



## Processing and characterization of $\text{CaTiO}_3$ perovskite ceramics

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Received 20 February 2014; Received in revised form 2 April 2014; Received in revised form 1 May 2014;  
Accepted 15 May 2014

### Abstract

Calcium titanate ( $\text{CaTiO}_3$ ) ceramics with perovskite structure were produced by solid state reaction. Calcium carbonate ( $\text{CaCO}_3$ ) and titanium dioxide ( $\text{TiO}_2$ ) were mixed (in molar ratios 1/1 and 3/2), and the obtained mixtures were calcined at 1150 °C in successive thermal cycles. The obtained samples were characterized by differential thermal analysis, thermogravimetry, X-ray diffraction, measurement of particle size distribution and linear thermal shrinkage. XRD results indicated that the samples have perovskite  $\text{CaTiO}_3$  structure with small amount of secondary  $\text{CaO}$  and  $\text{TiO}_2$  phases, and their phase composition depends on the heat treatment conditions. The measured values of electrical resistivity were within the characteristic range of insulating materials and approach values corresponding to semiconducting ceramics.

**Keywords:**  $\text{CaTiO}_3$ , structural characterization, conductivity, thermistor

### I. Introduction

Electroceramics have numerous applications due to their specific structures and physical properties, such as interconnect, packaging and substrates materials for microelectronics or as individual circuit components, particularly as capacitors or sensors [1–3].

Calcium titanate ( $\text{CaTiO}_3$ ) is a ceramic material with a perovskite structure. This compound does not show anisotropy, and its structure is cubic above 1307 °C, tetragonal between 1107 and 1227 °C and orthorhombic below 1107 °C [4]. The cubic perovskite structure can be obtained at room temperature when doped with cation receptors.  $\text{CaTiO}_3$  shows distinct structural, electrical and optical properties and, therefore, is of great scientific and technological interest [5]. Calcium titanate is also used as a resistor element with thermal sensitivity (thermistor), due to its negative temperature

coefficient (NTC), and is a refractory material with high resistance to caustic corrosion [6]. Thermistors are a type of resistors that change their electrical resistance depending on temperature. The resistance can be increased or decreased with temperature depending on the carrier mobility. Thermistors that exhibit a decrease in resistance with increasing temperature are called negative temperature coefficient (NTC) thermistors and those that exhibit an increased resistance with higher temperatures are known as positive temperature coefficient (PTC) thermistors. Thermistors can be classified according to electrical relationships, such as current-time, voltage-current and resistance-temperature [7].

The oxides with perovskite structure can be obtained by various methods of synthesis, particularly by solid state reactions (mixed oxides) or wet-chemical preparation (sol-gel, Pechini). The mixed oxide method is the reaction between oxides and/or carbonates, following milling, mixing and heat treatment at relatively high temperatures close to the melting points of components [8]. The method is widely used due to low cost, easy preparation and large amount of material produced, when compared with wet-chemical techniques. However, some drawbacks are firing at high temperatures,

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products with multiphase character, wide particle size distribution, loss of stoichiometry due to the volatilization of reactants at elevated temperatures and the presence of contaminants acquired during the grinding process. Thus, the reproducibility of the method is difficult [9].

The objective of this study is to evaluate the influence of heat treatments on the electrical properties of  $\text{CaTiO}_3$  obtained by the mixed oxides method from two different initial compositions.

## II. Materials and Methods

Calcium titanate powders were prepared from calcium carbonate ( $\text{CaCO}_3$ ) and titanium dioxide ( $\text{TiO}_2$ ) by solid state reactions under controlled conditions. Two different compositions (M1 and M2) were selected in accordance with the  $\text{CaO-TiO}_2$  phase diagram (Fig. 1). The phase diagram of the  $\text{CaO-TiO}_2$  system predicts the existence of three stable compounds:  $\text{Ca}_3\text{Ti}_2\text{O}_7$ ,  $\text{Ca}_4\text{Ti}_3\text{O}_{10}$  and  $\text{CaTiO}_3$ . The first two peritectic decomposition reactions should occur around 1750 °C and 1840 °C, respectively. The third compound,  $\text{CaTiO}_3$ , is formed congruently at 1960 °C with a eutectic at 1450 °C, between  $\text{CaTiO}_3$  and  $\text{TiO}_2$  [10]. Although thermodynamic equilibrium under normal industrial operating conditions is normally not reached, the phase diagram was used to predict adequate compositions and processing parameters.

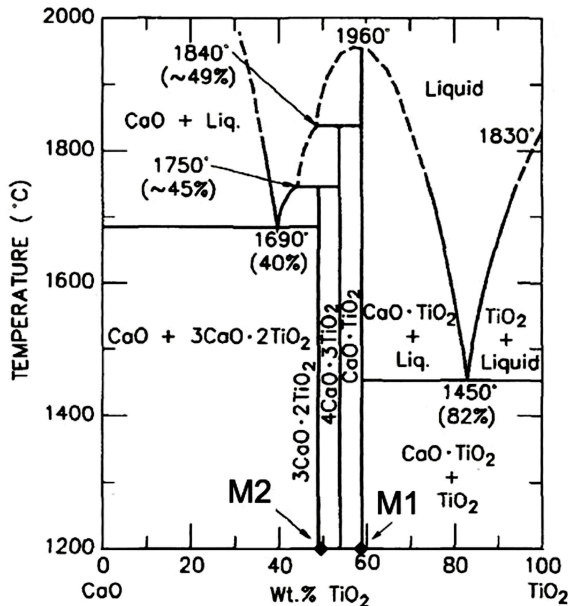


Figure 1. Location of compositions M1 and M2 in the diagram of the binary system  $\text{CaO-TiO}_2$  [10]

Two samples with the compositions M1 (51.9 wt.%  $\text{CaCO}_3$  and 48.1 wt.%  $\text{TiO}_2$ ) and M2 (41.1 wt.%  $\text{CaCO}_3$  and 58.9 wt.%  $\text{TiO}_2$ ) were prepared by mixing of  $\text{CaCO}_3$  (Vetec) and  $\text{TiO}_2$  (Aldrich) in dry ball mill jar over a period of 24 h. The obtained mixtures were transformed in calcium titanate powders by solid state reac-

tions at 1150 °C. The thermal treatment was performed in three successive cycles (Fig. 2) with a heating rate of 10 °C/min and 2 h holding times in a resistive furnace (Jung J200). Between the calcination steps, the powders were comminuted manually in an agate mortar, minimizing possible stoichiometric differences between the surface and the bulk of the particles.

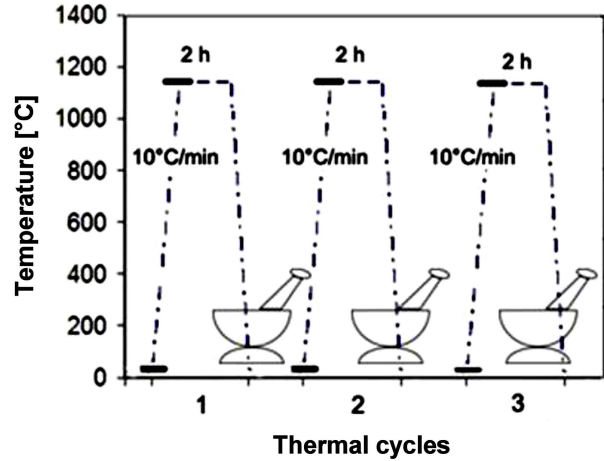


Figure 2. Experimental calcination cycles in successive stages followed by natural cooling and deagglomeration in agate mortar

The particle size distribution of the precursor mixtures M1 and M2 was measured with PTD Master Sizer 2000, Malvern. Linear thermal shrinkage was measured with an optical dilatometer (Misura) and the obtained data were used for optimizing the thermal treatment conditions. Differential thermal analysis and thermogravimetry (DTA/TG, EP STA 409, Netzsch) were carried out at 10 °C/min in an oxidizing atmosphere. Investigation of the crystalline phases present after every calcination step was performed on Philips XRD, PW 3710 using Ni-filtered  $\text{CuK}\alpha$  radiation.

Electrical conductivity measurements were carried out using cylindrical samples of the powders pressed in a manual hydraulic press at 100 MPa, with a 22 mm diameter and thickness between 1 and 3 mm. The electrical conductivity was measured at room temperature by the standard two-point method, using a DC power source (Keithley, 6220). The potential difference was measured with a voltmeter (Keithley, 6517A). The calculation of the resistivity was performed according to the following equation [11]:

$$\rho = \frac{d^2\pi}{4} \cdot \frac{V}{I} \cdot \frac{1}{L} \quad (1)$$

where  $\rho$  is the resistivity ( $\Omega\cdot\text{m}$ );  $d$ , the diameter of the sample (mm);  $V$ , the potential difference (V);  $I$ , the current (A); and  $L$ , the sample thickness (mm).

## III. Results and Discussion

Figure 3 shows the particle size distribution of the precursor powders M1 and M2. It can be seen that the

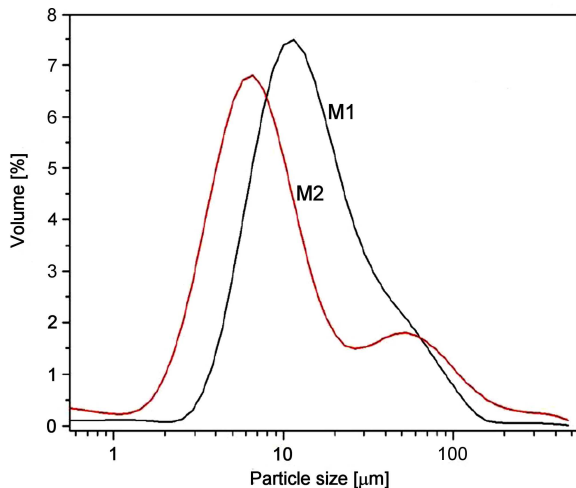


Figure 3. Particle size distribution

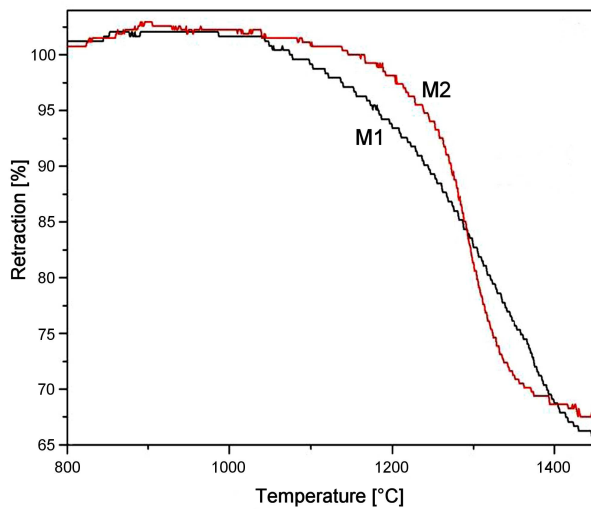


Figure 4. Linear thermal shrinkage of M1 and M2 samples

particle size distribution is bimodal with average particle sizes ( $d_{50}$ ) of  $10\mu\text{m}$  and  $8.4\mu\text{m}$  for the sample M1 and M2, respectively. Figure 4 shows dilatomet-

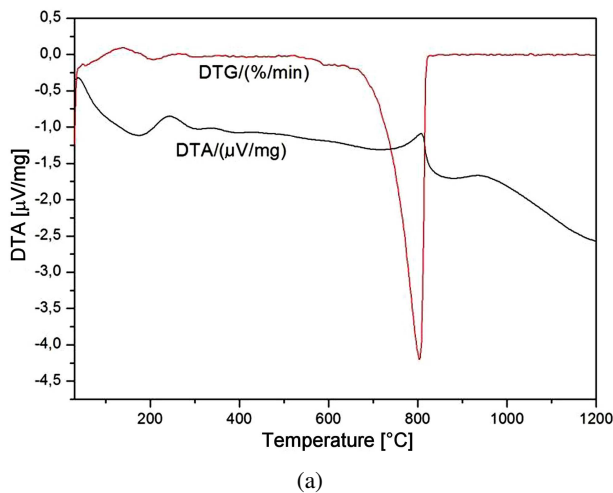
ric curves for both precursor mixtures. Softening of the sample M1 begins at  $\sim 1150^\circ\text{C}$  with shrinkage of  $\sim 33\%$ , whereas shrinkage of the sample M2 starts at  $\sim 1050^\circ\text{C}$ .

The results of differential thermal analysis (DTA/DTG) and thermogravimetry (TG) for the sample M1 are presented in Fig. 5. The formation of titanate takes place at temperatures above  $500^\circ\text{C}$  and the weight loss of the compound develops up to  $\sim 800^\circ\text{C}$ . Thus, the DTA exothermic peak between  $650$  and  $800^\circ\text{C}$  refers to the carbonate decomposition and formation of titanate. Above  $800^\circ\text{C}$  there is a slight weight loss as a result of the continuing reaction of residual carbonate and the formation of calcium titanate.

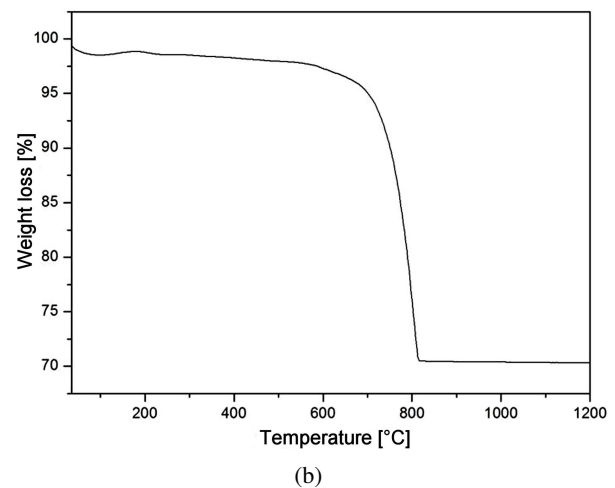
Figure 6 shows the XRD patterns of the samples M1 and M2, after three different thermal cycles (C1 to C3). The dominant XRD peaks belong to perovskite calcium titanate ( $\text{CaTiO}_3$ ) phase. However, peaks of minor intensity corresponding to the precursor phases  $\text{TiO}_2$  and  $\text{CaO}$  are still observed even after 3 cycles of thermal treatment. The intensity of diffraction peaks of the samples M1 and M2 are different. It seems that the sample M1 with molar ratio  $\text{Ca}/\text{Ti} = 1$  has smaller amount of undesirable secondary phases ( $\text{CaO}$  and  $\text{TiO}_2$ ).

Micrographs of the samples calcined at  $1150^\circ\text{C}$  in three cycles (M1-C3 and M2-C3) are shown in Fig. 7. The fracture surfaces have some interconnected porosity and the grain sizes around  $1\mu\text{m}$ , which are within the range found in the literature [12]. The microstructures are similar, but the pellet M2-C3 presents a greater variation in grain size in relation to the sample M1-C3.

Table 1 presents the resistivity and conductivity values measured after each calcination cycle (C1, C2, C3) for the pressed pellets M1 and M2. The electrical properties are also dependent on the  $\text{Ca}/\text{Ti}$  ratio. The pellet M1 has a lower resistivity compared to M2 for all heat treatments considered. Calcination led to decreased resistivity (increased conductivity) of the M1 samples. However, for M2 samples the subsequent calcination did not show a linear relationship with the conductivity;



(a)



(b)

Figure 5. Thermal analyses of precursor powder M1: a) DTA/DTG and b) TG

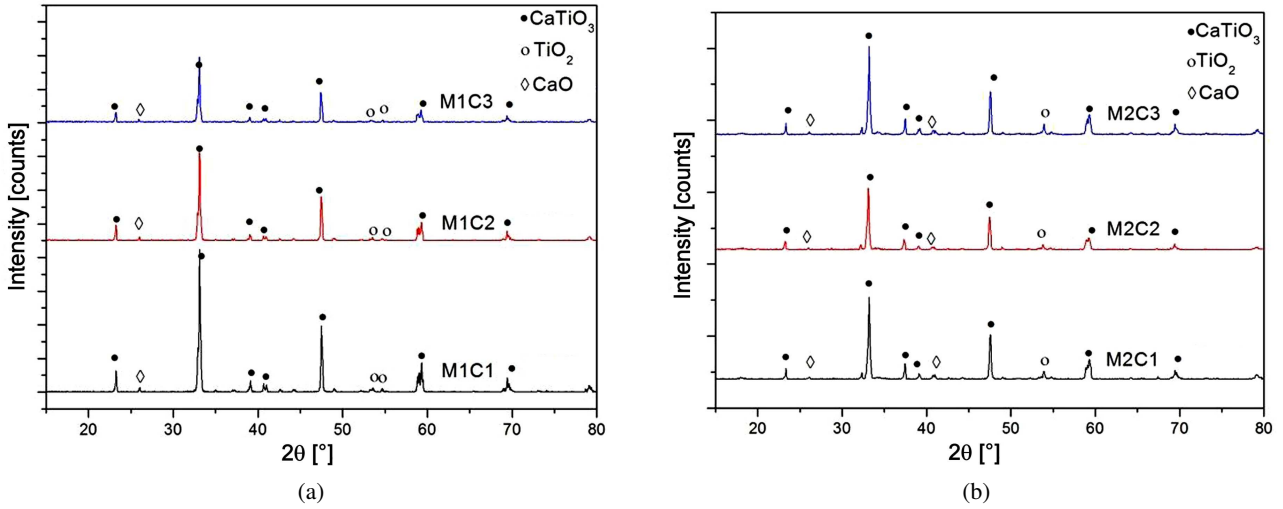


Figure 6. XRD patterns of samples: a) M1 and b) M2

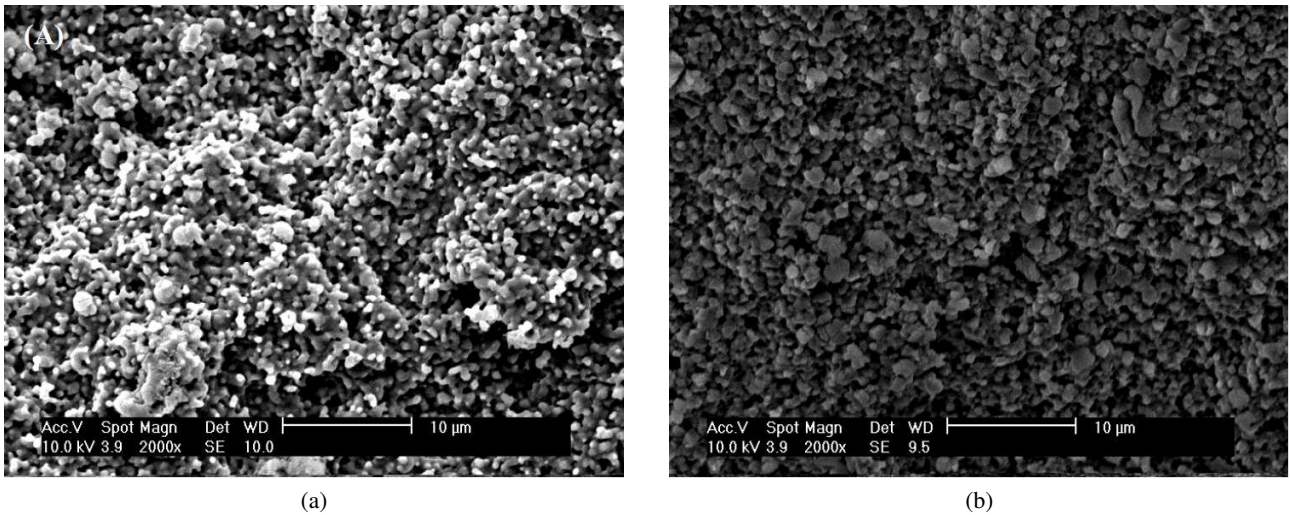


Figure 7. Scanning electron micrographs (SEM) of: a) M1-C3 and b) M2-C3

Table 1. Electrical resistivity and conductivity (at room temperature) of M1 and M2 pellets

Composition	CaO:TiO <sub>2</sub> molar ratio	Thermal cycle	Resistivity [Ω·m]	Conductivity [S/cm]
M1	1:1	C1	$1.5 \pm 0.4 \times 10^9$	$7.8 \pm 1.7 \times 10^{-10}$
		C2	$8.3 \pm 2.3 \times 10^8$	$1.4 \pm 0.3 \times 10^{-9}$
		C3	$6.0 \pm 1.6 \times 10^8$	$1.9 \pm 0.4 \times 10^{-9}$
M2	3:2	C1	$5.7 \pm 1.3 \times 10^{10}$	$2.0 \pm 0.3 \times 10^{-11}$
		C2	$2.8 \pm 0.7 \times 10^{10}$	$4.2 \pm 0.9 \times 10^{-11}$
		C3	$7.1 \pm 1.7 \times 10^{10}$	$1.6 \pm 0.3 \times 10^{-11}$

resistivity dropped after the first cycle but increased again after the third calcination.

Both pressed pellets (M1 and M2) have conductivity values within a range characteristic of insulating materials, which typically range from  $10^{-10}$  to  $10^{-22}$  S/cm [2]. However, conductivity of the sample M1 approaches values corresponding to semiconducting materials.

After each heating and subsequent grinding, the samples showed different values of electric conductivity, probably due to the formation of an oxide layer on the surface of the grains during sintering, which was not fully degraded after grinding. This layer might be responsible for incomplete reaction between CaO and TiO<sub>2</sub> and change of the electrical conductivity.

#### IV. Conclusions

Calcium titanate ceramics with perovskite structure were produced from mixture of  $\text{CaCO}_3$  and  $\text{TiO}_2$  powders by solid state reaction at  $1150^\circ\text{C}$ . Although the thermodynamic equilibrium in the course of investigation by solid state reaction at high temperature has not been reached, the samples with two different Ca/Ti molar ratios (1/1 and 3/2) showed trends suitable for obtaining  $\text{CaTiO}_3$  ceramics with perovskite structure. Calcium titanates with different compositions, obtained by solid state reaction at  $1150^\circ\text{C}$  in three different thermal cycles, have a high variation of the electrical conductivity from  $1.4 \times 10^{-9}$  to  $4.2 \times 10^{-11}$  S/cm. Thus, the obtained calcium titanates might be used as thermistors with a large resistivity at room temperature and thermally stable up to high temperatures ( $\leq 800^\circ\text{C}$ ).

**Acknowledgement:** The authors acknowledge the support of Brazilian agencies CNPq and CAPES.

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