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Major improvement of ferroelectric and optical properties in Na-doped Ruddlesden-Popper layered hybrid improper ferroelectric compound, $Ca_3Ti_2O_7$

C. Huang [a], Winnie Wong-Ng [b], W.F. Liu [a, b, *], X.N. Zhang [a], Y. Jiang [a], P. Wu [a], B.Y. Tong [c], H. Zhao [c], S.Y. Wang [c]

[a] *Tianjin Key Laboratory of Low Dimensional Materials Physics and Preparing Technology, School of Science, Tianjin University, Tianjin, 300072, China*
[b] *Materials Measurement Science Division, National Institute of Standards and Technology, Gaithersburg, MD, 20899, USA*
[c] *College of Physics and Material Science, Tianjin Normal University, Tianjin, 300074, China*

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ABSTRACT

Ruddlesden-Popper layered $Ca_3Ti_2O_7$ (CTO) and $Ca_{2.85}Na_{0.15}Ti_2O_7$ (CNTO) ceramics were successfully prepared by a conventional solid-state reaction process. The ferroelectric coercive field greatly decreased via Na doping. Interestingly, a diode-like electric transport effect was observed in the CNTO sample, which is most likely due to a newly formed p-n junction caused by the applied electric field. Optical characterization by UV–visible absorption showed a decrease of band gap from 3.55 to 3.41eV via Na doping. First-principles calculation showed a similar decreasing trend which confirmed the experimental results.

1. Introduction

Perovskite Ruddlesden-Popper (RP) structure (general formula $A_{n+1}B_nC_{3n+1}$, C typically represents oxygen) have gained much attention owing to a wide variety of important properties, such as catalytic activity, colossal magnetoresistance, superconductivity, and ferroelectricity [1–4]. Usually, as the temperature decreases, the structure undergoes phase transitions which are accompanied by octahedral rotations, resulting in many interesting electronic properties, including colossal magnetoresistance and metal-insulator transitions [5,6].

In the past few years, $n = 2$ perovskite RP structures have become important because of their 'hybrid improper ferroelectricity' (HIF) [7]. The main feature of HIF is that the ferroelectricity is generated by a complex distortion mainly consisting of two kinds of BO_6 octahedral rotations [8]. While (anti)ferromagnetism demands B ions with unfulfilled *d* orbitals, this is not in conflict with BO_6 octahedral geometry, therefore, HIF makes room temperature multiferroicity possible. HIF provides a mechanism for controllable polarization-magnetization coupling, leading to possible strongly coupled multiferroicity.

$Ca_3Ti_2O_7$, a typical $n = 2$ RP compound which consists of one layer of NaCl-type CaO blocks and two layers of perovskite-type $CaTiO_3$ blocks alternately stacked along the *b*-axis, recently gained much attention due to its ferroelectricity. Using first-principle calculations, Benedek et al. revealed a rich set of coupled structural and polar domains in which BO_6 octahedral rotations induce ferroelectricity [7]. Nonandic et al. then presented the domain and ferroelectric switching pathways in $Ca_3Ti_2O_7$ to illustrate the reverse polarization [9]. Recently, Liu et al. found that the amplitudes of oxygen octahedral rotation and tilt modes decrease with Sr content in $Ca_{3\text{-}x}Sr_xTi_2O_7$ ceramics, which affects the polarization [10]. In 2015, Oh et al. provided experimental demonstration of HIF and confirmed an interesting ferroelectric domain structure resulting from orthorhombic twins and switchable planar polarization in $(Ca,Sr)_3Ti_2O_7$. However, the exceedingly high coercive field of 120 kV/cm in $(Ca,Sr)_3Ti_2O_7$ prevented it from being used in other fields [8]. Recently in 2017, Li et al. found that the coercive field in the epitaxial thin films was unexpectedly low

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* Corresponding author. Tianjin Key Laboratory of Low Dimensional Materials Physics and Preparing Technology, School of Science, Tianjin University, Tianjin, 300072, China.
E-mail address: wfliu@tju.edu.cn (W.F. Liu).

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(2–5 kV/cm) compared with that of bulk crystals and ascribed the ultra-low coercive field to lattice imperfections in the thin films [11]. Their work provides important guidance for enabling this new ferroelectric material for potential applications.

As doping is often an effective way to achieve improved properties, Okazaki et al. [12] investigated the photocatalytic activities of Rh-doped $Ca_3Ti_2O_7$ and found that photocatalytic activities were enhanced in these materials after treated under a reducing atmosphere of 3% H_2. Cao et al. [13] demonstrated that the PL intensity of $Ca_3Ti_2O_7:Eu^{3+}$ phosphor can be improved significantly with Bi^{3+} co-doped due to an energy transfer between the Bi^{3+} and Eu^{3+} ions. Wang et al. [14] confirmed a continuous exponential distribution of trap depth of 0.69–0.92 eV in $Ca_3Ti_2O_7:Pr^{3+}$ phosphor, which is found to be responsible for the persistent luminescence behavior. Up to now, a few investigations have been focused on alkali elements as dopants in $Ca_3Ti_2O_7$. In fact, the substitution at the A-site could improve the properties of perovskite materials effectively, for example, it has been reported that substitution of the alkali element Na can further improve piezoelectric properties of the KNO_3 ceramic [15], while in Na-doped $BiFeO_3$ nanoparticles, an increased Na^+ doping could reduce the band gap and simultaneously cause the decrease of the leakage current [16]. Therefore, in this paper, we chose Na^+ ions as the low-valent dopant in $Ca_3Ti_2O_7$ and prepared the $Ca_3Ti_2O_7$ (CTO) and $Ca_{2.85}Na_{0.15}Ti_2O_7$ (CNTO) samples using the conventional solid-state reaction method. Interestingly, the coercive field was greatly decreased after Na doping. A diode-like effect was observed in the CNTO sample which may be due to the carriers rebalancing under the applied voltage. The band gap was decreased after Na doping, to gain theoretical understanding, electronic structures of the samples were analyzed by first-principles calculations.

2. Experiment

CTO and CNTO powders were prepared by a standard conventional solid-state reaction process. The starting materials $CaCO_3$ (99.99%), TiO_2 (99.99%), and Na_2CO_3 (99.99%) were accurately weighed in stoichiometric proportions and mixed by ball milling with agate balls in anhydrous alcohol for 10 h. All mixtures were calcined at 1273 K for 12 h in air to obtain the desired powders, and the calcined powders were subsequently pressed into cylindrical compacts under uniaxial compression. Finally, dense CTO and CNTO ceramics were obtained by sintering the compacts at 1673 K in air for 48 h, and the relative densities of all ceramics were greater than 98% of the theoretical densities.

Crystal structure analysis of the samples was carried out by powder X-ray diffraction (XRD, D/Max-2500 diffractometer with Cu Kα radiation; Rigaku Co., Tokyo, Japan).[1] UV–vis absorption spectra were recorded with a UV-3600UV-VIS-NIR spectrophotometer (Shimadzu Co., Tokyo, Japan). To study the electrical properties, samples were pressed into cylindrical compacts (about 0.20 mm thickness), and both sides of the compacts were coated with Ag paste to form two electrodes, followed by calcining at 573 K for half an hour. The leakage currents of all samples were recorded by an Axiacct TF2000 ferroelectric analyzer (aixPES Co., Aachen, Germany). The morphology of the samples was investigated by scanning electron microscopy (SEM) using a model SU8010 field-emission scanning electron microscope (Hitachi Co., Tokyo, Japan), before measuring SEM, both samples were polished in the acid solution (comprising HF and HCl mixed in a 1:9 ratio by volume) for 30s, after polishing the samples were rinsed in deionized water for about 5min. First-principles calculations were performed using the Vienna *ab initio* Simulation Package (VASP) with projector augmented wave (PAW) potentials with LDA+U ($U = 5.5$ eV and a plane wave energy cut off of 450 eV). The calculations were performed using a $1 \times 1 \times 1$ Monkhorst-Pack k-point mesh for band structure, and $2 \times 1 \times 2$ Monkhorst-Pack k-point mesh for density of states (DOS). DOS computations were performed for two compositions: (i) pure $Ca_3Ti_2O_7$ supercell and (ii) three Na ion substituted for three Ca ion per supercell (where 192-atoms cell corresponds to a supercell).

3. Results and discussion

The Crystal Structure of $Ca_3Ti_2O_7$ is shown in Fig. 1(a). The XRD patterns of CTO and CNTO samples after the Rietveld refinements are shown in Fig. 1(b). All reflections can be indexed using the perovskite structure (space group $Ccm2_1$ (No.36)) for CTO and CNTO. No trace of peaks due to impurity phases was found. Refined crystal structural parameters are given in Table 1. As can be seen from this table, Ti–O bond lengths showed a decreasing trend after Na-doping. Shrinkage of the unit cell can be attributed to the fact that the size of the mixed Ca/Na site is smaller than that of the Ca site. The slight increase of $Ti-O_1-Ti$ bond angle may be attributed to the corresponding interatomic stress adjustment [17]. The changes in bond lengths and bond angles reflect that the TiO_6 octahedral tilting behavior was modulated after Na doping. As the octahedral tilting behavior is related to ferroelectricity, the electrical properties of these samples were then investigated.

One of the key characteristics for ferroelectric materials is their ability to reverse their polarization dipoles with the application of an external electric field, which could be demonstrated by a hysteresis loop of electric polarization versus biased electric field (P-E). P-E loop measurements are performed by applying an ac biased voltage to a capacitor comprised with metal/ferroelectrics/metal. With the application of ac electric field that exceed the coercive field of the ferroelectric material, the measured electric displacement would include contributions from the ferroelectric polarization switching, leakage current, and dielectric displacement. P-E loops and displacement currents recorded at room temperature using different voltage at a fixed frequency of 100 Hz are presented in Fig. 2 (a) and (b). When the electric filed is ramped to about 50 kV/cm, the displacement current of the CNTO sample exhibits an obvious increase, giving rise to a peak in the I_s-E curve (as indicated by the green arrow). If the applied electric field is unable to reverse the polarization, the peak in the displacement current could not be observed. Since the displacement current peak can represent the ferroelectric domain switching [18], appearance of such peaks demonstrates the occurrence of polarization switching in the CNTO sample and confirms its ferroelectricity [19]. For the CTO sample, the displacement current does not show any displacement peak until the applied electric field is ramped to 120 kV/cm. The coercive field of CTO determined from the current peak position is estimated to be ~120 kV/cm, which agrees with the previous report [8]. While the coercive field of CNTO is estimated to be a much-reduced value of about 50 kV/cm.

From the report of Ca-site Sr doped CTO single crystals and ceramics [8,10], Sr doping induced dramatically the decrease of remnant polarization in CTO samples, and the lower polarization was ascribed to a smaller amplitude of octahedral rotation and tilt, but the coercive field shows different trend. The reasons for the coercive filed decreasing varies from lattice strain, domain structure, defect state, and some other factors. For example, it has been reported lattice imperfections can cause low coercive field in $Ca_3Ti_2O_7$ films and the coercive field of $Pb(Zr_{0.55}Ti_{0.45})O_3$ film was

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[1] The purpose of identifying the equipment in this article is to specify the experimental procedure. Such identification does not imply recommendation or endorsement by the National Institute of Standards and Technology.