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Centrosymmetric tetragonal tellurium doped calcium copper titanate and its dielectric tunability

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ABSTRACT

Calcium copper titanate on doping Te^{4+} at Ti^{4+} sites transformed structurally to centrosymmetric tetragonal double perovskite. Indeed selected area electron diffraction studies carried out on Te doped ceramics corroborate the refined X-ray diffraction data. The dielectric tunability obtained as a function of applied DC field in Te doped calcium copper titanate ceramics was superior to that of undoped samples.

1. Introduction

Perovskite (ABO_3) is one of the most common oxide structures and is composed of a three-dimensional framework of corner-sharing BO_6 octahedra. The ideal ABO_3 structure is cubic, but often distortion is introduced in the system through the tilting of BO_6 octahedra in the rigid corner-sharing framework. A standard notation developed by Glazer [1,2] describes this octahedral tilting through the rotation of the BO_6 octahedra about the three orthogonal Cartesian axes. When the A-site cation is too small for the cavity, an equivalent amount of octahedral tilting ($a^+a^+a^+$) can occur giving rise to A-site-ordered double perovskite ($Im\bar{3}$ space group symmetry) with the general formula $AA'_3B_4O_{12}$. In this type of crystal structures A and A′ sites have two different oxygen coordinations with 1:3 ratio. The A cations (alkali metals, alkaline-earth metals or lanthanides) are accommodated in a 12-fold-coordinated oxygen cage while the A′ cations (Jahn–Teller distorted transition metal ions) have a square-planar coordination of oxygen units that are aligned perpendicular to each other. The stabilization of Jahn–Teller cations at the A′ sub-lattice for most of the reported compounds [3–7] needs high pressure ($\sim$11 GPa) and temperature ($\sim$1300 K) during synthesis. Among the many investigated compounds, $CaCu_3Ti_4O_{12}$ [8–10] and $CaCu_3Ru_4O_{12}$ [11,12] are the only known A-site-ordered perovskites that could be prepared at ambient pressures.

$CaCu_3Ti_4O_{12}$ (CCTO) has a double perovskite unit cell, with Ca/Cu at the A/A′ distorted transition sites and Ti at the B sites [13]. Owing to the tilt of the TiO_6 octahedra, the A′ atoms are coordinated with four oxygen atoms forming a square with a Cu atom at the center. The A atoms adopt a bcc arrangement with 12-oxygen icosahedral environment. Ever since the first report appeared on the exceptionally high dielectric constant ($\sim 10^5$) of calcium copper titanate ($CaCu_3Ti_4O_{12}$) [14–16], the origin of it in macroscopically non-polar materials like CCTO has been a topic of active research. Although there have been several investigations, no consistent picture has emerged to date [17–23]. However, dipoles arising due to off-center displacements of Ti-ions, presence of conducting grains [24,25] and non-conducting grain boundaries [26,27] (interlayer barrier capacitance mechanism) are the most promising and convincing mechanisms to explain the incident of high dielectric constant. Based on neutron diffraction data, there is an evidence to show that collective ordering of local dipoles [28] could be a source of high dielectric constant. But nevertheless, there is an alternative way of looking at the problem from the cation non-stoichiometry in which pure CCTO ceramics are associated with heterogeneous microstructures having semiconducting grains (having compositional deviation owing to non-stoichiometric Ca–Cu anti-site disorder and mixed valence state of B-site atoms) and insulating grain boundaries (having smaller or no deviation in stoichiometry) [29]. A more recent report based on conductive Atomic Force Microscopy (c-AFM) studies on CCTO ceramics claims the presence of conducting grain boundaries, thus proposing the presence of a “percolation conducting network at the grain boundaries with intra-grain insulating interfaces” [30,31].

Interestingly, there was also a report on the uncertainty in the determination of the crystal structure of the perovskite compound $CaCu_3Ti_4O_{12}$ [32]. According to this report, there exist pronounced

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Bragg peak asymmetries in the observed X-ray diffraction patterns that should not be present in commonly accepted cubic crystal structure of $CaCu_3Ti_4O_{12}$ described by the space group $Im\bar{3}$. The asymmetries could be explained based on different structural models assuming the coexistence of two phases with different lattice constants. There are other reports on this group of compounds which reveal that in addition to Jahn–Teller cations such as Cu^{2+} cations with other ionic radii and oxidation states could be stabilized at the A′ sites. These double perovskite compounds provide opportunities to observe intriguing properties due to the additional $A-A'$, $A'-B$ and $A'-B$ interactions through the valence-variable ions at both A′ and B sites. Thus, there could be a microscopic origin for the observed dielectric properties as opposed to the macroscopic/microstructural models described above.

These aforementioned reports in the literature motivated us to explore the possibilities of partially replacing Ti^{4+} by Te^{4+} and its influence on physical properties of CCTO ceramics. Tellurium (Te) has usual oxidation state of (IV) same as that of titanium (Ti). Tellurium being a p-block element, like Pb^{2+} and Bi^{3+}, Te^{4+} tends to be in distorted environment according to 2nd order Jahn–Teller effect. The two electrons in 5s orbital retain “stereo-chemically active lone pair” which induces asymmetry in the electron cloud distribution. In most common perovskite compounds, this lone pair electrons of cations (Pb^{2+}, Bi^{3+}) give large ferroelectric polarization caused by the dumbbell-like extrusion of the electron density of the $6s^2$ filled subshell on one side of the cation. The electronic configuration of Te^{4+} is [Kr] $4d^{10}5s^25p^0$ and Ti^{4+} is [Ar] $3s^03d^0$. The presence of the $5s^2$ lone pair electrons in Te^{4+} leads to a change in the bond length between the cation and oxygen ion which may enhance the distorted polarization in the compound. Therefore, Te^{4+} doping on Ti^{4+} sites was carried out to visualize its effect on the physical properties (electrical) of CCTO ceramics. In this paper, we report our investigations into the structural aspects of the Te^{4+} doped CCTO compound ($CaCu_3Ti_{4-x}Te_xO_{12}$, CCTTO) along with its nonlinear dielectric behavior.

2. Experimental details

Polycrystalline samples of $CaCu_3Ti_{4-x}Te_xO_{12}$ ($x=0$, 0.05, 0.1, 0.2) were synthesized via solid-state reaction route using $CaCO_3$ (99.37% Aldrich), CuO, TiO_2 and TeO_2. Stoichiometric amounts of these raw materials were mixed in an agate pestle and mortar. For homogenization, the mixture was ball-milled for 3–4 h. This powder was initially heated at 600 °C/6 h. Subsequently, it was cooled down to room temperature at a rate of 2 °C/min and again ground well for 3–4 h to further homogenize the mixture. Thus obtained powder was subjected to calcination at 980 °C/8 h and cooled down to room temperature. X-Ray powder diffraction studies were carried out to confirm the phase formation. The structural analyses were carried out by the Rietveld and Pawley method with the program Jana-2006 and EXPGUI. The prediction of perovskite crystal structure and stability, including the tilt angle of the B-site octahedra, has been done using the software program SPuDS (Structure Prediction Diagnostic Software) [33–35]. The CCTO and CCTTO nanoparticles were probed using conventional transmission electron microscopy (TEM). Selected-area electron diffraction (SAED) and high-resolution TEM (HRTEM) studies were done using a Tecnai T-20 Super Twin microscope equipped with a LaB_6 thermionic emission, operating at 200 kV. Samples for TEM investigations were prepared by dispersing the powdered samples in isopropyl alcohol and was drop-casted the suspension on a carbon-coated copper grid.

The powders of CCTO and CCTTO were cold-pressed (at room temperature) to obtain pellets of 8 mm in diameter and sintered at 1050 °C/10 h. The density of sintered pellets was in the range of 95–98% as determined by the Archimedes method. The capacitance and dielectric loss were monitored as a function of frequency 100 Hz–100 MHz) at a signal strength of 0.2 V and at different DC bias fields using Agilent 4294A Impedance analyzer. The dielectric constant values were evaluated by taking the dimensions of the sample into account. Two-probe capacitor configurations were used for making the present measurements.

3. Results and discussions

The XRD patterns obtained for $CaCu_3Ti_{4-x}Te_xO_{12}$ ($x=0$, 0.05) powders calcined at 980 °C/8 h shown in Fig. 1a and b could be indexed to a pure cubic phase associated with the space group $Im\bar{3}$ (according to JCPDS 75-2188). The cubic phase refinement for undoped CCTO was done on the basis of the structural data available for the known cubic double perovskite phase in ICSD-database PDF No. 164546. The powders of $CaCu_3Ti_{4-x}Te_xO_{12}$ samples where in $x=0.1$, 0.2 (Fig. 1c and d) calcined at 980 °C/8 h in air could not be indexed to cubic phase. The insets in Fig. 1c and d, clearly demonstrate a split in the Bragg peak corresponding to (400). By taking this peak split or shoulder into consideration, we could index the XRD pattern of CCTTO1 ($x=0.1$) and CCTTO2 ($x=0.2$) to a tetragonal cell. The profile fit analysis in Jana2006 software shows the existence of tetragonality. Phase analysis and crystal structure prediction were done by combining Rietveld method based on the X-ray diffraction patterns and software package entitled SPuDS. The structural stability of a compound with a given composition was evaluated by comparing the quantity, referred to as the global instability index (GII),

$$GII = \left\{ \frac{(v_i^{ox} - v_i^{cal})^2}{N} \right\}^{1/2},$$

where, N is the number of atoms in the formula unit and and are respectively the formal valence and calculated BVS for the ith ion. Table 1 shows the global instability indices calculated for $Ca_{0.25}Cu_{0.75}Ti_{0.95}Te_{0.05}O_3$. The predicted value of GII for space group $I4/mmm$ is the lowest. Therefore, the tetragonal phase was refined by using a starting model of centric $I4/mmm$ space group associated with the lattice parameters $a=6.947$ Å and $c=7.3939$ Å. The calculated GII values different space groups are elucidated in Table 1.

The initial assigned atomic positions are Ca (0, 0, 0), Cu1 (0, 0, 0.5), Cu2 (0.5, 0, 0), Ti (0.25, 0.25, 0.25), O1 (0.2629, 02629, 0) and O2 (0, 0.2829, 0.3214). The primitive cell model is depicted in Fig. 1e. The Rietveld results gave a good fit with $R_{wp} \approx 4.36\%$ and $R_p \approx 3.36\%$ for $CaCu_3Ti_{4-x}Te_xO_{12}$ ($x=0.2$). The structural parameters after refinement of $CaCu_3Ti_{4-x}Te_xO_{12}$ ($x=0$, 0.1 and 0.2) are listed in Table 2. The XRD patterns recorded for CCTTO1 ($x=0.1$) and CCTTO2 ($x=0.2$) fit well with the structural model of $I4/mmm$ symmetry. The results obtained for structural refinement for CCTTO ($CaCu_3Ti_{4-x}Te_xO_{12}$, $x=0.1$, 0.2) confirm the presence tetragonal phase. $\Delta 2\theta$ calculated from the peak splitting of (400) indicates the tetragonality of the ceramic samples (Fig. 1) at room temperature. $\Delta 2\theta$ increase from CCTTO1 ($\sim 0.20°$) to CCTTO2 ($\sim 0.29°$) supporting the XRD refinement.

The structural refinement results of CCTTO2 obtained for perovskite structure with the general formula shows that 12-fold coordinated A-site (2a Wyckoff atomic position) occupied by Ca has 8 $Ca-O$ with a bond length of 2.5715(8) Å are shorter than $Ca-O$ bond length in pure CCTO and the remaining 4 $Ca-O$ bonds with a bond length of 2.8256(11) Å are longer than that of pure CCTO. Existence of two different bond lengths indicates that the coordination around the A-site is a distorted icosahedral coordination. The 12 co-ordination environment gives the Bond Valence