagonal $RMnO_3$ is ferroelectric with high Curie temperature T_C between 590 and 1000 K.[8] Below the Néel temperature, there exists an antiferromagnetic ordering of Mn^{3+} ions.[9,10] The magnetic moments of Mn^{3+} ions take a triangular long-range ordering arrangement within the c-plane.[11] The coexistence of magnetism and ferroelectricity is rare, especially in materials without lone pair ions.[12] Recent reports[3,13] of coupling between the magnetic and ferroelectric ordering in $YMnO_3$ have induced strong research interests in understanding the origin of its ferroelectric behavior. The mechanism of ferroelectricity in magnetoelectric hexagonal $YMnO_3$ has been found to be driven entirely by electrostatic and size effects and the ferroelectric phase is characterized by a bulking of the layered MnO_5 polyhedron, accompanied by displacements of the Y ions, leading to a net electric polarization.[14] Although the physical properties of the hexagonal $RMnO_3$ with R=Y, Ho, Lu, Sc, and Yb (Refs. 15 and 16) have been studied recently, little has been found about the physical and electronic properties of $TmMnO_3$.

Zhou *et al.* reported the high-pressure synthesis of cubic type $TmMnO_3$ perovskite and hexagonal structure without mentioning ferroelectric properties.[17] Although the frustrated magnetic structure[18] and the anomalies of dielectric constant at magnetic transition of hexagonal $TmMnO_3$ (Ref. 19) were studied, the ferroelectric properties have not been reported yet. This is ascribed mainly to the leakage current and the difficulty of obtaining high density polycrystalline $TmMnO_3$ ceramics. The problem of leakage current exists in many kinds of perovskite ferroelectrics.[20–22] In most cases, the leakage current may be attributed to oxygen ion vacancies due to high sintering temperature and low density of bulk samples. Therefore, reducing oxygen vacancy by postannealing sample in oxygen atmosphere is indispensable for obtaining improved ferroelectricity. Here, we report the pressure-assisted synthesis of hexagonal $TmMnO_3$ with high density and low leakage current by removing oxygen vacancies through postannealing sample in oxygen atmosphere. The ferroelectric properties of the obtained samples were characterized through dielectric constant and polarization-electric field hysteresis loop measurements.

Polycrystalline dense $TmMnO_3$ ceramics were synthesized by the conventional solid-state reaction technique under ambient pressure using cold-pressing method under 5 GPa. It is found that this high-pressure method can significantly increase the densification of the ceramic samples. To obtain appropriate valence, Mn_2O_3 was calcined at 400 °C in air for 48 h, then thoroughly mixed with oxides of Tm_2O_3 (99.5%) and Mn_2O_3 (99%) in 1:1 metal ratio and calcined in air at 900 °C for 24 h. To ensure better reaction, the calcined mixture was finely ground, pressed into small pellets, and sintered in air at 1200 °C for 24 h. The process was repeated for several times until a single phase 6*H* $TmMnO_3$ was obtained, which was indicated by powder x-ray diffraction. The samples were well ground, pressed into a cylinder (5 mm in diameter), and encapsulated in aluminum foil to prevent contamination. The capsule was put at the center of a NaCl cylinder (8 mm in diameter and 15 mm in height). The NaCl

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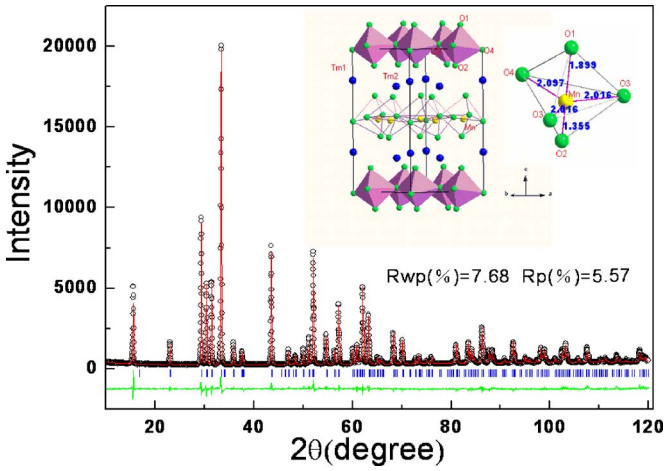

FIG. 1. (Color online) Observed (●) and calculated (-) powder x-ray diffraction for hexagonal $TmMnO_3$ polycrystalline ceramics at room temperature. Positions of Bragg reflections are indicated by tic marks. The difference between observed and calculated intensity is shown with bottom line. Inset: schematic of crystal structure of hexagonal $TmMnO_3$ and a MnO_5 polyhedron. The blue, green, and yellow spheres denote Tm, O, and Mn atoms, respectively. The numbers give the bond lengths.

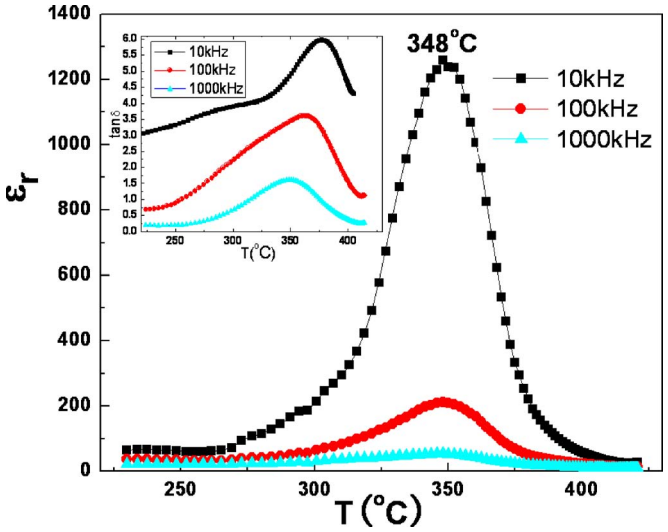

FIG. 2. (Color online) The temperature dependence of dielectric constant and loss of $TmMnO_3$ measured at different frequencies of 10, 100, and 1000 kHz. Inset: the inverse dielectric constant and high-T Curie-Weiss fit (red solid line).

powder serves as pressure medium and has been proven to be more efficient in keeping excellent quasihydrostatic pressure. The NaCl cylinder was then cold pressed under 5 GPa at room temperature for 10 min and sintered at 1350 °C for 24 h to obtain improved high density samples.

The recovered samples were annealed in oxygen atmosphere at 500 °C for 8 h to remove oxygen vacancies. The powder x-ray diffraction (XRD) experiments were performed with M18AHF diffraction meter (MAC Science, Japan) employing Cu $K\alpha$ radiation. The result of XRD indicates that fabricated sample is composed of single hexagonal $TmMnO_3$ phase without any trace of impurity within resolution, as shown in Fig. 1. Dielectric constant measurement was carried out on an HP4294A impedance analyzer above room temperature. The polarization-electric field (P-E) hysteresis loops and current-voltage (I-V) curve were measured using TF 2000 ferroelectric analyzer.

The crystal structure of hexagonal phase $TmMnO_3$ with space group $P6_3cm$ was refined from Rietveld analysis using GSAS program pocket. The calculated profile illustrated a good agreement with the observed one (Fig. 1). The obtained lattice parameters (a=6.08 Å, c=11.37 Å, and c/a=1.87) are in good agreement with single crystal results.[17]

The schematic views of the crystallographic structure of $TmMnO_3$ and MnO_5 polyhedra are shown in the inset of Fig. 1. In the ferroelectric phase, rare earth atom Tm located at two different symmetry sites: 2a (Tm1) and 4b(Tm2). They are connected to seven oxygen atoms (TmO_7 polyhedron). Mn atom is situated at the center of MnO_5 polyhedron, surrounded by bipyramid of oxygen atoms. Along the c direction, the crystal structure is composed of alternative Tm and corner-shared MnO_5 polyhedron layers.

The dielectric measurement was conducted on the sample annealed in oxygen atmosphere at 500 °C for 8 h. There are no remarkable peaks if the sample is not annealed owing to leakage current caused by oxygen vacancies. Post-annealing at temperature higher than 500 °C will introduce additional oxygen vacancies since the compound has to keep a dynamic equilibrium of suck in and breath out oxygen. Through systematic tests, it was found that 500 °C is around the optimal temperature to get maximum oxygen content. The temperature dependence of relative dielectric constant ε_r and dielectric losses (tan δ) of $TmMnO_3$ ceramic samples at different frequencies (10, 100, and 1000 kHz) is shown in Fig. 2. Divergent dielectric peaks in ε_r appearing in the vicinity of 348 °C could be found, similar to several other multiferroic oxide systems including $BiMnO_3$.[22] Since there is no remarkable shift of peaks being observed over the investigated frequency range, we believe that $TmMnO_3$ ceramics are not relaxor type materials. Compared to conventional ferroelectric such as $BaTiO_3$, the fluctuation in ε_r at transition point between ferroelectric and paraelectric phase is large. We also observed that dielectric peak became broadened and the magnitude of dielectric constant reduced with increasing frequency. The dielectric peaks at around 348 °C (621 K) in our experiments may be interpreted to be caused by the ferroelectric-paraelectric transition. In the paraelectric region above 380 °C, the dielectric data can be well described by the Curie-Weiss law. The experimental reciprocal dielectric constant ($1/\varepsilon_r$) and its high-T Curie-Weiss fit are shown in the inset of Fig. 3. The fitted Curie constant and Curie-Weiss temperature are $C \approx 6.79 \times 10^3$ K and θ

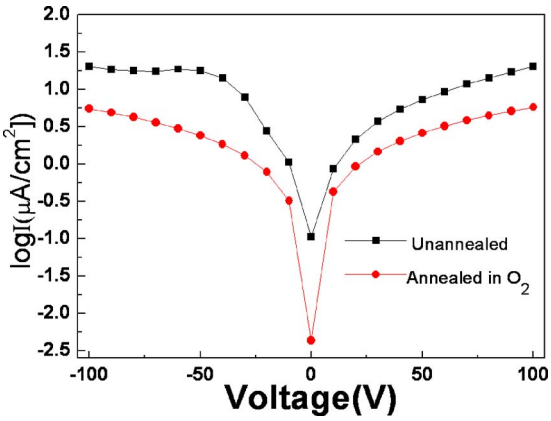

FIG. 3. (Color online) Logarithm of leakage current I vs applied voltage V for thin plate $TmMnO_3$ ceramics (solid square: unannealed, solid circle: annealed in O_2 at 500 °C for 8 h).

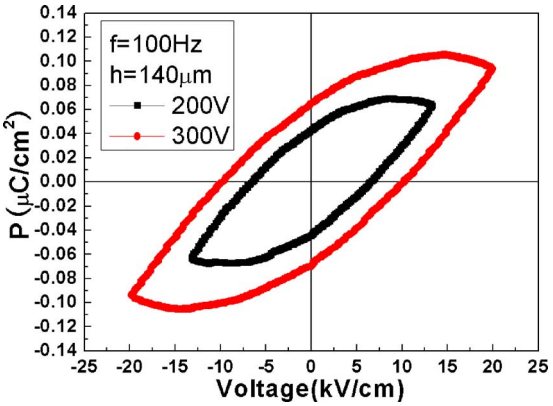

FIG. 4. (Color online) Polarization-electric field hysteresis loop collected at different applied fields and at a frequency of 100 Hz.

≈320.36 °C, respectively. The magnitude of dielectric loss is large compared with conventional ferroelectrics such as $BaTiO_3$.[23] This is likely to be induced by leakage current, which is hard to totally eliminate at the moment in ceramic samples since the grain boundaries usually have higher conductivity and the oxygen loss at high measuring temperature.

In order to estimate leakage current effect, we measured the leakage current for both unannealed and annealed $TmMnO_3$ ceramics in oxygen atmosphere. The results are displayed in Fig. 3. The measurements were carried out using thin $TmMnO_3$ capacitors with an upper limit of applied voltage up to 100 V. We can see from the figure that the leakage current was reduced by one to two orders of magnitude after annealing in oxygen atmosphere. The oxygen vacancies serve as charge carriers randomly distributed in the material and can be effectively removed by annealing in O_2 at proper temperature. With oxygen vacancies in the samples, the current will become considerably large with increasing applied voltage due to charge carriers caused by oxygen vacancies. Therefore, postannealing in oxygen atmosphere makes the $TmMnO_3$ samples become much more resistive and exhibit better ferroelectric properties.

The *P-E* hysteresis loops were also measured at different applied voltages at a frequency of 100 Hz. The result is shown in Fig. 4. The thickness of the sample is 0.14 mm. The maximum of polarization (P_{max}) and coercive electric field (E_c) obtained from the hysteresis loop under 19.94 kV/cm are 0.10 $\mu C/cm^2$ and 10.17 kV/cm, respectively, which are much smaller compared to other ferroelectric materials such as $BaTiO_3$.[23] The polarization tends to saturate with increasing applied field. Owing to the large leakage currents, a saturated ferroelectric loop is very difficult to obtain. Although the system shows very small hysteresis, the electric hysteresis loop provides the solid evidence of ferroelectricity in polycrystal hexagonal $TmMnO_3$ ceramics.

In summary, combining conventional solid state chemistry reaction with high pressure under 5 GPa and postannealing in oxygen atmosphere at 500 °C for 8 h, we obtained dense hexagonal $TmMnO_3$ ceramics which exhibit better ferroelectric properties. Postannealing in oxygen atmosphere can eliminate oxygen vacancies in the samples and reduce the leakage current, so that dielectric peaks can be observed through dielectric measurement. According to electric hysteresis loop and dielectric data, hexagonal $TmMnO_3$ ceramic exhibits ferroelectricity at room temperature and shows ferroelectric-paraelectric transition at around 348 °C.

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