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Optical modulation and magnetic transition in $PbTi_{1-x}Pd_xO_{3-\delta}$ ferroelectric thin films

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ABSTRACT

The $PbTi_{1-x}Pd_xO_{3-\delta}$ (*x*PTPO) thin films prepared by chemical solution deposition have been investigated by means of structural characterizations, optical and magnetic measurements. X-ray diffraction patterns show that all the films have a pseudotetragonal perovskite structure, but also exhibit a lattice dilatation behavior and increased internal strain as the *x* increases. A possible mechanism for strain-induced structural evolution is discussed. Raman scattering further corroborates this change in average structure, where the characteristic variation of phonon modes, indirectly reveal the incorporation of Pd^{2+} ions into host lattice. Transmittance spectra analysis indicates that Pd doping has a key effect on the energy band structure. The optical bandgap of *x*PTPO films decreases significantly with increasing Pd content, expressed by (3.5–9.0*x*) eV ($0 \le x \le 0.09$). Also, magnetic switching driven by doping has been confirmed in the films, which is attributed to the competition between ferromagnetic and paramagnetic/antiferromagnetic components.

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1. Introduction

Ferroelectric materials, which are characterized by a spontaneous polarization that occurs below the Curie temperature and can be switched using an external electric field, have attracted much attention for several decades because of their electrical and optical properties [1,2]. Recently, the need to create stable, single-phase perovskite-type (ABO_3) ferroelectrics to be used in photovoltaic (PV) devices has begun to generate great interest, though candidate materials are few and far between [3,4]. Ferroelectric perovskite oxides possess spontaneous polarization and show a bulk PV effect, where the spontaneous electric polarization promotes the desirable separation of photo-excited carriers (electrons and holes) 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 [5–7]. Therefore, it is beneficial to boost the conversion efficiency of solar cells based on theoretical consideration. However, most ferroelectrics (e.g., $PbTiO_3$ (PTO), $BaTiO_3$, etc.) exhibit a wide E_g of above 3.0 eV [8,9], absorbing primarily ultraviolet radiation, which comprises only 8% of the solar spectrum. This has become a major obstacle that limits their PV applications. Since light absorption and carrier concentrations are both bandgap dependent, small bandgap polar materials are thus highly desirable.

To search for such materials, one approach is to rely upon first-principles calculations. Recently, the theory calculations showed that the *B*-site substitution of PTO with an oxygen-vacancy-stabilized d^8M^{2+} cation (M=Ni, Pd, and Pt), whose bonds with oxygen are less ionic and more covalent, could considerably reduce the E_g while well maintaining the large spontaneous polarization [10,11]. However, there have been few experiments on such d^8M^{2+} doped PTO materials to be conducted so far, so the prediction remains not well understood. Additionally, the appropriate introduction of M^{2+} and oxygen vacancies would potentially give rise to increasing magnetization in the PTO-derived perovskite. Therefore, these motivate us to prepare the d^8M^{2+} doped PTO ferroelectric materials and investigate their structural, optical and magnetic properties.

In this work, we report a Pd-doped PTO material synthesized by a chemical solution deposition method. Lattice strain-induced structural evolution accompanied by E_g modulation and magnetic transition has been observed in $PbTi_{1-x}Pd_xO_{3-\delta}$ (*x*PTPO) thin films. These results are significant to gain insight into the PTO-based perovskite materials for ferroelectric PVs and magnetic

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2. Experimental details

The ferroelectric thin films were deposited on fused quartz substrates by chemical solution deposition employing a spin-coating process. In order to monitor the effect of Pd content on the microstructure, optical and magnetic properties, the *x*PTPO thin films were prepared in the Pd-doped range of $0 \le x \le 0.09$ at 0.03 intervals. Lead acetate [$Pb(CH_3COO)_2 \cdot 3H_2O$], palladium acetate ($C_4H_6O_4Pd$), and tetrabutyl titanate [$Ti(OC_4H_9)_4$] were used as the starting materials for the preparation of *x*PTPO precursor solutions. Acetic acid (CH_3COOH) and acetylacetone ($CH_3COCH_2COCH_3$) were used as the solvent and the chemical modifier, respectively. The concentration of the final solutions was adjusted to 0.25 mol/L and the pH value to 3–4 by using acetic acid. The precursor solutions were spin-coated on fused quartz substrates to form uniform wet films. The rotation speed and the spin time were fixed at 5500 rpm and 30 s, respectively. The thermal treatments of films were carried out in a rapid thermal processor. Each layer of the wet films was initially dried at 180 °C for 120 s to evaporate the solvent, and then rapidly heated to 380 °C for 180 s to remove the residual organics. Finally, the films were annealed at the optimum temperature 800 °C for 400 s. The spin-coating and thermal treatments were repeated several times to obtain the desired film thickness.

The crystal-structures of the as-prepared *x*PTPO ($x=0.00$, 0.03, 0.06, and 0.09) films were analyzed by X-ray diffraction (XRD) using a Bruker D8 Advance diffractometer with Cu Kα radiation ($\lambda=1.54056$ Å). In the XRD measurement, a continuous scanning mode ($\theta \sim 2\theta$) was selected with a step size of 0.2° and collection time of 0.1 s. The morphologies of the films were characterized with a field emission scanning electron microscopy (FE-SEM: Philips XL30FEG). Raman scattering experiments were carried out using a micro-Raman spectrometer (Jobin-Yvon LabRAM HR 800UV) equipped with a 633 nm He–Ne laser as the exciting light. The optical properties of *x*PTPO were investigated by the ultraviolet-visible-near-infrared spectrophotometer (cary500, USA Varian). The magnetization hysteresis loop measurement was performed in a physical property measurement system (PPMS-9, Quantum Design).

3. Results and discussion

Fig. 1 shows the XRD patterns of the *x*PTPO thin films grown on fused quartz substrates in the 2θ range of 10–70°. All the films are crystallized into a single-phase perovskite structure and no impurity phases could be certified, at least within the detection limits of the instrument. It is notable that the different peak shapes were involved as the composition changes. The difference in peak profiles at around 32° in the XRD patterns is usually used as evidence for the phase transition in terms of PTO tetragonal symmetry [12]. However, no evident characteristic peaks splitting appear and the XRD peaks at around 32° are partially overlapped for pure PTO film, suggesting its pseudotetragonal structure possibly due to the interface strain-induced tetragonal distortion [13,14]. Upon increasing *x*, the peak intensity, broadening and position present obvious change. As shown in the inset of Fig. 1, the intensities of (101) and (110) peaks increase drastically and vary gradually from overlapping to splitting as the *x* increases. It can be confirmed that the *x*PTPO films show a multiphase coexistence state of tetragonal and cubic symmetries. This variation of diffraction peaks depending on the composition indicates a gradual structural evolution process, which may be attributed to the

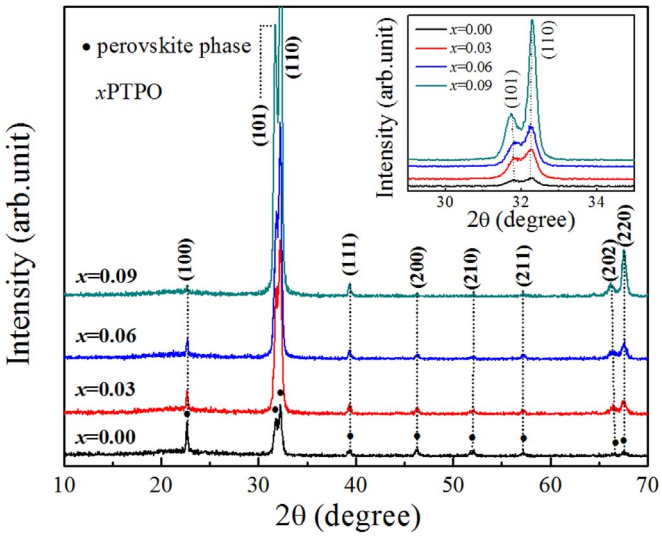

Fig. 1. XRD patterns of the *x*PTPO ($x=0.00$, 0.03, 0.06, and 0.09) films; inset: the magnified patterns around $2\theta=32°$.

incorporation of substitution ions into the PTO crystal lattice since the ionic radius of Pd^{2+} (0.86 Å) is larger than that of Ti^{4+} (0.61 Å).

From the XRD spectra, lattice parameters for PTO were calculated to be $a=b=3.914$ Å and $c=4.078$ Å, which matches with the literature values (JCPDS no. 70–0746). Fig. 2(a) illustrates both the variation of lattice parameters (a, c) and unit cell volumes (V) for *x*PTPO thin films with the *x*. The a continuously increases up to $x=0.09$, whereas the c lattice parameter decreases slowly. The cell volume increases from 62.472 $Å^3$ for PTO to 62.590 $Å^3$ for 0.09PTPO, which is consistent with the substitution of Ti^{4+} by the larger Pd^{2+}. This lattice dilatation behavior will favor solubility and accommodate an O-vacancy-stabilized Pd^{2+} substitution [15]. Moreover, it can be found that the difference between a and c changes a little but remains prominent, and the tetragonal lattice distorted ratio (c/a) decreases undesirably with doping but changes only 0.5% (see inset of Fig. 2(a)), indicative of the lattice deviation from the average structure. 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 visible c/a tetragonal distortion is an important condition for a good ferroelectric property. Since the separation of charge carriers depends on an internal electric field originating from the electric polarization, it can be inferred that the Pd-doped PTO thin films would nearly maintain the charge separation property of parent PTO in theory.

On the other hand, taking the effects of lattice strain (ε) into consideration, the Pd^{2+} cations doped PTO produces inner stress field to break the balance of Ti–O orbital hybridization, giving rising to structural distortions. The internal strain can be estimated by means of the Williamson–Hall (W–H) analysis method, which is subject to the relation $\beta_{hkl}\cos\theta=(K\lambda/D)+4\varepsilon\sin\theta$, where β_{hkl} 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 [16]. Fig. 2(b) shows the W–H plots of the quantity $\beta_{hkl}\cos\theta$ as a function of $4\sin\theta$ for the *x*PTPO thin films with the slope of the fitted line representing strain. The plots showed an increased positive strain as the *x* increases, as presented in the inset of Fig. 2(b), which is in agreement with the emergence of lattice dilatation behavior.

Raman scattering is sensitive to the change in the coordination of local symmetry, which gives information about the molecular vibrations and distortions of the crystal lattice [17,18]. Thus, it can be useful for the compositional and structural analysis in *x*PTPO.

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