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Original Article

CdO-CuO-TiO_2 ternary dielectric systems: Subsolidus phase diagram and the effects of Cu segregation

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ABSTRACT

Valence of Cu cations and Cu segregation of $CdCu_3Ti_4O_{12}$ ceramics are initially examined by establishing the subsolidus phase diagram of $Cd_{1\text{-}x}Cu_{3+x+2y}Ti_{4\text{-}y}O_{12}$ ($-7 \leq x \leq 0.07$, $-1.333 \leq y \leq 2.91$) systematically. Different from CaO-CuO-TiO_2 system, the co-existence of hexagonal and orthorhombic $CdTiO_3$ phases is observed in the line between $CdTiO_3$ and CuO. Basing on the obtained phase diagram, three typical ceramics with Cu-equal ($CdCu_3Ti_4O_{12}$), Cu-rich ($Cd_{0.930}Cu_{3.070}Ti_4O_{12}$), and Cu-poor ($Cd_{1.137}Cu_{2.863}Ti_4O_{12}$), showing high dielectric constant, are chosen as target samples to investigate the role of Cu valence and segregation in dielectric behaviors. Cu^{3+} ions, rather than Cu^+ ones as reported previously, forms in the grain to act as the hopping charge carriers as demonstrated by X-ray photoelectron spectroscopy and High-energy X-ray absorption Near Edge Structure. This work would give a hint in tuning the stoichiometry for achieving more fascinating structures and properties in new ceramic material design.

1. Introduction

Perovskite $CaCu_3Ti_4O_{12}$ (CCTO) belongs to one class of important ceramics and has shown giant dielectric constant ($\varepsilon' > 10^4$) in a wide temperature region (*e.g.* approx. 100–600 K) [1]. Many great efforts have been devoted to study CCTO-based/related materials [2–6]. It is well established that when Ca sites in CCTO-type ceramics are substituted by several other metal ions, like $Bi_{2/3}$ [7], $Na_{1/2}Y_{1/2}$ [8], Dy [9], $Na_{1/3}Bi_{1/3}$ [10], or $Ln_{2/3}$ (Ln = lanthanide), high dielectric constant could also be retained [11]. Simultaneously, some mechanisms have been proposed to explain the origin of abnormal dielectric behaviors for CCTO, which include the models of barrier layer in twin boundary [12], internal barrier layer capacitors (IBLC) [13,14], surface barrier layer capacitors (SBLC) [15,16], and nanoscale barrier layer capacitors (NBLC) [17]. Among these, IBLC model, based on semiconducting grains that were surrounded by insulating boundaries, is widely accepted. Capsoni et al. have asserted that the existence of semiconducting grains is attributed to Cu^{3+} in the bulk, and that CuO segregation accounts for the improved giant permittivity of CCTO [18]. Although barrier layer capacitor (BLC) effect has been used to explain the high dielectric constant, either the origin of conductive-grain-based BLC or the impacts of CuO segregation (located within the grain boundaries) on dielectric response is still unclear, likely because (i) CCTO-based materials belong to the multi-component systems with high possibilities of formation of different phases or intermediates, and (ii) the lower-valence Cu^+, other than Cu^{3+}, has widely been considered as an important contribution to the grain conduction in such sorts of material systems [19,20].

Thus, it is fundamentally important to build a clear picture for well understanding the varied Cu-content in the ceramics' grains and/or boundaries and the effect of Cu valence on the dielectric behavior. In this regard, phase diagram strategy is a powerful tool to tune the stoichiometry by deliberately introducing phase segregation (*e.g.* the presence of Cu-based phases) at grain boundaries and in turn controlling the deficiency of grains [21–24]. Up to date, only a few investigations have been reported on the subsolidus phase relationship of CCTO-related systems, mainly in CaO-CuO-TiO_2 and SrO-CuO-TiO_2 systems [25–28], but no further investigations about the influences of valence variations and phase segregations on dielectric properties. As an important member of CCTO-related sorts, $CdCu_3Ti_4O_{12}$ (CdCTO)

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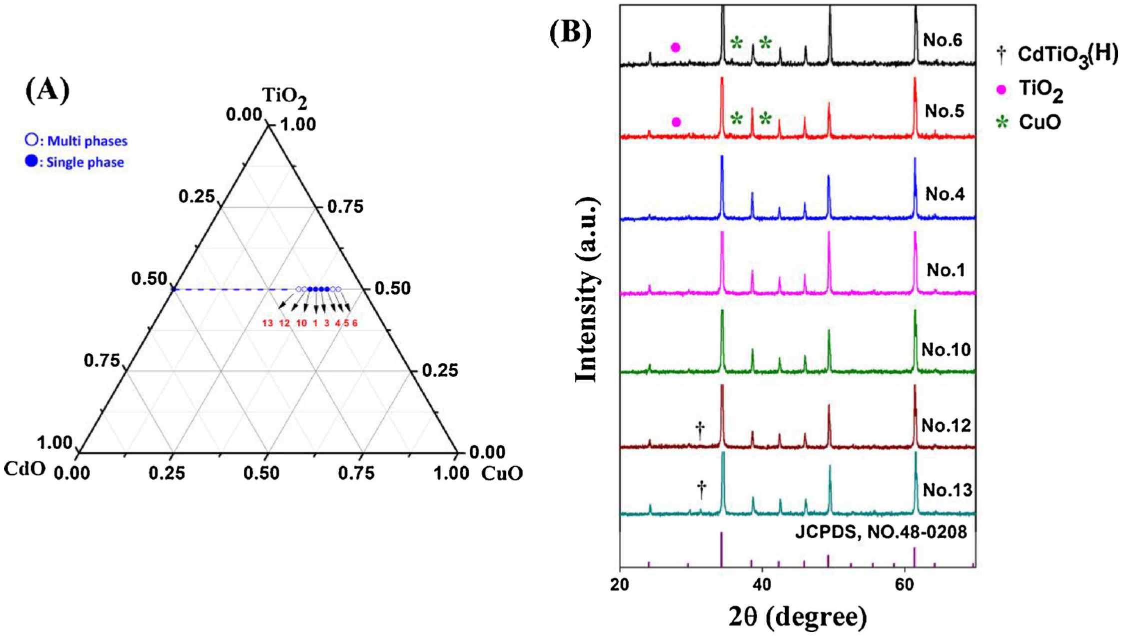

Fig. 1. (A) Phase diagram of $Cd_{1-x}Cu_{3+x}Ti_4O_{12}$ ($-0.137 \le x \le 0.059$) and (B) corresponding powder XRD patterns of samples.

also exhibits an interesting high permittivity (ε' can be up to 9000) [29], while the site occupancy factors (SOF) of Cd/Cu sites, Cu segregation, and the valence of the cations in CdCTO ceramic are not accessible in literature reports [30]. All these are highly dependent on the determination of subsolidus phase diagram of CdO-CuO-TiO_2 system. Unfortunately, the phase diagram of CdO-CuO-TiO_2 is not well established. Considering that CdO and CaO have the different physicochemical properties, especial the thermodynamic feature, the phase behavior of CdO-CuO-TiO_2 could not be exactly same as that of CaO-CuO-TiO_2 system.

In this work, we synthesized $CdCu_3Ti_4O_{12}$-based ceramics *via* solid-state reaction and further build up the CdO-CuO-TiO_2 subsolidus phase diagram. Through carefully tuning the Cu contents in ceramics by controlling the cation stoichiometry to form CuO at grain boundaries and to produce Cu^{3+} species in the grains, we established the relationship among the segregation of Cu, Cu^{3+} ions in the grain and dielectric properties of $CdCu_3Ti_4O_{12}$-based ceramics and further discussed the contribution of CuO segregation to IBLC mechanism, which had been long-term debated.

2. Experimental procedure

2.1. Sample preparation

Ceramic samples with various stoichiometric ratios (see Table S1) in the CdO-CuO-TiO_2 ternary systems were prepared by a conventional solid state reaction method. Chemicals, CdO (99.9%), CuO (99.9%), and TiO_2 (99.99%) were used as raw materials, which were weighted carefully, milled thoroughly in an agate mortar, and then pressed into pellets by an uniaxial press. The pressed pellets were calcined at 950 °C for 24 h in air. Then, the pellets underwent a calcination process at 950 °C for 12 h in air, and such a process was repeated twice to reach a sufficient reaction.

2.2. Sample characterization

Powder X-ray diffraction (XRD) data of the samples were collected by a Rigaku Miniflex apparatus (Cu Kα, λ = 0.15418 nm). High purity KCl was used as an internal standard for peak positions calibration. Structural refinement was performed using General Structure Analysis System (GSAS). Raman spectra were collected on a Raman spectrophotometer (T64000) with the laser beam of 532 nm. X-ray photoelectron spectroscopy (XPS) analysis was carried out with an ESCALAB250 equipment. Charging shift was calibrated using C1s photoemission line at a binding energy of 284.8 eV. Microstructures and element contents of the ceramics were examined by scanning electron microscope (SEM) and energy dispersive spectroscopy (EDS) on a HITACHI SU8020 analyzer. High-energy X -ray Absorption Near Edge Structure (XANES) of the Cu K-edge were measured at the beamline BL14W1 (Shanghai Synchrotron Radiation Facility). A standard Cu foil was introduced to realize energy calibration. XANES spectra of Cu K-edge were recorded from 8950 eV to 9050 eV. The software package IFEFFIT was used to analyze and fit the experimental data.

2.3. Performance measurements

Dielectric properties of the samples were measured in a frequency range from 10 Hz to 20 MHz using a Novocontrol Concept 41 dielectric/impedance spectrometer at an AC voltage of 1 V.

3. Results and discussion

3.1. Determination of sub-solidus phase diagram of CdO-CuO-TiO_2 ternary systems

Samples with nominal compositions of $Cd_{1-x}Cu_{3+x+2y}Ti_{4-y}O_{12}$ ($-7 \le x \le 0.07$, $-1.333 \le y \le 2.91$) were prepared to set up the sub-solidus phase diagram and further to clarify whether stoichiometric $CdCu_3Ti_4O_{12}$ (CdCTO) compound is the only one equilibrium ternary phase. Many techniques could help to establish sub-solidus phase diagram for multiple component oxides. The accurate analysis of Powder X-ray diffraction (XRD) is widely used until now to investigate the phase composition and content, as well as determine the phase diagram [25,31,32]. Table S1 lists the information about phase contents of 30 samples with various nominal compositions in CdO-CuO-TiO_2 ternary systems obtained by XRD analysis. Based on the information of phase contents, we constructed a phase diagram of CdO-CuO-TiO_2 system. Phase diagram and XRD patterns for the corresponding samples are shown in Fig. 1. The samples from No. 1 ($x = 0$) to No. 4 ($x = 0.036$)