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Combined theoretical and nanoscale experimental study of Pb(Ca,Ba)TiO$_3$, Pb(Sr,Ba)TiO$_3$, and Pb(Sr,Ca)TiO$_3$ complex perovskite structures: An investigation of the ferroelectric and electronic properties

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ABSTRACT

Combined experimental and first-principles studies have been conducted to obtain a fundamental understanding of the effect of A-site chemical doping on the electronic structure and ferroelectric behavior of Pb(Ca,Ba)TiO$_3$, Pb(Sr,Ba)TiO$_3$, and Pb(Sr,Ca)TiO$_3$ perovskite complex solid solutions. Rietveld refinement of powder X-ray diffraction data shows that the crystal structure of all the three compounds is distorted from the ideal cubic perovskite structure. At the nanoscale, piezoresponse force microscopy (PFM) studies show low-performance ferroelectric properties of Pb(Sr,Ca)TiO$_3$ thin films when compared to Pb(Ca,Ba)TiO$_3$ and Pb(Sr,Ba)TiO$_3$ films. Theoretical analysis of the electronic band structure performed on the basis of density functional theory (DFT) allows to elucidate the origin of the different ferroelectric behaviors observed in Pb(Ca,Ba)TiO$_3$, Pb(Sr,Ba)TiO$_3$, and Pb(Sr,Ca)TiO$_3$ thin films. DFT-based computational calculations reveal that there is a strong correlation between the effects of Ti 3d non-bonding orbitals (responsible for π Ti–O bonding) and the ferroelectric polarization behavior of A(A′A″)BO$_3$ complex perovskite solid solutions. In our study, very low Ti 3d$_{xy}$, d$_{xz}$, and d$_{yz}$ non-bonding electronic density state contributions were observed and the presence of mainly ionic Ca–O and Sr–O bonds. These effects are the reason for the unusually weak polarization, low tetragonality, and poor ferroelectricity of Pb(Sr,Ca)TiO$_3$ thin films. This is in contrast to the observed behaviors of Pb(Ca,Ba)TiO$_3$ and Pb(Sr,Ba)TiO$_3$ thin films. However, our first-principles calculations agree well with the PFM-based experimental results obtained in the nanometer scale.

1. Introduction

Notably intense global research has been directed toward the exhaustive study of the wide spectrum of properties (ferroelectricity, piezoelectricity, sensors, ferromagnetism, photocatalysis, and photovoltaics) of inorganic and hybrid organic-inorganic perovskites classes [1–5]. Previous studies have demonstrated that the increasing capabilities of first-principles calculations and the advances in characterization techniques in the nanoscale range have become powerful tools for the interpretation of both theoretical and experimental data; and therefore, the number of ab initio and experimental studies continues to grow [6–11]. From the perspective of inorganic perovskite ABO$_3$-type materials, the prototype PbTiO$_3$ ferroelectric oxide and their Pb-based oxide solid solutions provide most of the technologically useful ferroelectric materials, which are dominant candidates for electro-active material applications [12,13]. Their corresponding properties, such as ferroelectric, piezoelectric, dielectric, optical, and electronic states are strongly influenced by the amount of substitution in the A (twelve-fold coordination) and/or B (six-fold coordination) sites [14–16].

In particular, the density functional theory (DFT) approach offers an opportunity for a rational design of new materials with improved properties, even before they are observed

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experimentally. Brehm et al. [17] reported physical and electronic properties of hypothetical $PbTiO_3$-based oxysulfides, $PbTiO_{3-x}S_x$ using first-principles calculations. Theoretical analysis indicates that this compound should be considered a solar bulk photovoltaic material candidate [17]. First-principles calculations conducted by Cohen [18] revealed that the strong interaction between the Ti 3d orbitals and O 2p orbitals, or in other words covalent bonding, is crucial for large polarization of lead titanate, $PbTiO_3$. In addition, the fundamental characteristics of the hybridization between Pb 6s, 6p, and O 2p orbitals (also responsible for the large tetragonality of lead titanate, $PbTiO_3$) has been demonstrated by first principles calculations using full potential linearized augmented plane wave (FLAPW) method with the local density approximation (LDA) [19]. Because of $PbTiO_3$ structure to be capable of accommodating a large number of cation substitutions, a meaningful development of new semiconducting ferroelectric complex perovskite oxides is opened up.

Previous studies [20] on structural and electronic behaviors of two possible (001) surface terminations of cubic $PbTiO_3$ using first-principles calculations based on density functional theory (DFT) showed a partial covalent character of the Ti—O bonds, especially in the TiO_2-terminated surface layer, and of the (110) plane, whereas the Pb—O bonds showed a very low covalent character. Recently, Shimada et al. [21] investigated whether or not ferroelectricity can exist in $PbTiO_3$ nanotubes using first-principles density functional theory calculations. Paris et al. [22] also reported experimental and theoretical studies on the $(Pb_{1-x}Sm_x)TiO_3$ system. Recently, first-principles studies on $PbTi_{1-x}Ni_xO_{3-x}$ solid solutions have indicated the important role of B-site Ni and Ti cation ordering [23]. A combined experimental and theoretical study has shown that $PbZr_{0.30}Ti_{0.70}O_3$ doped with tungsten thin films deposited on $LaNiO_3$ bottom electrodes by pulsed laser deposition are less susceptible to fatigue than undoped-PZT films [24]. Furthermore, theoretical investigations have shown that the fatigue phenomenon in the PZT system is associated with a small overlap of π bonds between Ti 3d and O 2p states. A recent publication by Lee et al. [25] reported a combination of theoretical and electrical studies on the effect of nanometer-thick in $SrTiO_3$ films. They presented evidence of room temperature ferroelectricity in thinning $SrTiO_3$ films. Seidel et al. conducted a theoretical and experimental study using a combination of conductive atomic force microscopy, transmission electron microscopy, and first-principles density functional calculations for $BiFeO_3$ [26].

The purpose of the present work is to perform a combination of nanoscale piezoresponse force microscopy experimental analysis and first-principles calculations based on density functional theory (DFT) to study the ferroelectric and electronic properties of the $Pb(Ca,Ba)TiO_3$, $Pb(Sr,Ba)TiO_3$, and $Pb(Sr,Ca)TiO_3$ complex perovskite solid solutions, classified as $A(A'A'')BO_3$ ($A = Pb$, $A' = Ca$ and Sr and $A'' = Ba$ and Sr).

2. Experimental procedures

The synthesis of $PbTiO_3$-based complex perovskite oxides co-substituted at the A-site with isovalent cation pairs (Ca^{2+}/Ba^{2+}), (Sr^{2+}/Ba^{2+}), and (Sr^{2+}/Ca^{2+}) was based on the chemical solution deposition (CSD) method commonly known as the polymeric precursor route. Details of the preparation method can be found in the literature [27,28]. Ceramic and thin film samples with nominal chemical compositions of $Pb_{0.60}(Ca_{0.20},Ba_{0.20})TiO_3$, $Pb_{0.60}(Sr_{0.20},Ba_{0.20})TiO_3$, and $Pb_{0.60}(Sr_{0.20},Ca_{0.20})TiO_3$, hereafter referred to as PCBT-60, PSBT-60, and PSCT-60, respectively, were prepared. The precursor solution was deposited onto a $Pt/Ti/SiO_2/Si$ commercial substrate by spin coating at 6000 rpm for 20 s using a spin coater (KW—4B, Chemat Technology) via a syringe filter to avoid particulate contaminations.

After spin coating, the films were preheated to 200 °C for 10 min on a hot plate to remove residual water. Then, the films were annealed using a stepwise/successive growth and crystallization engineering method at 400 °C for 4 h and 700 °C for 2 h in air to remove residual organic components at a heating rate of 5 $°Cmin^{-1}$, respectively. The film thickness was adjusted by repeating the deposition and pyrolysis/growth/crystallization cycle. The thicknesses of PCBT-60, PSBT-60 and PSCT-60 films were adjusted to 300, 280, and 310 nm, respectively.

The phase structures of the samples were identified using a Rigaku MiniFlex600 X-ray diffractometer ($CuK_\alpha = 1.54056$ Å radiation). In order to more accurately determine the crystallographic structure, the Rietveld refinement technique was performed using the General Structure Analysis System (GSAS) software.

The surface morphology, polarization patterns of the ferroelectric domain structures, and the local hysteresis loops of ferroelectric films were investigated at the nanoscale level using a commercial atomic force microscope (AFM) (MultiMode Nanoscope V, Bruker) modified to function as a piezoresponse force microscope (PFM). The system was equipped with a lock-in amplifier (SR850, Stanford) and a function generator (33220A, Agilent). During all PFM measurements, the conductive probe was electrically grounded and an external voltage was applied to the bottom Pt electrode operated at a driving amplitude of 1 V (rms).

3. Computational methods and model systems

To further study the effect of AO_{12}-site double chemical substitution by either (Ca^{2+}/Ba^{2+}), (Sr^{2+}/Ba^{2+}), or (Sr^{2+}/Ca^{2+}) isovalent cation pairs of the $PbTiO_3$ perovskite lattice, first-principles calculations within the framework of density functional theory (DFT) were used. Using this method, energy variations of the different structure symmetries can be evaluated and the corresponding ferroelectric, optical, and electronic properties can be obtained with precision. Calculations were carried out with the CRYSTAL06 [29] package using the gradient-corrected correlation functional by Lee, Yang, and Parr, combined with the Becke3 exchange functional, B3LYP [30,31].

The Pb, Ti, O, Ba, Sr and Ca atomic centres were described by all electron basis sets [DB]-31G, 86-411(d31), 6-31G*, 311(1d)G, 311(3d)G, and 86-511d(21)G, respectively. Here [DB] denotes the Durand—Barthelat non-relativistic large effective core potential, and all basis sets can be found at the CRYSTAL home page. In the theoretical calculations, 1 × 1 × 5 supercells for all systems were built, as shown in Fig. 1. To initiate structural modeling, tetragonal symmetric $PbTiO_3$ (space group *P4mm*), PCBT-60, PSBT-60, and PSCT-60 systems were constructed based on the Rietveld refinement analysis using lattice parameters and atomic positions displayed in Table 1.

4. Results and discussions

Fig. 2(i) shows the XRD patterns of the PCBT-60, PSBT-60, and PSCT-60 thin films on platinum-coated silicon substrates. All the thin films are found to possess polycrystalline features with pure perovskite phases within the detection limits of XRD. In addition, the diffraction peaks for all the thin films are indexed to the tetragonal phase by considering the obvious splitting of the (101)/(110) peaks. In order to clarify the structure evolution, Fig. 2(ii) shows in detail that the (101) and (110) peaks clearly overlap and shift towards higher scattering angles for the PSCT-60 thin film compared with the PCBT-60 and PSBT-60 thin films, indicating both a decrease in the *d* spacing and tetragonality (*c/a* ratio).

To further confirm the structural evolution, the crystal