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Bandgap modulation and magnetic switching in $PbTiO_3$ ferroelectrics by transition elements doping

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Abstract

Transition metal (TM = Fe, Ni and Mn) ions doped $PbTiO_3$ perovskite ferroelectric ceramics prepared by a solid state reaction method have been studied by means of structural characterizations, optical and magnetic measurements. All the samples have pure tetragonal perovskite structure, but exhibit different grain shapes and sizes with the introduction of TM ions and oxygen vacancies. The observed structural changes arise from internal lattice strain, which is estimated by Williamson–Hall (W–H) analysis model. Moreover, TM ions doping plays simultaneously an important role on the energy band structure and magnetic orderings. The energy gap of $PbTi_{0.95}TM_{0.05}O_{3-\delta}$ shows a drastic decrease compared to that of $PbTiO_3$. Furthermore, $PbTi_{0.95}TM_{0.05}O_{3-\delta}$ materials possess multiple magnetism switching, in which diamagnetic–ferromagnetic transition and ferromagnetic–paramagnetic transition occur. In particular, the Fe-doped $PbTiO_3$ ceramic presents a typical ferromagnetic hysteresis, originating from the effective exchange coupling interaction between oxygen vacancies and Fe 3*d* spins.

Keywords: C. Optical properties; $PbTi_{0.95}TM_{0.05}O_{3-\delta}$; Ferroelectric ceramics; Ferromagnetism

1. Introduction

Ferroelectrics, which are characterized by a spontaneous polarization that occurs below the Curie temperature and can be switched using an external electric field, have attracted great interest as a candidate class of materials for use in photovoltaics and for the coupling of light absorption with other functional properties [1]. Ferroelectric ABO_3 perovskite materials possess spontaneous polarization and show a bulk photovoltaic effect, where the spontaneous electric polarization promotes the desirable separation of photo-excited carriers and allows voltages higher than the bandgap (E_g). This may enable efficiencies beyond the maximum possible in a conventional p–n junction solar cell [2–5]. Therefore, it is beneficial to boost the conversion efficiency of solar cells based on theoretical consideration. However, the most solid oxide ferroelectrics exhibit a wide E_g of above 3.0 eV, absorbing primarily in the ultraviolet region (UV). Since UV light comprises only 8% of the solar spectrum, new materials with a decreased E_g and large polarization would be highly desirable. Recent work has showed that substituting the *B*-site of $PbTiO_3$ (PTO) perovskite with transition-metal (TM) ions whose bonds with oxygen are less ionic and more covalent, could decrease the bandgap [6–8]. The first principle density functional theory calculations also suggested doping the TiO_6 network with an oxygen-vacancy-stabilized d^8 M^{2+} (M = Ni, Pd, and Pt) may remarkably reduce the E_g while maintaining spontaneous polarization [8,9]. However, few experiments on the E_g tunability in PTO with vacancies by introducing TM elements (Mn, Fe, Ni, etc.) into the crystal structure of ferroelectric PTO have been systematically reported so far.

In addition, the appropriate introduction of magnetic TM cations and oxygen vacancies potentially give rise to ferromagnetism in the

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PTO perovskite based on a theoretical carrier-mediated mechanism [10,11]. Therefore, the magnetism of TM cations-doped PTO is also worth studying to see if such materials present room-temperature ferromagnetism for promising multiferroic applications. These motivate us to synthesize the TM-doped PTO ferroelectrics and investigate their crystal structure, optical, and magnetic properties. In this work, we report systematically TM (TM = Fe, Ni and Mn) doped PTO and study ions substitution-dependent structural, optical and magnetic properties of perovskite ferroelectric ceramics. These results are significant to gain insight into the PTO-derived perovskite materials for photovoltaic and multiferroic applications.

2. Experimental details

$PbTi_{0.95}TM_{0.05}O_{3-\delta}$ ferroelectric ceramics for TM = Mn, Fe, and Ni (abbreviated as PTMO, PTFO, and PTNO, respectively) were prepared by a solid-state reaction method using PbO (99%), TiO_2 (99%), MnO (99.5%), Fe_2O_3 (99%), and NiO (99%) as starting raw materials. For each composition, the starting materials were weighed in required molar ratios and ball-milled in an alcohol medium with zirconia balls. The dried slurries were pre-sintered first at 700 °C, then uniaxially pressed into pellets, and finally sintered at the optimum temperature range 900–1000 °C for the different element doping. For comparison, the ceramic PTO was also prepared using the same method at a sintering temperature of 800 °C.

The phase composition and crystalline structures of the as-prepared ceramics were analyzed by X-ray diffraction (XRD, Bruker D8 Advance, with Cu Kα radiation) from 10° to 60°. Raman scattering analysis for the samples was performed with a micro-Raman spectrometer (Renishaw plc InVia plus, 514.5 nm). The surface morphologies were figured directly using a scanning electron microscopy (SEM, Philips XL30FEG). The optical absorption experiments were carried out by ultraviolet–visible–near-infrared (UV–vis–NIR) spectrophotometer (cary500, USA Varian) equipped with integration sphere. The magnetic properties were investigated using a vibrating sample magnetometer (VSM) integrated in a physical property measurement system (PPMS-9, Quantum Design). All measurements of the samples were performed at room-temperature.

3. Results and discussion

Fig. 1(a) shows the XRD patterns of the $PbTi_{0.95}TM_{0.05}O_{3-\delta}$ ferroelectric ceramics. All the samples show a polycrystalline perovskite structure with clearly visible characteristic peaks, and the peaks agree well with the PTO diffraction standard card (JCPDS no. 06-0425). Besides, no diffraction peaks from the impurity phases can be detected. The obvious splitting of main characteristic peaks at 2θ around 32° indicates the tetragonal structure of the $PbTi_{0.95}TM_{0.05}O_{3-\delta}$ crystals [12,13]. From the XRD spectra, the lattice parameter of PTO were calculated to be $a = 3.9064$ Å, which is in good agreement with the experimental data of 3.904 Å [13], and that of PTMO, PTFO, and PTNO was $a = 3.9086$ Å, 3.895 Å, and 3.9074 Å, respectively, as shown in Fig. 1(b). It can be found that the difference between a and c changes a little but remains prominent, demonstrating a stable tetragonal phase obtained in the $PbTi_{0.95}TM_{0.05}O_{3-\delta}$ ceramics. Although the tetragonal lattice distorted ratio (c/a) decreases undesirably with doping, the largest change value is only 0.015. The existence of spontaneous ferroelectric polarization in the PTO crystal is well known due to the off-centered displacement of Ti^{4+} ion in the octahedral cage [TiO_6], which is directly proportional to the c/a. For this reason, the large c/a tetragonal distortion is an important condition for a good ferroelectric property. Since the separation of charge carriers for ferroelectrics depends on an internal electric field originating from the electric polarization, it can be inferred that the appropriate introduction of TM elements would nearly maintain the charge separation property of PTO based on above analysis.

On the other hand, taking the effects of lattice strain (ε) into consideration, the TM cations doped PTO can produce inner stress field to break the balance of Ti–O orbital hybridization, which induces local lattice distortions. In order to get more details about structural properties, the internal strain in the samples was estimated by Williamson–Hall (W–H) analysis method [14]. The strain is calculated by using the following equation: $\beta\cos\theta = (K\lambda/D) + 4\varepsilon\sin\theta$, where β is the full width at its half-maximum, K is a shape factor, λ is the X-ray wavelength, and D is the crystallite size. Fig. 2 shows the

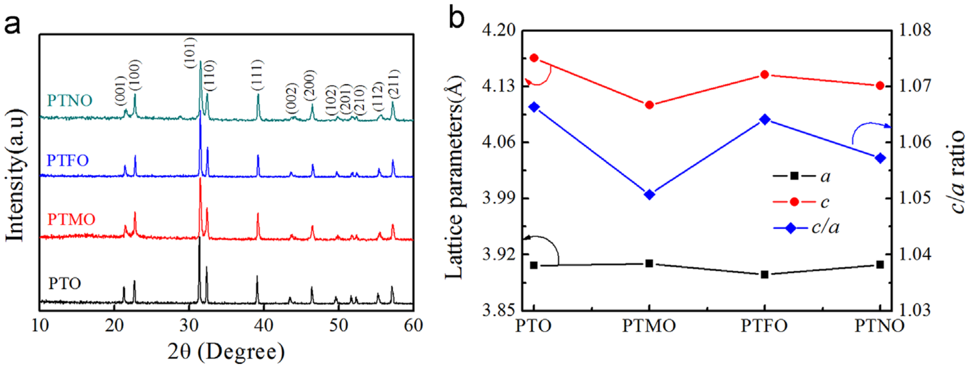

Fig. 1. (a) XRD patterns of the samples. (b) Lattice parameters and tetragonal lattice distorted ratio (c/a) of the samples.

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