Materials Research Bulletin 48 (2013) 310–314

Contents lists available at SciVerse ScienceDirect

Materials Research Bulletin

journal homepage: www.elsevier.com/locate/matresbu

Effect of sintering in oxygen on electrical conduction and dielectric properties in $CaCu_3Ti_4O_{12}$

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ARTICLE INFO

Article history:
Received 4 August 2012
Received in revised form 7 October 2012
Accepted 17 October 2012
Available online 26 October 2012

Keyword:
A. Ceramics
B. Sol-gel chemistry
C. Impedance spectroscopy
D. Dielectric properties

ABSTRACT

$CaCu_3Ti_4O_{12}$ (CCTO) ceramics were sintered in air and in oxygen, and the oxygen pressures are 1 atm and 3 atm, respectively. The results of dc electrical conduction and dielectric measurement show that for the CCTO ceramics sintered in oxygen, leakage, grain conductivity and the low-frequency dielectric constant are greatly reduced; these changes of electrical properties may be attributed to the enhancement of activation energies for electrical conduction in grain. In addition, for the CCTO ceramics sintered in oxygen, in the spectra of dielectric loss the strong peaks appear in the low-frequency range, which may be attributed to the contact-electrode effect on ceramic surface.

1. Introduction

A giant dielectric constant (larger than 10^4) with good temperature stability was discovered in cubic-perovskite compound $CaCu_3Ti_4O_{12}$ (CCTO) [1,2]. Unlike some other ferroelectric materials with perovskite structure, such as $BaTiO_3$, $CaTiO_3$ and $Pb(Zr_xTi_{1-x})O_3$, the spontaneous long-range ferroelectric order is not observed in CCTO. Till now, many mechanisms have been put forward, among which, the internal-boundary-layer-capacitor (IBLC) model is the most widely accepted one for the ceramic of CCTO [3–5].

According to the IBLC model, in CCTO ceramic the dielectric response may be contributed from the extrinsic polarization at the insulating grain boundary between the n-type semiconducting grains, thus the change on electrical properties of grain and grain boundary can make a considerable impact on dielectric behaviors. For example, it is reported that the dielectric constant can be greatly reduced if grain resistivity is enhanced [6–10], and the composition change at grain boundary also makes a great impact on dielectric properties [11–17].

It is noticed that the electrical properties in grain and at grain boundary are both related to oxygen vacancies. For example, some results of experiments and calculation show that the conducting electrons in grain may be contributed from the ionization of oxygen vacancies, in this process, the electrons released from neutral oxygen vacancies will be accepted by Ti^{4+}, and the conductive Ti^{3+} ions are formed [18–20]. Recently, Yu et al. [21] and Zhang et al. [22] also reported their interesting works which depict the impacts of oxygen sintering atmosphere on the electrical properties at grain boundary in CCTO ceramics.

In the present work, the CCTO ceramics were sintered in air and in pure oxygen with different pressures. It is shown that the sintering in oxygen greatly impacts the electrical conduction and dielectric properties, which may be attributed to the change of electronic structures *in grain*.

2. Experimental methods

The $CaCu_3Ti_4O_{12}$ ceramics were synthesized by the sol–gel method. The raw materials are $Ca(NO_3)_2{\cdot}4H_2O$, $Cu(NO_3)_2{\cdot}3H_2O$, butyl titanate ($C_{16}H_{36}O_4Ti$), ethanol and glacial acetic acid. All of the reagents used in the experiments are of analytical grade.

The precursor dry gel was firstly prepared according to the procedures reported in Ref. [23]. The gel was annealed in air at 700 °C for 2 h to remove the organic materials, and then the obtained powders were calcined in air at 1035 °C for 48 h. Finally, under the pressure of 20 MPa, the powders were pressed into pellets with diameter of 15 mm, and the pellets were sintered in air and in pure oxygen at 1080 °C for 6 h, the pressures of oxygen are 1 atm and 3 atm, respectively.

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http://dx.doi.org/10.1016/j.materresbull.2012.10.029

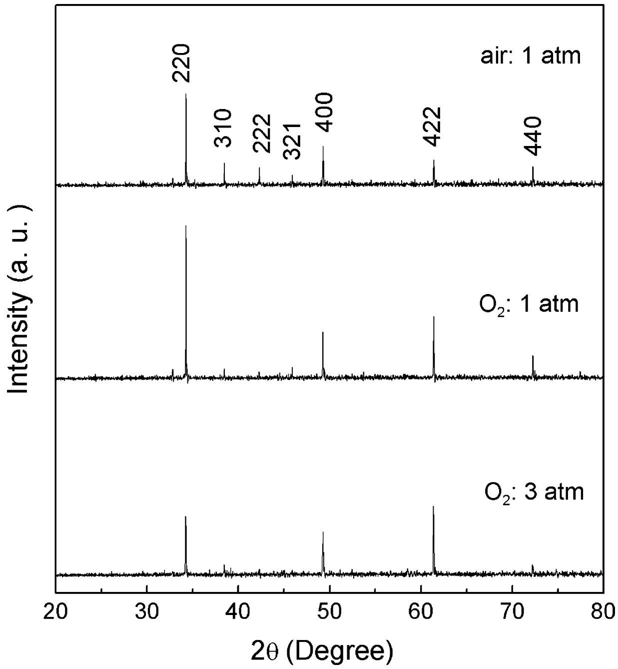

Fig. 1. The XRD patterns for the CCTO ceramics sintered in air and in oxygen with different pressures.

The composition and structure were characterized by X-ray diffraction (XRD, D8-Advanced) technology with CuKα radiation in a 2θ scanning from 20 to 80°. The surface morphologies and composition distribution of the ceramics were collected by a scanning electron microscopy (SEM, FEI Sirion Field Emission Gun). The dc current density-electric field intensity (*J*–*E*) plots were collected at room temperature (*RT*) by an electrometer (Keithley 6517A) with a computer-controlled program. The complex plane of impendence (Z^*) plots and the spectra of dielectric constant and loss were collected at different temperatures (*RT*, 320 K, 340 K, 360 K and 380 K) by using a precision impedance analyzer (WK

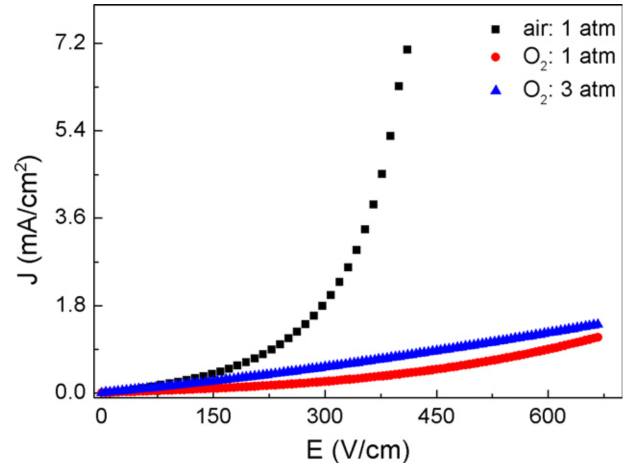

Fig. 3. The room-temperature dc *J*–*E* curves for the CCTO ceramics sintered in air and in oxygen with different pressures.

6500B). Before the measurements of dielectric properties and electrical conduction, the ceramic surfaces were polished, and Ag electrode materials were brushed and annealed at 650 °C for 0.5 h.

3. Results and discussion

Figs. 1 and 2 show the XRD patterns and SEM images for the CCTO ceramics sintered in air and in oxygen. For all samples, the XRD peaks are consistent well with the values in the Committee for Powder Diffraction Standard (JCPDS) card for CCTO (No. 75-2188), and nearly no second phase is detected. From the SEM images, it can be seen that the CCTO ceramics are composed by the particles with sizes of tens of μm, and sintering in different atmosphere seems to show little impact on morphologies.

Fig. 3 shows the *RT* dc *J*–*E* curves. For the ceramic sintered in air, the *J*–*E* curve shows a clear non-Ohmic characteristic, and leakage enhances drastically under the higher electrical fields. For the samples sintered in oxygen, on one hand, leakage is greatly reduced;

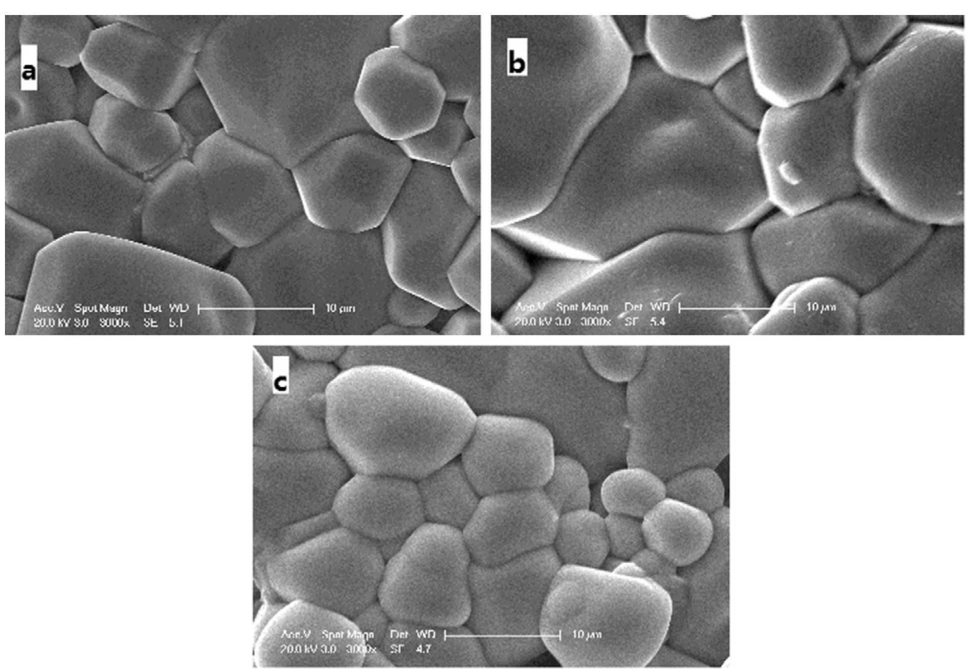

Fig. 2. The SEM images for the CCTO ceramics sintered (a) in air, (b) in 1-atm oxygen, and (c) in 3-atm oxygen.