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Room temperature photoluminescence of BCT prepared by Complex Polymerization Method

F.V. Motta [a,*], A.P.A. Marques [b], J.W.M. Espinosa [c], P.S. Pizani [d], E. Longo [a], J.A. Varela [a]

[a] LIEC, Departamento de Físico-química, Instituto de Química, Universidade Estadual Paulista, R. Francisco Degni, s/n, Bairro Quitandinha, 14801-907 Araraquara-SP, Brazil
[b] LIEC, Departamento de Química, Universidade Federal de São Carlos, P.O. Box 676, 13565-905 São Carlos, SP, Brazil
[c] Departamento de Engenharia de Produção, Universidade Federal de Goiás, 75704-020 Catalão, GO, Brazil
[d] Laboratório de Semicondutores, Departamento de Física, Universidade Federal de São Carlos, 13565-905 São Carlos, SP, Brazil

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ABSTRACT

It was used the Complex Polymerization Method to synthesize barium calcium titanate powders (BCT). Crystalline $Ba_{0.8}Ca_{0.2}TiO_3$ perovskite-type phase could be identified by X-ray diffraction and confirmed by Raman spectroscopy in the powders heat treated at 600 °C. Inherent defects, linked to structural disorder, facilitate the photoluminescence emission. The photoluminescent emission peak maximum was around of 533 nm (2.33 eV) for the $Ba_{0.8}Ca_{0.2}TiO_3$. The photoluminescence process and the band emission energy photon showed dependence of both the structural order–disorder and the thermal treatment history. The results revealed that $Ba_{0.8}Ca_{0.2}TiO_3$ (BCT20) is a highly promising candidate material for optical applications.

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1. Introduction

The barium titanate ($BaTiO_3$) perovskite, that is one ferroelectrics material, has been extensively studied due several possible applications such as electronic and optical devices [1–4]. The substitution of Ba by Ca in the $BaTiO_3$ perovskite results in an improvement of the stability of the piezoelectric properties, consequently the barium calcium titanate ($Ba_{1-x}Ca_xTiO_3$) solid solution has attracted great attention for use in the laser systems, electro-optic material for various photorefractive and holographic applications [5–8].

$Ba_{1-x}Ca_xTiO_3$ (BCT) has usually been prepared by the solid state reaction method. In the solid state reaction method the mixture of $BaCO_3$, $CaCO_3$ and TiO_2 is heat treated at high temperatures for long times and requires two successive calcinations to get high solubility of Ca^{+2} in the $BaTiO_3$ matrix [9–11]. It has been observed that Ca^{+2} replaces Ba^{+2} in $Ba_{1-x}Ca_xTiO_3$ to form tetragonal BCT solid solutions when x is less than ~0.23 [5,12]. Moreover, Cheng and Shen [12] obtained pure tetragonal phase for $x \leqslant 0.25$ and mixture of phases for x in the range of 0.3–0.85. The synthesis by soft-chemical methods, as the Complex Polymerization Method (CPM), used to synthesize high pure $BaTiO_3$ powders, occur at lower temperature that the solid state reaction method. The immobilization of the metal complexes in such rigid organic polymeric networks can reduce the metal segregation, thus ensuring the compositional homogeneity at the molecular scale [13,14].

Jastrabik et al. [8] reported the photoluminescence (PL) and optical absorption in the pure and Cr-doped $Ba_{0.77}Ca_{0.23}TiO_3$ single crystals at temperatures of the 5–300 K in the 300–800 nm spectral. Interband excitation of pure BCT crystals at $\lambda = 350$ nm results in the well-known visible wide-band emission with a maximum at ~552 nm (green) at 10 K.

Photoluminescence property at room temperature occurs due to structural disorder existing in the perovskite system [15,16]. However, the system can not be fully disordered owing to present a minimal order in the structure. This means that there is an order–disorder rate which favors the PL phenomenon in the system. It has been demonstrated that a series of structurally disorder titanates synthesized by a soft-chemical process have shown intense photo-

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[*] Corresponding author. Fax: +55 16 33518214.
E-mail address: fabiana@liec.ufscar.br (F.V. Motta).

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luminescence (PL) at room temperature [17–19]. In such cases, a minimal order in the system is necessary for the material exhibit PL property at room temperature.

In previous PL studies, the analysis of X-ray absorption near-edge structure (XANES) spectra pointed out the coexistence of two types of environments for titanium atoms, namely, fivefold (TiO_5) square–base pyramid or trigonal bipyramidal and sixfold coordination (TiO_6) octahedron. The order parameter is related to the presence of TiO_6 clusters, whereas the disorder is related to the presence of TiO_5 clusters. It is believed that PL occurs due to interaction of TiO_5–TiO_6 clusters [20,21]. de Figueiredo et al. [22] observed the PL phenomenon in $Ca_{0.95}Sm_{0.05}TiO_3$ (CT:Sm) only in disordered structure. Experimental observations suggest that PL emission of CT:Sm is related both to the TiO_5–TiO_6 and CaO_{11}–CaO_{12} concentrations; consequently, depends on both the modifier lattice (Ca and Sm ions) and the former lattice (Ti ions) [22,23].

Considering that the CPM is efficient to promote produce structural order–disorder complexes oxides powders and few have has been reported about the property PL of the barium calcium titanate (BCT). This paper reports the synthesis and the structural effect of $Ba_{0.8}Ca_{0.2}TiO_3$ (BCT20) powders in the conditions that favor the PL emission at room temperature.

2. Experimental detail

BCT20 was prepared by CPM [24,25]. In this synthesis, the titanium citrate was formed by dissolution of titanium (IV) isopropoxide in aqueous solutions of citric acid (CA). This solution was mixed in a stoichiometric molar proportion of 4:1 CA:titanium. The citrate solution was homogenized under constant stirring at a temperature of ~80–90 °C, pH ~ 1.5. After complete dissolution were added $BaCO_3$ and $CaCO_3$. Ammonium hydroxide was used to adjust the pH of the solution (pH 7–8). The molar ratio between barium, calcium and titanium cations was 0.80:0.20:1. After homogenization of this solution was added ethylene glycol to promote the polymerization.

After partial evaporation of the water, the polymeric resin was heat treated at 300 °C (10 °C/min) for 4 h, forming an expanded resin, constituted of partially pyrolyzed material. The resin became a dark-brown powder and was crystallized at several temperatures between 400 and 700 °C for 2 h using a heating rate of 5 °C/min.

BCT20 powders were characterized by X-ray diffraction (XRD) using Cu Kα radiation in order to determine the structural evolution and the lattice parameters *a* and *c*. The average crystallite diameter (D_{crys}) was determined by XRD, from the (1 0 1) and (1 1 0) diffraction peaks of the $BaTiO_3$ phase (2θ at around 31.5° and 31.6°, respectively), according to the Scherrer equation as described by Suryanarayana and Norton [26].

The Raman spectroscopy data were obtained at room temperature by a RFS/100/S Bruker FT-Raman equipment attached to a Nd:YAG laser promoting an excitation light of 1064 nm with spectral resolution of 4 cm^{-1} and range of 0–1100 cm^{-1}.

The photoluminescence (PL) spectra of the BCT20 powders were collected with a U1000 Jobin-Yvon double monochromator coupled to cooled GaAs photomultiplier and a conventional photon counting system. The 488.0 nm exciting wavelength of an argon ion laser was used. The maximum output power of the laser was 20 mW. All measurements were taken at room temperature.

3. Results and discussion

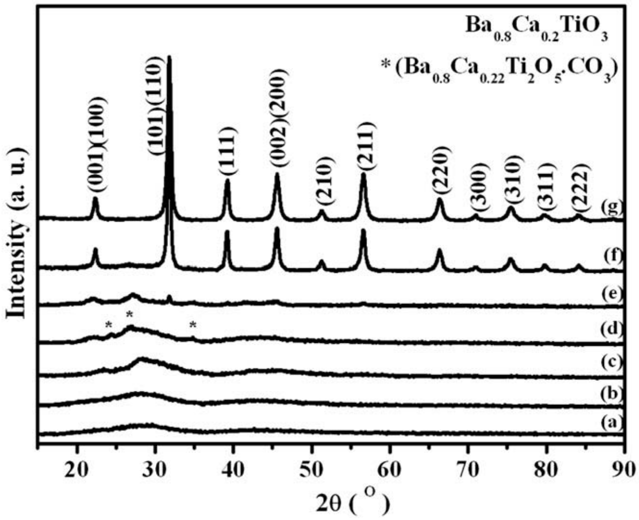

Fig. 1. X-ray diffraction patterns of $Ba_{0.8}Ca_{0.2}TiO_3$ powders heat treated at (a) 400 °C, (b) 450 °C, (c) 500 °C, (d) 550 °C, (e) 575 °C, (f) 600 °C and (g) 700 °C.

Fig. 1 shows the XRD patterns of the BCT20 powders heat treated at different temperatures, from 400 to 700 °C. In this figure, it is observed that the BCT20 heat treated at 400 °C is disordered. The materials heat treated between 450 and 550 °C present only broad diffraction reflections at 2θ ~ 24.3°, 26.7° and 34.7° referent to the barium titanium oxycarbonate, $(Ba_{0.8}Ca_{0.2})_2Ti_2O_5 \cdot CO_3$ [27]. This barium titanium oxycarbonate is an intermediate metastable phase that disappears when the material is heat treated at 575 °C, remaining only the reflections referent to $Ba_{0.8}Ca_{0.2}TiO_3$ perovskite-type phase. These XRD patterns indicate that the powders samples heat treated at 575 °C and higher temperatures are structurally ordered at long range.

The pure $BaTiO_3$ (BT) ceramic shows a tetragonal phase as identified and indexed using the standard XRD data of the corresponding BCT20 powders [5,9]. The lattice parameters and the mean crystallite sizes were calculated from the peak positions displayed in Fig. 1. The ordered BCT20 calculated crystallite sizes were around of 17 nm. The lattice parameters *a* and *c* were obtained using the least square refinement from the REDE93 program. The lattice parameters *a* and *c* were around of 3.9607(3) and 3.9941(3) Å, respectively; similar to the values reported for $Ba_{0.773}Ca_{0.227}TiO_3$ crystals (*a* = 3.962 Å and *c* = 3.999 (Å)) [5].

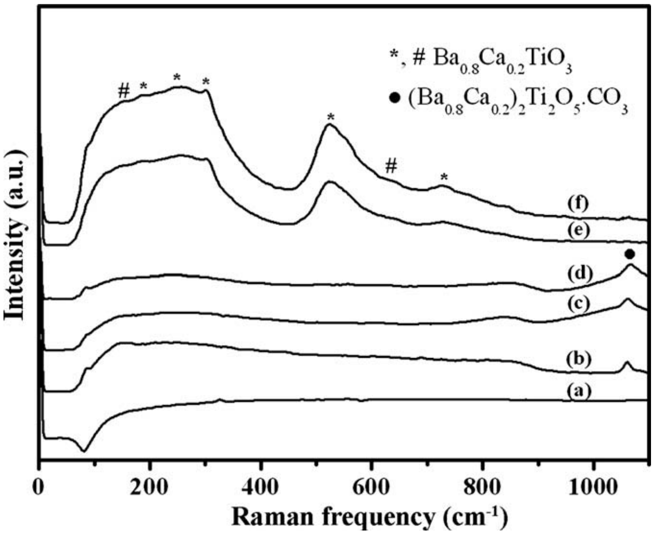

Fig. 2. Spontaneous Raman spectra of BCT20 powders heat treated at (a) 400 °C, (b) 500 °C, (c) 550 °C, (d) 575 °C, (e) 600 °C and (f) 700 °C.

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