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Elastic modulus and hardness of $CaTiO_3$, $CaCu_3Ti_4O_{12}$ and $CaTiO_3/CaCu_3Ti_4O_{12}$ mixture

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ABSTRACT

Three ceramic systems, $CaTiO_3$ (CTO), $CaCu_3Ti_4O_{12}$ (CCTO) and intermediate nonstoichiometric $CaTiO_3/CaCu_3Ti_4O_{12}$ mixtures (CTO.CCTO), were investigated and characterized. The ceramics were sintered at 1100 °C for 180 min. The surface morphology and structures were investigated by XRD and SEM. Elastic modulus and hardness of the surfaces were studied by instrumented indentation. It was observed that CCTO presented the higher mechanical properties ($E = 256$ GPa, hardness = 10.6 GPa), while CTO/CCTO mixture showed intermediate properties between CTO and CCTO.

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1. Introduction

The efficient miniaturization of electronic devices is a challenge in microelectronics and depends on the discovery of new and suitable materials. Supercapacitors and random access memory devices often require materials with high dielectric permittivity and low loss. In this way, $CaCu_3Ti_4O_{12}$ (CCTO), an unusual cubic perovskite structure, exhibits a giant relative dielectric permittivity at room temperature and thermal stability over a wide temperature range [1–4].

Compared to traditional $CaCu_3Ti_4O_{12}$-based composition, Ca excess and Cu deficiency in $CaCu_3Ti_4O_{12}$ ($Ca_{(1+x)}Cu_{(3-x)}Ti_4O_{12}$ with $x = 1$) causes the formation of a polyphasic system presenting 66.7 mol% of $CaCu_3Ti_4O_{12}$ (CCTO) and 33.3 mol% of $CaTiO_3$ (CTO). The effects of this different stoichiometry are a decrease of the dielectric property and a higher nonlinear electrical behavior, which is of interest for varistors and gas-sensing applications [5].

Varistors are used in the protection of electric and electronic circuits, whereas lightning rods remain the principal application. The varistors inside the lightning rods experience a high compression stress when all the elements of the device are kept close together (to provide a good electrical contact between the single pieces). Then, the characterization of the mechanical properties of ceramic varistors is an important subject, and still seldom studied in the literature. In addition, the characterization of the mechanical properties of CCTO and CTO/CCTO mixture is an important subject and has been scarcely reported. The systematic interests stem from the possibilities to apply their properties in different branches of new engineering. For this reason, in this work the experimental values elastic of modulus and hardness of CTO, CCTO and CTO/CCTO mixture were investigated by nano-indentation and correlated with the microstructure of the ceramics.

2. Experimental

$CaTiO_3$, $CaCu_3Ti_4O_{12}$ and $CaTiO_3/CaCu_3Ti_4O_{12}$ mixtures were prepared based on traditional reagent mixture processing. All the precursors were of analytical grade: $CaCO_3$ (J.T. Baker 99.99%), TiO_2 (Aldrich 99.8%), and CuO (Riedel 99%). The ratio used was 66.7 mol% of CCTO and 33.3 mol% of CTO. The mixed reagents were ball milled for 24 h in isopropyl alcohol using a polyethylene bottle and zirconium balls. Dispersions were dried at 110 °C and heat-treated at 900 °C in ambient atmosphere for 12 h.

The ceramic powders were slightly compressed into discs of 10 mm in diameter and about 1 mm in thickness, and then isostatically pressed under 210 MPa. The discs were sintered at 1100 °C for 180 min in a conventional furnace at ambient atmospheres. The heating and cooling rates applied were 5 °C/min. The density of the sintered bodies was determined by the Archimedes method.

The present phases were analyzed by X-ray diffraction using a Rigaku 20000 diffractometer with Cu Kα radiation. The samples were examined by scanning electron microscopy (SEM) by means of a Zeiss DSM 940 A using samples thermally etched at 50 °C below the sintering temperature for 5 min. Average grain size was determined by the interception method, using at least 300 grains.

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Elastic modulus and hardness were measured by means of a Hysitron Triboindenter. A Berkovich diamond indenter with a total included angle of 142.3° was used for every measurement of 50 load–unload cycles with 2500 and 5000 μN. The data sets were processed using appropriate software to produce load-displacement curves.

The Oliver–Pharr method [6], which proposes the estimation of the slope of the unloading curve by first fitting the entire unloading data, was employed to determine the reduced elastic modulus (E_r) and the hardness (H) of the materials. The reduced elastic modulus is related to the elastic modulus of the sample (E) and the contact stiffness (S) by Eqs. (1) and (2) [7]:

$$1/E_r = \left(1-\upsilon^2\right)/E + \left(1-\upsilon_i^2\right)/E_i \quad (1)$$

$$E_r = S.(\pi/4A_{max})^{1/2} \quad (2)$$

where υ is the Poisson's ratio and subscript i denotes the indenter material. A_{max} is the surface contact area at the maximum displacement. The contact stiffness (S) is the slope of the unloading curve taken as the first derivative in the maximum depth of a fitted power law function of the unloading segment of the curve. For our indenter tip, E_i is 1140 GPa and υ_i is 0.07, while ceramics poisson's ratio was assumed to be 0.25 [8].

The material hardness (H) is defined as the maximum load, P_{max}, divided by the projected area of the indentation under this load, see Eq. (3):

$$H = P_{max}/A_{max} \quad (3)$$

The tip area function $A(hc)$ was calibrated from indentations upon a fused silica sample of known E.

3. Results and discussion

The X-ray difraction patterns are provided in Fig. 1 and the SEM microstructures of CTO, CCTO and CTO/CCTO mixture sintered pellets are shown in Fig. 2. The X-ray difraction patterns were indexed to perovskite-related structures of CCTO and CTO according to JCPDS 75-1149 and 82-0231 files, respectively. Secondary phases were not observed in the diffractograms and CTO/CCTO mixture sample showed clear differences between both present phases (CTO and CCTO).

In addition, it can be seen that all samples exhibited uniform microstructures with low porosity (Fig. 2). $CaTiO_3$ showed very small grains sizes (<1 μm), while CCTO showed an average grain size of 10 μm. As expected, the microstructure of the CTO/CCTO mixture

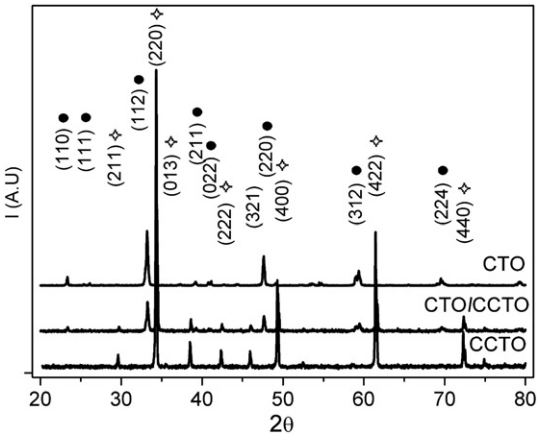

Fig. 1. X-ray diffraction patterns of $CaTiO_3$ (CTO), $CaCu_3Ti_4O_{12}$ (CCTO) and $CaTiO_3$/$CaCu_3Ti_4O_{12}$ mixtures (CTO/CCTO mixture). ✧ $CaCu_3Ti_4O_{12}$ (JCPDS 75-2188); ● $CaTiO_3$ (JCPDS 81-0561).

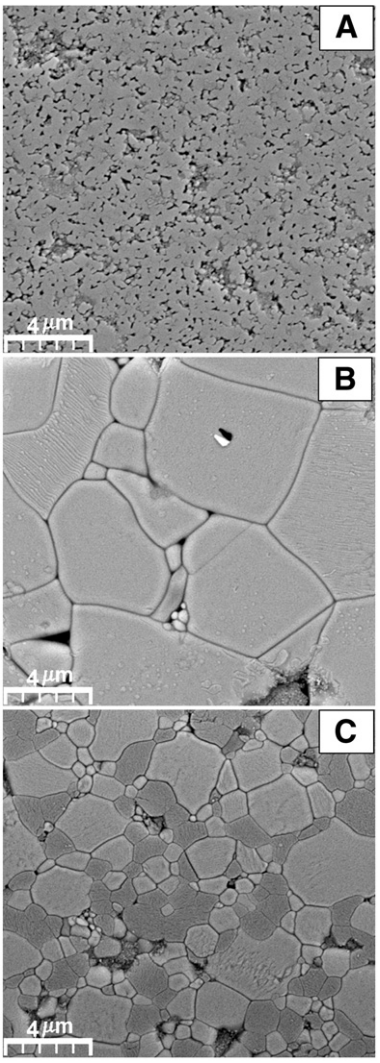

Fig. 2. Scanning electron microscopy images of $CaTiO_3$ (CTO), $CaCu_3Ti_4O_{12}$ (CCTO) and $CaTiO_3$/$CaCu_3Ti_4O_{12}$ mixture (CTO/CCTO mixture).

sample (Fig. 2c) was heterogeneous. In this sample (CTO/CCTO mixture) the CCTO phase consists in two families of grains with average grain sizes of about 10 and 2 μm, respectively. The CTO is usually outside the CCTO grains, although it has also been detected inside grains [5].

Fig. 3 shows representative load-displacement curves of CTO, CCTO and nonstoichiometric CTO/CCTO mixture. It can be observed that the maximum displacement is smaller for CTO and nonstoichiometric CTO/CCTO mixture than CCTO. This suggests that CCTO is harder and stiffer than CTO, while CTO/CCTO mixture showed an intermediate behavior.

The measured hardness and elastic modulus of the three ceramics is shown in Table 1. Compared with other traditional electroceramics (114, 107 and 280 Gpa for ZnO, $BaTiO_3$ and SnO_2, respectively) CCTO showed good stiffness and hardness performances [9–12]. The scattering on elastic modulus and hardness data could be due to porosity effects. Also, it can be seen that CCTO displayed better mechanical properties than CTO (almost 26%) or CTO/CCTO mixture (almost 31%), and that CTO values are consistent with the literature [13,14]. In this way, the mechanical properties of CTO/CCTO mixture almost follow a classical mixture rule ($H_{CTO.CCTO} \sim 2/3\ H_{CCTO} + 1/3\ H_{CTO}$ or $E_{CTO.CCTO} \sim 2/3\ E_{CCTO} + 1/3\ E_{CTO}$). The grain size apparently did not have a significant effect on mechanical properties analyzed and the results showed an average value.

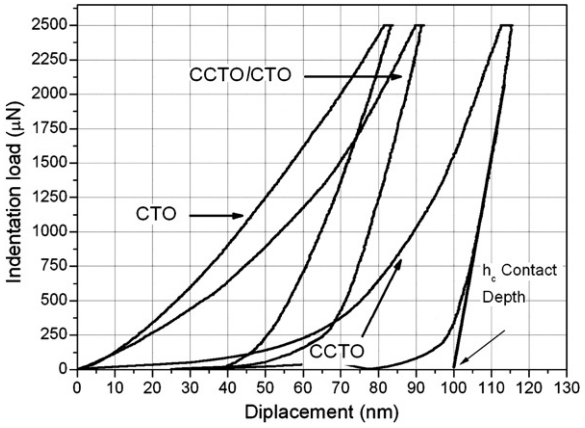

Fig. 3. Typical load-displacement curves.

The good mechanical properties of CCTO can be associated to the high density and homogeneous microstructure of sintered ceramics, in contrast to CTO/CCTO mixtures and CTO samples that showed grains of different sizes, at least two phases (CCTO/CTO mixture) and lower density (CTO).

4. Conclusion

Nano-indentation provided an easy and accurate method for the measurement of mechanical properties of CTO, CCTO and CTO/CCTO mixture ceramics. Obtained values of CTO hardness and elastic modulus are in agreement with those reported in the literature.

Nonstoichiometric CTO/CCTO mixture ceramics showed intermediate properties between CTO and CCTO. Hardness and elastic modulus of CTO/CCTO mixture a mixture rule and apparently the grain size did not show significant effects on the mechanical properties analyzed. Finally, CCTO displayed good mechanical properties compared with other typical electroceramic materials.

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Table 1
Density (ρ_r), grain size (D_{50}), reduced modulus of elasticity and modulus of elasticity of $CaTiO_3$ (CTO), $CaCu_3Ti_4O_{12}$ (CCTO) and $CaTiO_3/CaCu_3Ti_4O_{12}$ mixture (CTO/CCTO mixture) ceramics.

System	ρ_r (%)[a]	D_{50} (μm)	E_r (GPa)	E (GPa)	H (GPa)
CTO	92	<1	142 ± 24	161	5.0 ± 1.8
CCTO	95	10	212 ± 26	256	10.6 ± 3.6
CTO.CCTO	96	15 − 4	169 ± 29	196	7.9 ± 3.2

[a] This values were obtained by considering ideal theoretical density values of $CaCu_3Ti_4O_{12}$ (5.07 g/cm^3) and $CaTiO_3$ (4.67 g/cm^3).

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