Quantification of Calcium Titanate ($CaTiO_3$) by the Rietvield Method in Different Molar Proportions

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O objetivo do presente estudo é produzir titanato de cálcio (CT) com estrutura perovskita (ABO_3) a partir de rutilo comercial (TiO_2) e carbonato de cálcio comercial ($CaCO_3$). As matérias-primas foram caracterizadas por difração de raios X (DRX). Diferentes composições foram formuladas, as amostras foram comprimidas a 150 MPa e sinterizadas em forno resistivo a temperaturas de 1300 °C por 3h. As amostras foram analisadas por DRX após o processo de sinterização e as fases foram quantificadas de acordo com o método de Rietveld. As imagens foram representadas por meio de microscopia eletrônica de varredura (MEV), a fim de mostrar as características das microestruturas formadas. A densidade dos pellets sinterizados foi medida usando o método de Arquimedes. De acordo com os resultados, a formação do CT depende da razão molar entre os cátions cálcio e titânio nas composições analisadas.

Palavras-chave: *titanato de cálcio; método rietvield.*

The aim of the current study is to produce calcium titanate (CT) with perovskite structure (ABO_3) from commercial rutile (TiO_2) and commercial calcium carbonate ($CaCO_3$). The raw materials were characterized through X-ray diffraction (XRD). Different compositions were formulated, the samples were compressed at 150 MPa and sintered in resistive furnace at temperatures at 1300 °C for 3h. The samples were analyzed through XRD after the sintering process and the phases were quantified according to the Rietveld method. The images were depicted through scanning electron microscopy (SEM) in order to show the features of the formed microstructures. The density of the sintered pellets was measured using the Archimedes method. According to the results, the CT formation depends the molar ratio between calcium and titanium cations in the analyzed compositions.

Keywords: *calcium titanate; rietveld method.*

Introduction

The perovskite structure presents the ABX3 type formula and due to its excellent electrical and magnetic properties is extensively used in sensors and electronic devices[1-3]. The perovskite structure is represented as a cube with cations A and B located in its vertices and the anion X located in its centers of the face. It is a quite flexible structure, so a variety of foreign cations can be placed in its lattice, in different degrees. Thus, it lets a great co-substitution scope to the tailor properties of many ferroelectric and piezoelectric materials used for different applications[4].

The CT perovskite structure is more easily seen in the tetragonal or orthorhombic structures, due to the distortion in the octahedron structure (TiO^6). The CT transition temperature may be found in four different space groups depending on the phase, namely: the orthorhombic (Pbnm), orthorhombic (Cmcm), tetragonal (I4/mcm) and cubic (Pm3m) groups. Among these groups there are the cubic phase, at high temperatures (above 1306°C) and the orthorhombic (Pbnm)[5,6] one, which is stable at room temperature. Kennedy *et al* (6) suggest that the orthorhombic structure (Cmcm) is an intermediate stage; however, Ali *et al*[7] disagree with such theory, therefore, the existence of these four stages is controversial.

CT is a material with substantial interest to areas such as geology, metallurgy and ceramics, since it is a promising material to be used in sensors and electronic devices[8]. Some other CT applications such as that of biomaterial used to coat titanium prosthesis[9] have been developed. CT is also used as a resistor element with thermal sensitivity, due to its negative temperature coefficient (NTC)[10], another application for particulate CT is its use for the separation of hydrogen and oxygen from distilled water during light energy conversion[11]. The structurally disordered CT photoluminescent properties are reported in the literature[12,13]. Moreover, this material can be used in communication systems operated by microwave frequencies (UHF and SHF)[14,16] because of its high dielectric constant, low dielectric loss and large temperature coefficient of resonant frequency[17,19].

The traditional process of synthesizing CT is by a solid-state reaction based on calcining the mixed oxide or carbonate powders. Other techniques such as organometallic[20], liquid mix[21], plasma spray[22] and mechanochemical[23,25] processes have also been reported. Reaction-sintering process is a simple and effective route to syntheses ceramics.

Therefore, the aim of the present study is synthesis $CaTiO_3$ ceramics by a reaction-sintering process and quantification of phases formed in different proportions between the oxides TiO^2 and CaO.

Materials and Methods

A commercial calcium carbonate ($CaCO_3$, 99%, Merck) was used as calcium source, and commercial rutile was used as titanium source (TiO^2, 99%, Brazil Crystal). The raw materials were characterized through X-ray diffraction (Shimadzu XDR 6000) under 2θ diffraction conditions ranging from 10° to 80°, at scanning speed 2°/min, in order to verify the chemical and mineralogical composition of the raw materials.

The power mixing method was used to formulate the compositions, which were weighed in an analytical scale (Metler Toledo AX 504). The proper molar ratio between the oxides titanium/calcium analyzed was: 1.1; 1.2; 1.3; 1.4; 1.5, 1.6. The mixtures were manually homogenized for 15 min., with the aid of high gassing ethyl alcohol and a pestle, after they were weighed; all the compositions were prepared according to table 1.

The samples were compressed in a manual hydraulic press at 150 MPa into a disc-like shape after the milling process. Each disc was approximately 10 mm diameter and 2 mm thick. The samples were sintered in resistive furnace (Jung J200) under oxidizing atmosphere at temperatures that ranged at 1300°C, for 3 h (in air) at heating rate of 10°C/min and naturally cooled to room temperature. The samples were named according to the Table 1.

Table 1. Compositions analyzed, molar ratios, proportions used

Sample	Relation TiO_2/CaO	TiO_2 (g)	CaO (g)
C1	1.1	52.20	47.20
C2	1.2	54.70	45.51
C3	1.3	56.58	43.42
C4	1.4	58.40	41.71
C5	1.5	60.00	40.00
C5	1.6	61.51	38.55

After the sintering process, the compositions were characterized through X-ray diffraction (XRD, Rigaku Geigaku Geigerflex) for 2θ from 15° to 80°. The goniometer-scanning rate was 2°/min. The compositions were milled and sieved through 200 Tyler mesh.

The phases were quantified according to the Rietveld method using the GSAS/EXPGUI[26,27] software. The quantification combined alumina (Al_2O_3), as the internal standard (30%) under zero offset correction condition, and amorphous phase quantification. The cell unit and background parameters were used in the space group Pbnb, and the orthorhombic perovskite structure was performed after the work offset. The background was corrected using the Chebyschev polynomial of the first kind, the diffraction peak profiles were fitted through pseudo-Voigt function. The quality of the least squares refinement was assessed according to quality indices of optimal range between 2 and 4%, as well as to residual graphic analysis[28].

Microstructures were analyzed using scanning electron microscopy (SEM). The samples were manually fractured, ultrasound-cleaned for 15 min and oven dried for 60 min at 105 °C, for scanning electron microscope (SEM) analysis. The samples were subjected to porosimeter (NANNETI) - using the ASTM standard ISO 10545 as reference, weighed in analytical scale (Gilbertini E42, accuracy 0.001 g), dried in an oven at 110 °C/4h and cooled at room temperature to determine the apparent density (hydrostatic); then, they were weighed again in order to determine the dry mass.

Results and Discussion

The calcium carbonate (Sigma-Aldrich) used in the solid state reaction for CT obtainment is a commercial product mainly featured by its high purity (≥99.0%) and 47.8% loss on fire. The used anatase is a white titanium pigment commercially named TIONA (≥99.0%) and manufactured by Crystal Brazil S.A. The XRD patterns of used raw materials are show in Figure 1.

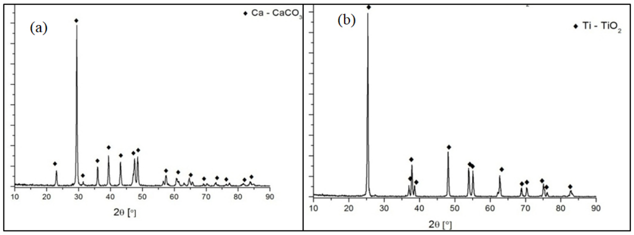

Figure 1: XRD patterns of the used raw materials. (a) XRD patterns of calcium carbonate, (b) XRD patterns of titanium dioxide.

The XRD pattern of calcium carbonate Figure 1a just shows the peaks related to calcium carbonate (ICSD - 73446) itself - which is a high-purity commercial material free of different phases and the most intense peak happens at 29°. The XRD pattern of titanium dioxide Figure 1b just shows peaks related to rutile (ICSD - 94566), TiO2 is a high-purity commercial material and its most intense peak takes place at 27°. The XRD patterns of ceramics sintered are show in Figure 2.

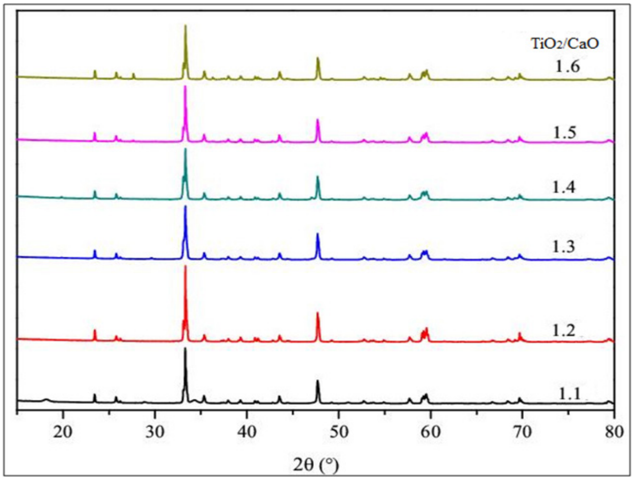

Figure 2: XRD patterns of the analyzed compositions in different molar proportions.

The phase composition of sintered ceramic samples was studied through XRD analysis; the CT orthorhombic phase formation is seen in all the samples and is confirmed as the XRD patterns are matched with the crystallography information file (ICSD - 82487) with (Pbnm) space group, the rutile phase matched with the crystallography information file (ICSD - 94566) and Portlandite is matched with the crystallography information file (ICSD - 20224). Table 2 shows the samples and phases formed and their quantifications.

Table 2. Phases formed and their quantifications in compositions C1, C2, C3, C4, C5, and C6.

Sample	CT ($CaTiO_3$) (%)	Rutile (TiO_2) (%)	Amorphous phase (%)	Portlandite ($Ca(OH)_2$) (%)
C1	68.36	0.63	15.79	15,22
C2	95.19	0.19	4.62	-
C3	86.05	1.26	12.69	-
C4	85.06	0.69	14.25	-
C5	67.77	1.43	30.80	-
C6	60.27	4.06	35.67	-

In Figure 3 can observe the refinements of the compositions C_1, C_2, C_3, C_4, C_5 and C_6.

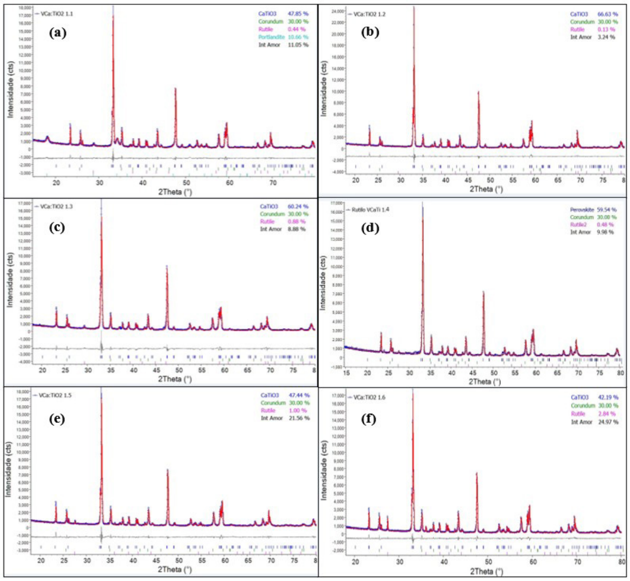

Figure 3: Refinements of the compositions: (a) sample C_1, (b) sample C_2, (c) sample C_3, (d) sample C_4, (e) sample C_5, (f) sample C_6

The composition C_1 presented formation of calcium titanate with the perovskite structure in amount of 68.36%, with a remanescent of TiO_2 in 0.63% with a remanescent of $Ca(OH)_2$ in 15.22% and amorphous phase in 15.79%. The composition C2 presented the formation of calcium titanate in amount of 95.19%, with a remanescent of TiO_2 in 0.19% and amorphous phase in 4.62%. The composition C_3 presented the formation of calcium titanate in amount of 86.05%, with a remanescent of TiO_2 in 1.26% and amorphous phase in 12.69%. The composition C4 presented the formation of calcium titanate in amount of 85.06%, with a remanescent of TiO_2 in 0.69% and amorphous phase in 14.25%. The composition C_5 presented the formation of calcium titanate in amount of 67.77%, with a remanescent of TiO_2 in 1.43% and amorphous phase in 30.80%. The composition C6 presented the formation of calcium titanate in amount of 60.27%, with a remanescent of TiO_2 in 4.06% and amorphous phase in 35.67%.

The SEM photographs of as-fired CT ceramics sintered are illustrated in Figure 4. Porous pellets with grain size 1 – 5 µm formed at C_1 and C_2 samples. The grain growth increase clearly at C_3, C_4, C_5 and C_6.

The apparently density of CT ceramics sintered increase with relation TiO_2/CaO. The maximum apparently density 3.71 g/cm3 is obtained in a relation 1,6 between TiO_2 and CaO (sample C_6), and the minimum density 2.04 g/cm^3 is obtained in a relation 1,1 between TiO_2 and CaO (sample C_1). Therefore, the densification in CT can be improved by adding TiO_2 due to the liquid phase sintering and the increased diffusivity of grain boundary produced a dense microstructure with large grains.

Phase relations in the Ca-Ti-O system have been studied extensively and are widely reported[29,34]. The eutectic point in the CaO-TiO_2 system occurs at about 1450°C. Perovskite ($CaTiO_3$) is the typical phase melting or crystallizing at these temperatures[30,34]. However reported the crystallization of an additional phase with the composition $4CaO._3TiO_2$ at low TiO_2 concentrations than the stoichiometric requirement for $CaTiO_3$ crystallization is reported[32,33].

In some recent work[29] studied the Ca-Ti-O system at 1200 K in pure oxygen and Ar. In this testwork, four ternary oxides without detectable range were identified:

$CaTiO_3$, $4CaO._3TiO_2$, $3CaO._2TiO_2$ and $CaO.Ti_2O_3$. It is important to note that $CaO.Ti_2O_3$ contains trivalent titanium. Thus, in the system Ca-Ti-O, a combination of trivalent and tetravalent titanium species can co-exist under reducing conditions, in the present study, these intermediate phases mentioned were not found/ quantified due thermodynamic equilibrium under normal operating conditions is normally not reached.

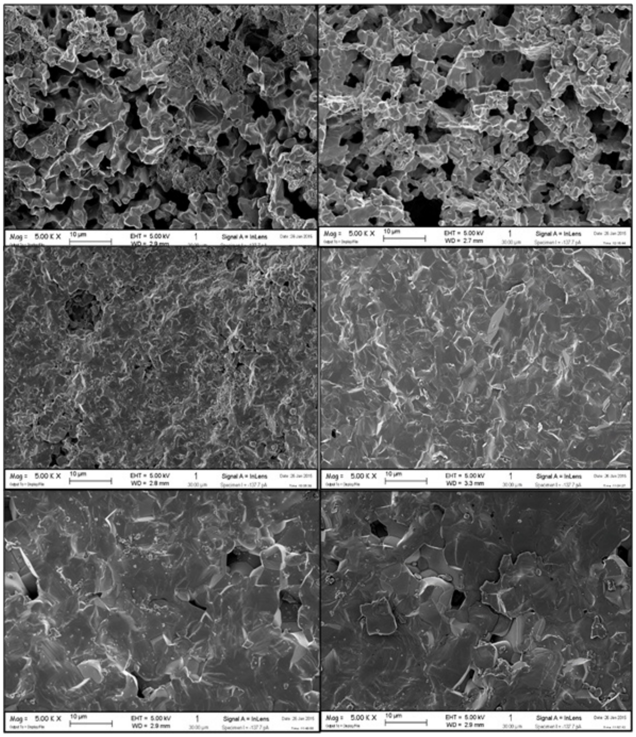

Figure 4: SEM photographs of CT ceramics: (a) sample C1, (b) sample C2, (c) sample C3, (d) sample C4, (e) sample C5, (f) sample C6.

Conclusions

The Perovskite $CaTiO_3$ ceramics could be obtained by a simple and effective reaction-sintering process successfully and its Rietveld refinement revealed that it was crystallized in orthorhombic symmetry at room temperature with Pbnm space group from all samples. The maximum apparently density (3.71 g/cm3) was obtained in sample C_6 whose TiO_2/CaO ratio is 1.6. The highest amount of CT (95.19%) was obtained in sample C_2 whose TiO_2/CaO ratio is 1.2, intermediate compounds were not found in the analyzed compositions.

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