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Effects of strontium/lanthanum co-doping on the dielectric properties of $CaCu_3Ti_4O_{12}$ prepared by reactive sintering

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ABSTRACT

The extremely high dielectric constant of the cubic perovskite $CaCu_3Ti_4O_{12}$ (CCTO) has attracted increasing attention for a variety of capacitive elements in microelectronic device applications. In this research, the influence of Sr and La replacing Ca and Cu, respectively, to simultaneously controlling the intrinsic properties of grain boundaries in a co-doped CCTO ceramic has been investigated. The preparation was done using high purity compounds milled and mixed by mechano-synthesis and further consolidated by reactive sintering without calcination. Characterization by XRD confirmed the formation of single-phase CCTO ceramic and a residual amount $CaTiO_3$. The microstructure and composition analyzed by SEM/EDX showed a smaller grain size for the co-doped CCTO. Impedance measurements indicated the smallest dielectric loss for the co-doped ceramics compare to pure and single-doped CCTO, while reaching a higher dielectric permittivity than single-doped ceramics. The CCTO-SrLa sample also showed high thermal stability of the dielectric permittivity between 100 and 470 K, and the lowest loss between 200 and 300 K. This behavior was attributed to the lower bulk resistance exhibited by the co-doped sample.

1. Introduction

Ceramics with colossal dielectric constant (CDC) have been intensively studied for their potential use as supercapacitors and in microelectronic applications [1–3]. One of the interesting candidates is the ceramic compound, calcium copper titanate, $CaCu_3Ti_4O_{12}$ (CCTO) that has attracted the attention of many researchers due to its CDC. CCTO is a well-known ceramic material that has a dielectric constant in the order of 10^4 and a dielectric loss of around 0.1 at 1 kHz; and a nonlinear current voltage characteristic up to 10^6 Hz over a broad temperature range (from 100 to 600 K) [4]. CCTO is a body-centered cubic oxide with four $ATiO_3$ units per primitive cell, where Ca^{2+} and Cu^{2+} ions reside in the A-sites while Ti cations occupy the B-sites. The size difference between the A-site causes a substantial tilting in the TiO_6 octahedra, leading to a body centered cubic super cell [5]. Several researchers have tried to explain the origin of giant dielectric constant of this material by different models. Sinclair et al. [6] demonstrated that CCTO ceramic consists of semiconducting grains with insulating grain boundaries. Thus, the higher dielectric constant would come from an internal-barrier-layer-capacitance (IBLC) effect. Ramirez et al. [7] proposed that the collective ordering of local dipole moments is the source of unusual high dielectric response and explained it by a highly polarizable relaxational excitations model. On the other hand, Lunkenheimer et al. [8] considered the contact-electrode depletion effect as an explanation for the high value of the dielectric constant.

In order to promote the practical applications of CCTO, many studies have been done to reduce the dielectric loss in this material. Much of this work is based upon cation substitution at A- or B-sites to improve the dielectric properties and extend the understanding on the origin of the CDC [9–18]. Different authors [11–13] have doped CCTO by adding La^{3+} in Ca position and showed a reduction of the real part of the dielectric constant (ε_r) and also of the dielectric loss (tanδ) compared to pure CCTO. Similarly, Xue et al. [14] doped CCTO by using Sr in Ca position, which decreases the dielectric constant but with a minor reduction of the dielectric loss. Analogous results were published by Vangchangyia et al. [16] and Yang et al. [15].

Recently, co-doping has been established as a new strategy to suppress the grain growth and grain boundary resistivity [19–24] with a significant impact on the dielectric properties. The strategy behind co-doping is to simultaneously suppress the grain growth and to enhance the grain boundary resistivity in order to reduce the dielectric loss [19] by doping different sites in the CCTO crystalline structure. Boonlakhorn

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et al. reported promising results by using combinations of dopants in the Ca^{2+} and Cu^{2+} sites like for example Sm/Mg [19], Y/Mg [20] and Yb/Mg [21].

Alternatively, reaction-sintering has been used to prepare CCTO obtaining a very similar dielectric behavior compared to those prepared by conventional synthesis [25,26]. Rubia et al. studied Hf-doped CCTO ceramics prepared by reaction sintering, demonstrating a higher incorporation of the dopant during reactive sintering. Espinoza et al. [26] also used reactive sintering in CCTO powders milled in a Spex mill. They obtained similar dielectric properties to CCTO prepared by conventional solid state reaction, without an intermediate calcination step meaning a reduction of the energy required for the preparation of the ceramic.

In this communication, the dielectric properties of Sr/La co-doped CCTO, prepared by reactive sintering, were investigated and compared with results obtained for un-doped and single-doped CCTO with Sr and La. The aim of this work is the reduction of the dielectric loss to promote the use of CCTO ceramic in microelectronic applications.

2. Experimental procedure

The starting materials for the synthesis of CCTO powders were $CaCO_3$ (Merck, 99.95%), CuO (Sigma-Aldrich, 99.99%), and anatase-TiO_2 (Sigma-Aldrich, 99.8%). The corresponding stoichiometric amounts of precursor powders were weighed with the respective amounts of dopants La_2O_3 (Sigma-Aldrich, 99.99%), $SrCO_3$ (Sigma-Aldrich, 99.9%) to prepare pure and doped CCTO by high-energy mechano-synthesis in a Spex Dual Mill 8000D, which operates at 875 cycles per minute. Based upon preliminary experiments, the selected dopant concentrations and cation replacement were as follows: $Ca_{0.6}Sr_{0.4}Cu_3Ti_4O_{12}$, $CaCu_{2.85}La_{0.15}Ti_4O_{12}$, $Ca_{0.6}Sr_{0.4}Cu_{2.85}La_{0.15}Ti_4O_{12}$ and, pure $CaCu_3Ti_4O_{12}$. The samples prepared for each composition were named: CCTO-Sr, CCTO-La, CCTO-SrLa and CCTO, respectively.

The powders were wet milled with ethanol as milling media during 2 h using stainless steel vials and balls, with a ball to powder ratio (BPR) of 5:1. Subsequently, reactive sintering was used to simultaneously obtain the CCTO phase and to consolidate the powders. Thus, the milled powders were compacted into discs by uniaxial pressing and sintered in air at 1050 °C for 18 h. The samples after sintering had a thickness of 1.6 mm and a diameter of 8.8 mm. Sintered pellets were characterized by X-ray diffraction (XRD) in a Bruker D8 diffractometer using CuKα radiation. The data were collected at room temperature with a step size and scan rate of 0.01° and 0.1 s, respectively. The X-ray tube was operated at 40 kV and 30 mA. Rietveld refinement of XRD patterns was performed using TOPAS software, for which pseudo-Voigt function was chosen as a profile function. In all refinements, the good of fitness (GOF) parameter was smaller than 1.8. The microstructure and composition were studied by field emission scanning electron microscopy (FESEM, FEI microscope, model Quanta 250) with an EDAX detector for energy-dispersive X-ray spectroscopy (EDX). Prior to SEM/

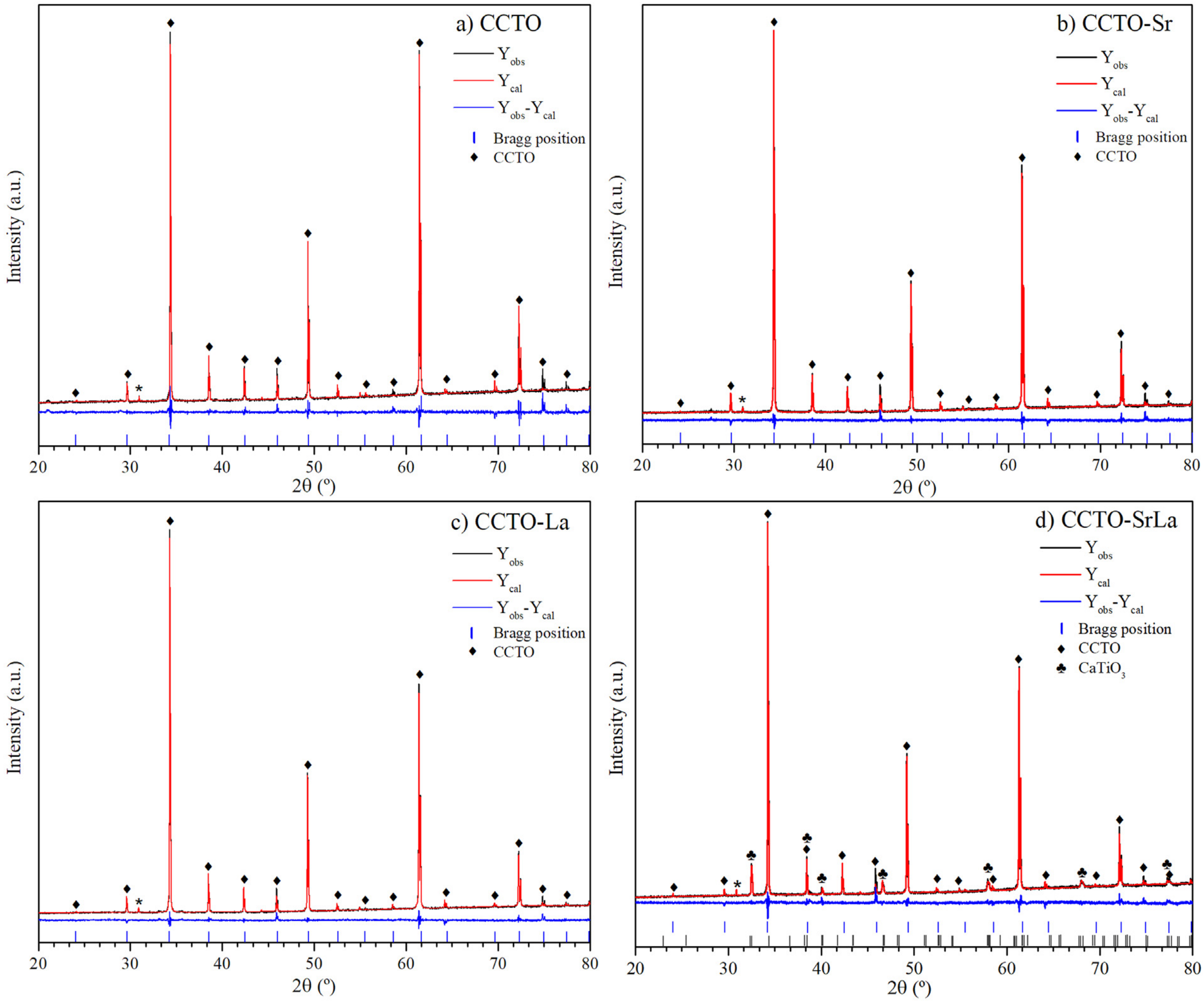

Fig. 1. Structure refinements of pure and doped CCTO samples: a) pure CCTO, b) CCTO-Sr, c) CCTO-La, and d) CCTO-SrLa. (*) Peaks corresponding to K_β reflection of CCTO (022).