Dielectric behaviour of Hf-doped $CaCu_3Ti_4O_{12}$ ceramics obtained by conventional synthesis and reactive sintering

M.A. de la Rubia [a,*], P. Leret [a], A. del Campo [a], R.E. Alonso [b], A.R. López-Garcia [b], J.F. Fernández [a], J. de Frutos [c]

[a] Electroceramic Department, Instituto de Cerámica y Vidrio, CSIC, Kelsen 5, 28049 Madrid, Spain
[b] Physics Department, Fac. Cs. Exactas, Universidad Nacional de la Plata, Calles 115 y 49, 1900 La Plata, Argentina
[c] Física Aplicada a las Tecnologías de la Información, ETSI Telecomunicación (UPM), Ciudad Universitaria, s/n, 28040 Madrid, Spain

Abstract

$CaCu_3(Ti_{4-x}Hf_x)O_{12}$ ceramics ($x = 0.04$, 0.1 and 0.2) were prepared by conventional synthesis (CS) and through reactive sintering (RS), in which synthesis and sintering of the material take place in one single step. The microstructure and the dielectric properties of Hf-doped CCTO (CCTOHf) have been studied by XRD, FE-SEM, AFM, Raman and impedance spectroscopy (IS) in order to correlate the structure, microstructure and the electrical properties. Samples prepared by reactive sintering show slightly higher dielectric constant than those prepared by conventional synthesis in the same way than the pure CCTO. Dielectric constant and dielectric losses decrease slightly increasing Hf content. For CCTOHf ceramics with $x > 0.04$ for CS and $x > 0.1$ for RS, a secondary phase $HfTiO_4$ appears. As expected, the reactive sintering processing method allows a higher incorporation of Hf in the CCTO lattice than the conventional synthesis one.
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1. Introduction

Recently, the compound $CaCu_3Ti_4O_{12}$ (CCTO) has attracted much interest due to its high dielectric constant, (up to 10^5), which is almost frequency independent up to 10^6 Hz and shows a good temperature stability in the range between 100 and 400 K.[1] The main disadvantage of this material is the high dielectric losses that limits its use. Although materials with very high dielectric constant are generally ferroelectric or relaxor, CCTO is centrosymmetric in the temperature range under study and it does not present phase transition. The system presents distorted cubic perovskite structure with Im3 space group and a lattice parameter of 7.391 Å. The TiO_6 octahedron is tilted and, as a consequence, the coordination of Ca and Cu cations is altered, producing a square planar arrangement of the oxygen around the Cu^{2+} cations and a 12-coordinate icosahedral environment for Ca.[2]

The origin of the high dielectric constant of CCTO is still a source of controversy. It is in doubt if the high dielectric constant is due to intrinsic effects such as stoichiometric changes, oxygen vacancies, Cu segregation, and different oxidation states of Ti and Cu or due to extrinsic effects related to the microstructure, as stated by the Internal Barrier Layer Capacitance (IBLC) model. According to this model the material can be considered as an ensemble of n-type semiconducting CCTO grains and insulating barriers, corresponding to a very thin Cu-rich secondary phase observed at the grain boundary.[3,4] This characteristic microstructure with semiconducting grains and insulating barriers (including domain boundaries and grain boundaries) gives place to electrostatic barriers at the grain boundaries which are responsible for the nonlinear current–voltage behaviour that this material presents. Oxygen vacancies may be proposed as a possible cause for the electron formation.[5] At room temperature, dc resistivity of undoped CCTO is principally determined by the grain boundary resistivity and therefore this resistivity depends on processing. In CCTO ceramics, a clear increase of the dielectric constant has been observed with sintering time due to the incorporation of the Cu-rich secondary phase into the CCTO

grains.[6] There are very few reports related to the impurity effect on CCTO. Based in the IBLC mechanism, HfO_2 can create new insulating barrier layers at the grain boundaries or inside grains, i.e. domain boundaries, resulting in a different microstructure and improved dielectric properties. In a very recent work, Yuan and Hark[7] prepared composites in the full range of compositions in the CCTO–HfO_2 system. Previously to the addition of HfO_2, CCTO was synthesized at $900\,°C$–$10\,h$ and then, mixtures of HfO_2 and CCTO were sintered at $1000\,°C$–$10\,h$. According with the authors the objective of this work is preparing CCTO–HfO_2 composites and not Hf-doped CCTO samples and in agreement all the identified phases in the composites prepared were CCTO and/or HfO_2. The authors point to abnormal grain growth that for composites with an HfO_2 content higher than $20\,wt.\%$ is suppressed although the dielectric constant of the CCTO phase remains constant.

The electrical properties of both doped and undoped CCTO depend as much on the raw materials as on processing.[8] Reaction sintering method has been used recently to prepare CCTO obtaining a very similar dielectric behaviour to those prepared by conventional synthesis.[9]

The ionic radii of Ti^{4+} and Hf^{4+} in octahedral coordination are different, $0.74\,Å$ and $0.84\,Å$, respectively. In ABO_3 perovskites, it is known that the nature of the B cation plays an important role in the resulting crystalline structure of these oxides. In these compounds it should be expected a competition between Ti–O and Hf–O bonds exists, as to both ionic radius of Ti^{4+} and Hf^{4+} and the covalence grade of the bonds are different.[10]

The aim of this work is to study Hf-doped $CaCu_3Ti_4O_{12}$ ceramics prepared by reaction sintering without an intermediate calcination step and by conventional synthesis and verify depending on the processing method which is the replacement of Ti by Hf in the CCTO lattice. Microstructural and dielectrical behaviour is compared with undoped CCTO.

2. Experimental procedure

Ceramic samples of $CaCu_3(Ti_{4-x}Hf_x)O_{12}$ ($x = 0.04$, 0.1 and 0.2) that correspond to the substitution of 1, 2.5 and 5 wt.% of TiO_2 by HfO_2 were prepared by two different synthesis routes: a conventional solid state reaction and by means of reaction sintering. Following the samples will be denoted as CS or RS and 1, 2.5 and 5 according to the wt.% replacement of Ti by Hf. In all cases, TiO_2 powder (rutile, 99.9%, Aldrich, $d_{50} = 0.5\,\mu m$), CuO (99.9%, Aldrich, $d_{50} = 3.3\,\mu m$), $CaCO_3$ (Aldrich, $d_{50} = 0.9\,\mu m$) and HfO_2 (98%, Aldrich, $d_{50} = 1.25\,\mu m$) were mixed in attrition mill for 3 h with zirconia balls using de-ionized water and 0.3 wt.% of Dolapix C64 as dispersant. The milled powders were dried and sieved through a 100 μm mesh.

Conventional solid state reaction consisted in the calcination at $900\,°C$–$12\,h$ of the milled mixture of raw materials in adequate amounts (synthesis of CCTO). Then the CS synthesized powder was attrition milled during 3 h (after milling $d_{50} = 0.8\,\mu m$). Dry and sieved powders were pressed into disks of 8 mm in diameter and 1.3 mm in thickness at 200 MPa by using 0.6 wt.% of polyvinyl alcohol PVA and 0.3 wt.% of polyethylene glycol

PEG as organic binders to favour the pressing step. The disks were sintered at $1100\,°C$–$32\,h$. In the reaction sintering method, RS, the synthesis and sintering of CCTO pellets were carried out in the same step at $1100\,°C$–$32\,h$. All thermal treatments were carried out with a heating and cooling rate of $3\,°C/min$. The density of the samples for both synthesis routes after sintering was $\geq 4.8\,g/cm^3$ (>95% of the theoretical density). Samples prepared by RS shrunk ~6% in diameter more than those prepared by CS ones. X-ray diffraction analysis was performed on a diffractometer X'Pert PRO of Panalytical using $CuK\alpha1$ radiation. RS samples were polished and thermally etched at $1000\,°C$ for 5 min. The microstructure was observed using a Hitachi SEM TM-1000, AFM characterization was carried out with a Solver Probe Microscope of NT-MDT equipped with the software NOVA 1238 and Raman characterization with a Confocal Raman microscope Alpha 300 of WITec Focus Innovations. The Raman laser excitation wavelength used was 532 nm with a power of 7.6 mW. To perform the electrical characterization, polished parallel disks were electroded with Pt by sputtering with a DSC-050 of BALTEC. Dielectric characterization was measured at RT in the range $10^{-2}\,Hz$–$1\,MHz$ in a Solartron 1296 dielectric interface.

3. Results and discussion

Fig. 1a and b shows the XRD patterns of the Hf-doped CCTO sintered samples (s) obtained by CS and RS processing methods, respectively. In Fig. 1A it is included too the XRD analysis for the calcined powders (c). In calcined powders, cubic perovskite CCTO phase (JCPDS 75-2188) is identified as the main phase and monoclinic HfO_2 one (JCPDS 74-1506) as secondary phase are identified. Diffraction peaks of HfO_2 become stronger with increasing Hf content. XRD analysis of the sintered samples (s) shows the presence of the cubic perovskite CCTO phase as the only phase for the CS-1 composition. In both CS-2.5 and CS-5 samples, pure CCTO is identified as the main phase and orthorhombic $HfTiO_4$ (JCPDS 40-0794) and CuO tenorite (JCPDS 41-0254) as secondary phases are identified. Diffraction peaks of $HfTiO_4$ become stronger with increasing Hf content. For RS-1 and RS-2.5 samples, CCTO is the only phase identified. For the composition with higher content of HfO_2 (RS-5) the same phases than in the case of CS-5 are identified, CCTO and $HfTiO_4$ and CuO as secondary phases. According to this result, the reactive sintering allows a higher incorporation of Hf in the CCTO lattice. CCTOHf compositions with Ti replacement by Hf $\geq 2.5\,wt.\%$ in CS processing method and $\geq 5\,wt.\%$ in RS one, give place to the appearance of $HfTiO_4$ as secondary phase. Therefore the solid solution limit of HfO_2 in CCTO is lower than the substitution of 5 wt.% of TiO_2 by HfO_2 when samples are prepared by RS.

CS of CCTO occurs in solid state because there is not unreacted TiO_2 nor CuO that can develop an eutectic liquid around $1000\,°C$[11] to assist sintering. However, in RS the elimination of the calcination step allows a possible reaction between CuO and TiO_2 at high temperature (~$1000\,°C$) to form the eutectic liquid that assists the first steps of sintering.