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

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O objetivo do presente estudo é produzir titanato de cálcio (CT) com estrutura perovskita (ABO3) a partir do minério rutilo e carbonato de cálcio comercial. As matérias-primas foram caracterizados por fluorescência de raios-X e difração de raios-X (XRD). Diferentes composições foram formuladas, as amostras foram comprimidas a 150 MPa e sinterizadas em forno resistivo em temperaturas de 1300 ° C por 3h. As amostras foram analisadas através de XRD após o processo de sinterização e as fases foram quantificadas de acordo com o método Rietveld. As imagens foram obtidas por meio de microscopia eletrônica de varredura (MEV) a fim de mostrar as características das microestruturas formadas. De acordo com os resultados, a formação do CT depende da razão molar entre os cátions de cálcio e titânio nas composições.

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

The aim of the current study is to produce calcium titanate (CT) with perovskite structure (ABO3) from rutile ore and commercial calcium carbonate. The raw materials were characterized through X-ray fluorescence and 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. 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 ABX_3 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 raw material sources of titanium in the synthesis of calcium titanate is minerals rutile and its main features is rutile is a scarce mineral, it crystallizes in the tetragonal system and a density of 4.18 g/cm^3 [20,21].

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[22], liquid mix[23], plasma spray[24] and mechanochemical[25-27] 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; 1.3; 1.5. 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	22.00	40.00
C2	1.3	26.00	40.00
C3	1.5	30.00	40.00

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 [28, 29] 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 [30].

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.

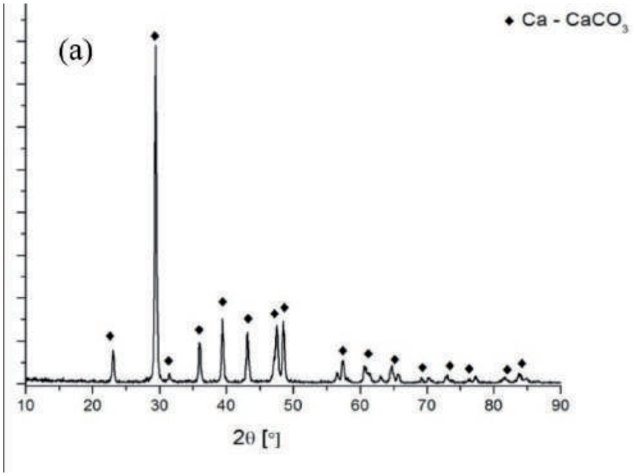
Results and Discussion

Table 1 shows the main chemical elements present in the characterized minerals (XRF).

Table 1: Main chemical elements present in the raw materials.

Materials (%)	**$CaCO_3$**	**TiO_2**	**SiO_2**	**Fe_2O_3**	**Al_2O_3**	**ZrO_2**	**P_2O_5**
Calcium carbonate	99.94	-	-	-	-	-	-
Rutile ore	-	87.91	2.14	1.35	2.38	4.41	1.32

The rutile ore has 87.91% titanium dioxide (TiO2) in the rutile phase, and the second most abundant phase present is zirconium (ZrO2) with 4.41%. The calcium carbonate (Sigma-Aldrich) used in the solid state reaction for CT obtainment is a commercial product mainly featured by its high purity (≥99.94%) and 47.8% loss on fire. The rutile ore comes from the Guaju mine (PB) ore, the XRD patterns of used raw materials are show in Figure 1.



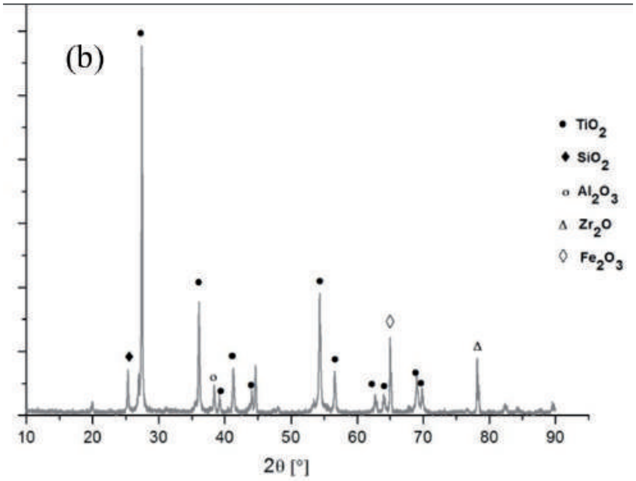


Figure 1: XRD patterns of the used raw materials. (a) XRD patterns of calcium carbonate, (b) XRD patterns of titanium dioxide.

The XRD pattern of calcium carbonate (Figure 1a) just shows the peaks related to calcium carbonate 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) shows peaks related to rutile (TiO_2), silica (SiO_2), corundum (Al_2O_3), and some others phases with less intense peaks. The XRD patterns of ceramics sintered are show in Figure 2.

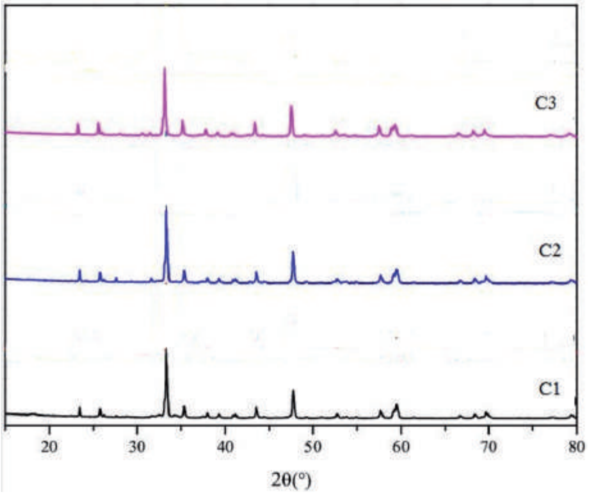


Figure 2: XRD patterns of the analyzed compositions in different molar proportions.

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 and C3.

Sample	**CT ($CaTiO_3$) (%)**	**Rutile (TiO_2) (%)**	**Amorphous phase (%)**	**Portlandite ($Ca(OH)_2$) (%)**
C1	76.87	0.32	15.41	7.34
C2	85.06	0.69	14.24	-
C3	80.01	1.15	18.84	-

In Figure 3 can observe the refinements of the compositions C1, C2 and C3. The composition C1 presented formation of calcium titanate with the perovskite structure in amount of 76.87%, with a remanescent of TiO_2 in 0.32% with a remanescent of $Ca(OH)_2$ in 7.34% and amorphous phase in 15.41%. The composition C2 presented the formation of calcium titanate in amount of 85.06%, with a remanescent of TiO_2 in 0.69% and amorphous phase in 14.24%. The composition C3 presented the formation of calcium titanate in amount of 80.01%, with a remanescent of TiO_2 in 1.15% and amorphous phase in 18.84%.

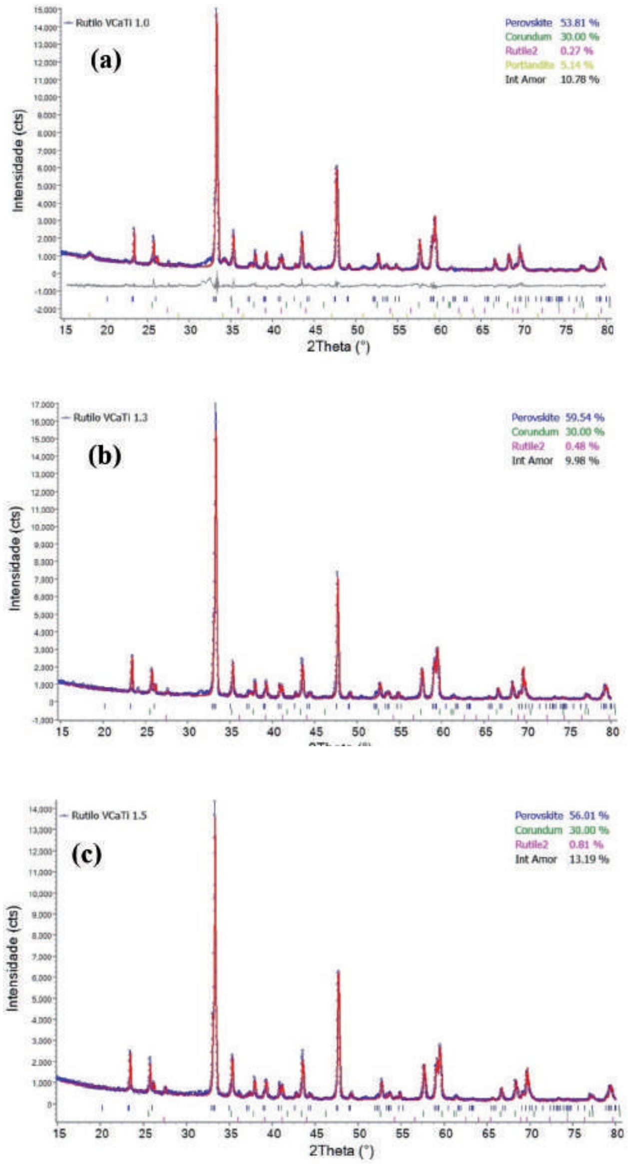


Figure 3: Refinements of the compositions: (a) sample C1, (b) sample C2, (c) sample C3.

The SEM photographs of as-fired CT ceramics sintered are illustrated in Figure 4.

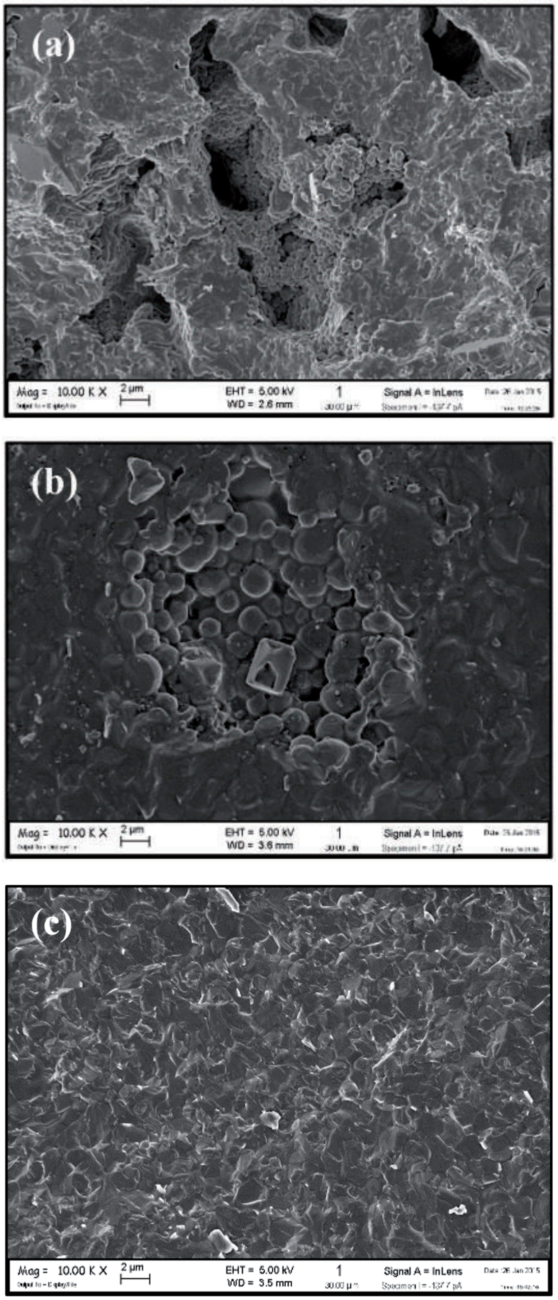


Figure 4: SEM photographs of CT ceramics: (a) sample C1, (b) sample C2, (c) sample C3

Phase relations in the Ca-Ti-O system have been studied extensively and are widely reported [31-36]. 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[32, 36]. 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[34, 35].

In some recent work[31] 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.

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 highest amount of CT (85.06%) was obtained in sample C2 whose TiO_2/CaO ratio is 1.3, intermediate compounds were not found in the analyzed compositions.

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