

SYNTHESIS and QUANTIFICATION OF CALCIUM TITANATE (CaTiO₃) BY THE RIETVELD METHOD, FROM THE RUTILE ORE.

Guilherme Gralik.⁽¹⁾

¹ Serviço Nacional de Aprendizagem Industrial/SENAI-PR, R. Joaquim de Paula Xavier, 1050 - Estrela, Ponta Grossa, CEP 84050-000, PR
guilherme_gralik@yahoo.com.br

ABSTRACT

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 1000 to 1400 °C for 3h. The samples were analyzed through XRD after the sintering process and the phases were quantified according to the Rietveld method. According to the results, the CT formation depends on the temperature of sinterization of analyzed compositions.

Keywords: calcium titanate, Rietveld method, rutile ore.

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]. 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^[2].

The CT perovskite structure is more easily seen in the tetragonal or orthorhombic structures, due to the distortion in the octahedron structure (TiO₆). 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 phases, at high temperatures (above 1306°C) and the orthorhombic (Pbnm)^[3, 4] one, which is stable at room temperature. Kennedy et al^[4] suggest that the orthorhombic structure (Cmcm) is an intermediate stage; however, Ali et al^[5] 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^[6]. Some other CT applications such as that of biomaterial used to coat titanium prosthesis^[7] have been developed. CT is also used as a resistor element with thermal sensitivity, due to its negative temperature coefficient (NTC)^[8]. 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^[9], liquid mix^[10], plasma spray^[11] and mechanochemical^[12-14] processes have also been reported. The raw material sources of titanium in the synthesis of

calcium titanate is mineral rutile and its main features is rutile is a scarce mineral, it crystallizes in the tetragonal system and a density of 4.18 g/cm³ [15, 16].

Reaction-sintering process is a simple and effective route to syntheses ceramics. Therefore, the aim of the present study is synthesis CaTiO₃ ceramics by a reaction-sintering process and quantification of phases formed in different temperatures.

MATERIALS AND METHODS

A commercial calcium carbonate (CaCO₃, 99%, Merck) was used as calcium source, rutile ore were used as mineral alternative sources of titanium, from Guaju Mine (PB – Brazil).

The raw materials were ground in a vibratory mill for 8 hours and past in of mesh size 200. The raw materials were characterized through X-ray fluorescence and 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: 1.4. The mixtures were manually homogenized for 15 min., with the aid of high gassing ethyl alcohol and a pestle, after they were weighed.

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 at 1000 to 1400 °C, for 3h (in air) at heating rate of 10°C/min and naturally cooled to room temperature. Each sintering temperature has the nomenclature: C1 = 1000°C, C2 = 1100°C, C3 = 1200°C, C4 = 1300°C, C5 = 1400°C.

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 [17, 18] software. The quantification combined alumina (Al₂O₃), 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 Chebyshev 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 [19].

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 ₂ O ₃	Al ₂ O ₃	ZrO ₂	P ₂ O ₅
Calcium carbonate	99.94	-	-	-	-	-	-
Rutile	-	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 ($\geq 99.94\%$) 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 Fig. 1.

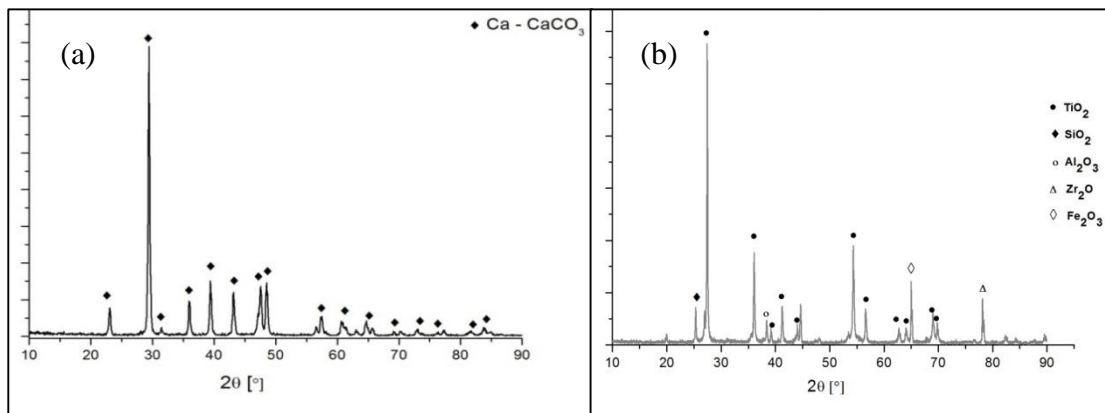


Figure 1 - XRD patterns of the used raw materials. (a) XRD patterns of calcium carbonate, (b) XRD patterns of titanium dioxide.

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 (TiO₂), silica (SiO₂), corundum (Al₂O₃), and some others phases with less intense peaks. The XRD patterns of ceramics sintered are show in Fig. 2.

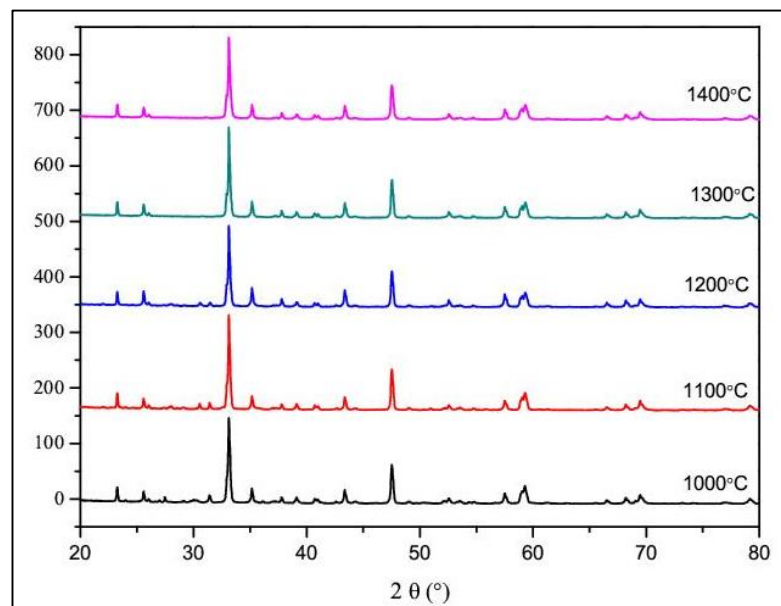


Figure 2 - XRD patterns of the analyzed compositions in different temperatures.

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(ICSD - 94566), gehlenite phase(ICSD - 86455), quartz low phase (ICSD - 79634), matched with the crystallography information file.

In Figure 3 can observe the refinements of the compositions C1, C2, C3, C4 and C5.

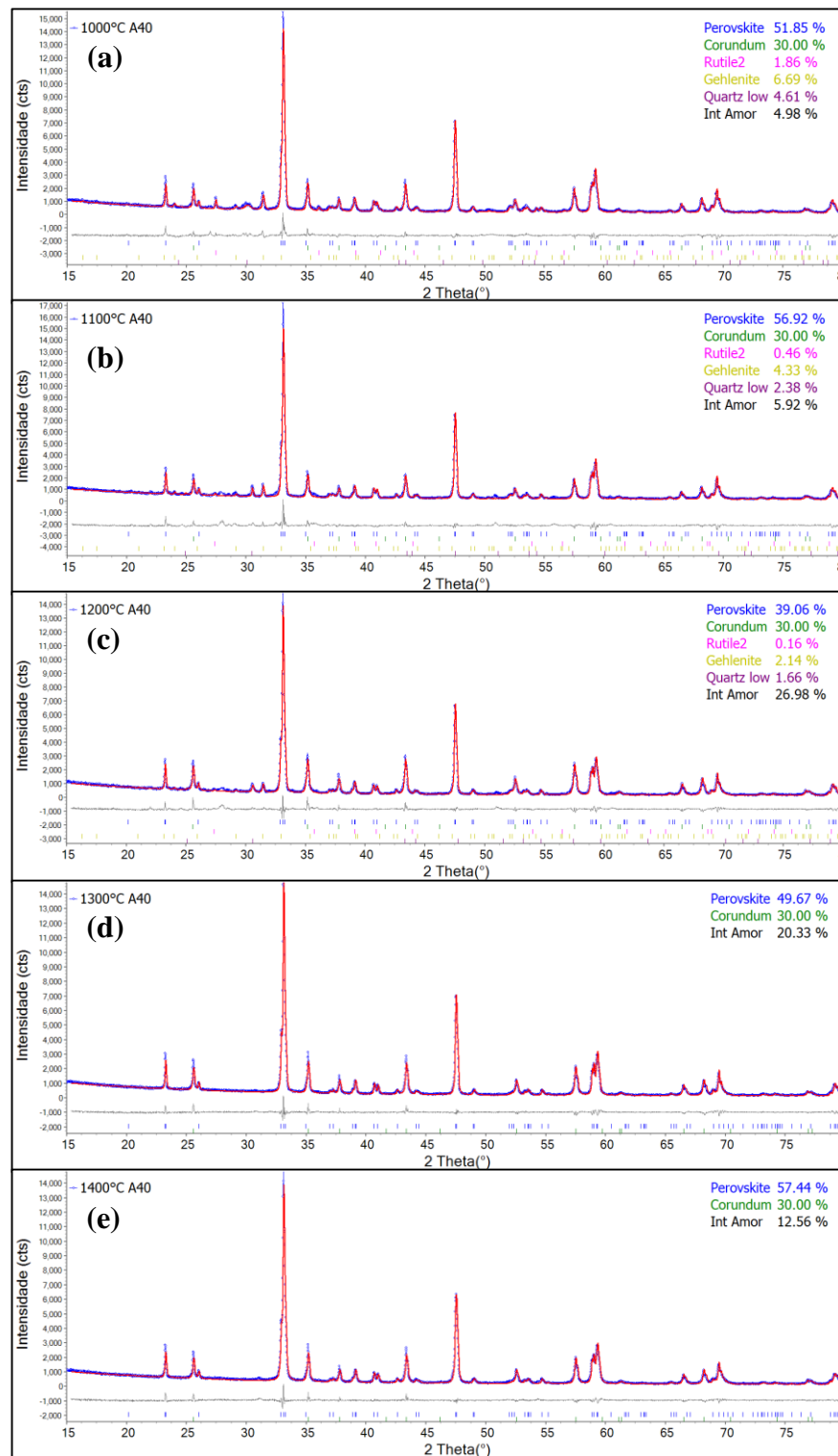


Figure 3 - Refinements of the compositions: (a) sample C1, (b) sample C2, (c) sample C3, (d) sample C4, (e) sample C5.

Table 1 shows the samples and phases formed and their quantifications.

Sample	*CT (%)	Rutile (%)	Gehlenite (%)	Quartz low (%)	**A.P. (%)
C1	74.07	2.66	9.56	6.59	7.12
C2	81.31	0.65	6.19	3.40	8.45
C3	55.80	0.23	3.06	2.37	38.54
C4	70.96	-	-	-	29.04
C5	82.05	-	-	-	17.94

*CT: calcium titanate **AP: amorphs phase

Table 1 – Phases formed and their quantifications in compositions C1, C2, C3, C4 and C5.

The composition C1 presented formation of calcium titanate with the perovskite structure in amount of 74.07%, and amorphous phase in 7.12%. The composition C2 presented the formation of calcium titanate in amount of 81.31%, and amorphous phase in 8.45%. The composition C3 presented the formation of calcium titanate in amount of 55.80%, and amorphous phase in 38.54%. The composition C4 presented the formation of calcium titanate in amount of 70.96% and amorphous phase in 29.04%. The composition C5 presented the formation of calcium titanate in amount of 82.05%, and amorphous phase in 17.94%. The intermediate phases (Rutile, Gehlenite, Quartz low), are present up to the sintering temperature of 1200 ° C, after this temperature they are no longer identified, they are probably present in the amorphous phase.

Phase relations in the Ca-Ti-O system have been studied extensively and are widely reported [20-25]. The eutectic point in the CaO-TiO₂ system occurs at about 1450°C. Perovskite (CaTiO₃) is the typical phase melting or crystallizing at these temperatures [21, 25]. However reported the crystallization of an additional phase with the composition 4CaO.3TiO₂ at low TiO₂ concentrations than the stoichiometric requirement for CaTiO₃ crystallization is reported [23, 24].

CONCLUSIONS

The Perovskite CaTiO₃ 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 (82.05%) was obtained in sample C5 whose sintered temperature is 1400°C, intermediate compounds were found in the analyzed compositions. Rutile ore can be used as source of Ti (titanium) for CaTiO₃ (CT) synthesis.

REFERENCES

1. BELL A. J., “Ferroelectrics: The role of ceramic science and engineering”, Journal of the European Ceramic Society, **28**, n. 7, pp. 1307-1317, Jan. 2008.
2. LEMANOV, V. V., SOTNIKOV, A. V., SMIRNOVA, E. P., WEIHNACHT, M., KUNZE, R., “Perovskite CaTiO₃ as an incipient ferroelectric”, Solid State Communications, **110**, n. 11, pp. 611-614, Abr.1999.
3. KENNEDY, B. J., HOWARD, C. J., CHAKOUMAKOS, B. C., “High-temperature phase transitions in SrZrO₃”, Physical Review. B 59 (6), 1999, pp. 4023-4027.
4. KENNEDY, B. J., HOWARD, C. J., CHAKOUMA, B. C., “Phase transitions in perovskite at elevated temperatures – a powder neutron diffraction study”, Journal of Physics Condensed Matter. **11**, n. 6, pp. 1479-1488, Out. 1999.
5. ALI, M., YASHIMA, R., “Space group and crystal structure of perovskite CaTiO₃ from 296 to 1720 K.”, Journal Solid State Chemistry. 178 pp. 2867-2872 (2005).

6. HAO, J., SI, W., Xi, X. X., GUO, R. A. S., BHALLA, L. E. “Dielectric properties of pulsed-laser- deposited calcium titanate thin films”. *Applied Physics Letter*, **76**, n. 21, pp.3100-3102, May 2000.
7. WEBSTER, T. J. et al. “Increased osteoblast adhesion on titanium-coated hydroxylapatite that forms CaTiO_3 ”. *Journal of Biomedical Materials Research Part A*, **67**, n. 3, p. 975-980, 2003.
8. MI, G. M., MURAKAMI, Y., SHINDO, D., SAITO, F., “Microstructural investigation of CaTiO_3 formed mechanochemically by grinding of a CaO-TiO_2 mixture”. *Powder Technology*, n. 104, **1**, 1999. p.75.
9. YANG, Z. Z., FUJII, T., SUWA, K., IWAHARA, H., *Solid State Ionics* 40/41 (1990) 544.
10. BALACHANDRAN, U., ODEKIRK, B., EROR, N. G., “Defect structure of acceptor-doped calcium titanate at elevated temperatures.” *Journal of Materials Science* **17**, pp. 1656–1662(1982).
11. NEUFUSS, K., A., RUDAJEVOVÁ, “Thermal properties of the plasma-sprayed $\text{MgTiO}_3\text{-CaTiO}_3$ and CaTiO_3 ”. *Ceramic International* 28 (1): pp.93–97 · December 2002.
12. MI, G., SAITO, F., SUZUKI, S., WASEDA. Y., “Formation of CaTiO_3 by grinding from mixtures of CaO or Ca(OH)_2 with anatase or rutile at room temperature”, *Powder Technology*. **97**, 15 June 1998, Pages 178-182.
13. EVANS, I. R., HOWARD, J. A., K SRECKOVIC, T. RISTIC, M. M. “Variable temperature in situ X-ray diffraction study of mechanically activated synthesis of calcium titanate, CaTiO_3 .”, *Materials Research Bulletin*, **38** (2003) 1203–1213.
14. G. Mi, Y. Murakami, D. Shindo, F. Saito, “Microstructural investigation of CaTiO_3 formed mechanochemically by dry grinding of a CaO-TiO_2 mixture”. *Powder Technology*. **104** (1999) 75.
15. MINDAT.ORG. Perovskite. Disponível em: <<http://www.mindat.org/min-3166.html>>. Acesso em: 11 set. 2013.
16. MINERALOGY DATABASE. Disponível em: <<http://webmineral.com/>>. Acesso em: 14 set. 2013.
17. A. C. LARSON, DREELE R. B. B., GSAS, https://permalink.lanl.gov/object/tr?what=info:lanlrepo/lareport/LA-UR-86-0748_REV, acessado em outubro de 2019. Los Alamos National Laboratory Report LAUR (2000) 86.
18. B. H. TOBY, “EXPGUI, a graphical user interface for GSAS” *Journal Applied Crystallography*, 2001. **34**, 210-213.
19. GRAFF, M. D., MCHENRY, M. E., *Structure of Materials*, Cambridge University Press, 2007.
20. JACOB, K. T., GUPTA, S., 2009. “Phase diagram of the system Ca-Ti-O at 1200 K”. *Bulletin of Materials Science*, **32** (6), pp. 611-616.
21. TULGAR, H. E., “Solid state relationships in the system calcium oxide-titanium dioxide”, *Istanbul Technical. University Bulletin*, 29 (1), pp. 111-129, 1976.
22. SHULTZ, R. L., 1973. “Effects of titanium oxide on equilibria among refractory phases in the system $\text{CaO-MgO-iron oxide}$ ”, *Journal American Ceramic Society*, 56 (1), pp. 33-36.
23. JONGEJAN, A., WILKINS, A. L., 1970. “A re-examination of the system CaO-TiO_2 at liquidus temperatures”, *Journal of the Less-Common Metals*, 20 (4), pp. 273-279.
24. ROTH, R. S., 1958. “Revision of the phase equilibrium diagram of the binary system calcititania, showing the compound $\text{Ca}_4\text{Ti}_3\text{O}_{10}$ ”. *Journal of Research of the National Bureau of Standard*, RP 2913, 61(5), pp. 437-440
25. DE VRIES, R. C., ROY, R., OSBOM, E. F., 1954. “The system $\text{TiO}_2\text{-SiO}_2$ ”. *Transactions and journal of the British Ceramic Society*, 53(9), pp. 525-540.