Structural refinement and photoluminescence properties of irregular cube-like (Ca$_{1-x}$Cu$_x$)TiO$_3$ microcrystals synthesized by the microwave–hydrothermal method
Structural refinement and photoluminescence properties of irregular cube-like (Ca$_{1-x}$Cu$_x$)TiO$_3$ microcrystals synthesized by the microwave–hydrothermal method

L.H. Oliveira$^{a,*}$, A.P. de Moura$^b$, T.M. Mazzo$^b$, M.A. Ramírez$^c$, L.S. Cavalcante$^b$, S.G. Antonio$^b$, W. Avansi$^b$, V.R. Mastelaro$^d$, E. Longo$^{a,b}$, J.A. Varela$^b$

$^a$DQ-UFSCar-Universidade Federal de São Carlos, P.O. Box 676, 13565-905 São Carlos, SP, Brazil
$^b$UNESP-Universidade Estadual Paulista, P.O. Box 355, 14801-907 Araraquara, SP, Brazil
$^c$UNESP-Universidade Estadual Paulista, 12516-410 Guaratinguetá, SP, Brazil
$^d$IFSC-USP, AV. Trabalhador São Carlense 400, 13560-970 São Carlos, SP, Brazil

HIGHLIGHTS

- Any secondary phases were detected in the (Ca$_{1-x}$Cu$_x$)TiO$_3$ powders.
- Cu atoms are able to induce a local polarization in [CaO$_{12}$] and [TiO$_6$] clusters.
- Ostwald-ripening and self-assembly are dominant mechanisms of these microcrystals.
- PL emission presents a shift to green region as the concentration of Cu increases.

ABSTRACT

In this paper, calcium copper titanate (Ca$_{1-x}$Cu$_x$)TiO$_3$ microcrystals with (x = 0, 0.01 and 0.02) were synthesized by the microwave–hydrothermal method at 140 °C for 30 min. These crystals were analyzed by X-ray diffraction (XRD), Rietveld refinement, X-ray absorption near-edge structure spectroscopy (XANES), micro-Raman spectroscopy, field emission scanning electron microscopy (FE-SEM). Its optical properties were investigated by ultraviolet–visible (UV–vis) absorption and photoluminescence (PL) measurements. XRD patterns, Rietveld refinement and micro-Raman spectroscopy indicated that these crystals present a perovskite-type orthorhombic structure. The Rietveld refinement data, micro-Raman and XANES spectra suggested that the substitution of Ca by Cu in A-site promoted a displacement of Ti atoms to off-center symmetric, which leads distortions on the cuboctahedral [CaO$_{12}$] clusters neighboring and consequently promotes a strain into the CaTiO$_3$ lattice. FE-SEM images showed that these cube-like microcrystals have an irregular shape due to Ostwald-ripening and self-assembly of plates and cubes in growth process. The defects and distortions into lattice at medium- and short-range on the [CaO$_{12}$]/[TiO$_6$] clusters promotes the structural order–disorder responsible by the intense PL properties of these microcrystals. The microcrystals are promising candidates for future applications in optical devices.

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1. Introduction

Crystalline ceramics mainly perovskite-type mixed metal oxide of chemical formula (ABO₃) have attracted attention over the years due to their physical and chemical properties, which can be changed by easy substitution in both the A and B-sites with several compositions [1,2]. In particular, titanium-based perovskite oxides with formula ATiO₃ (A = Pb, Sr, Ba, Zn, Ni, or Fe) presents outstanding potential in electronics [3], gas sensors [4], catalysis [5], memory devices [6], magnetic material [7], and so on. Moreover, the photoluminescence (PL) properties were observed in perovskite-type titanates, such as: (Ba,Ca)TiO₃ [8], Pb(Zr,Ti)O₃ [9], SrTiO₃ [10], and MgTiO₃ [11]. These compounds present broad and intense PL emission at room temperature that can provide the comprehension of energetic levels, defects formation, surface states, which are intrinsically related to its optical response.

Among these titanates, the CaTiO₃ presents a good chemical, physical and thermal stability even in some corrosive environments; and it is also employed as component of microwave technology, field emission displays and sensors [12]. CaTiO₃ is known through its use as the host of rare earth-doped, for its applications in integrated light-emission devices, field emission displays (FED’s), and all-solid compact laser devices operating in the blue-green region and positive temperature coefficient (PTC) resistors [13]. The demand for high-resolution and efficiency of waveguides, lamps and other optical devices has stimulated the discovery of new luminescent materials with enhanced properties [14].

Recently, Mazzo et al. [15] have reported the PL properties of CaTiO₃:Eu³⁺ crystals prepared by the microwave—hydrothermal (MH) method. Unlike other chemical methods, the MH process can be an efficient synthesis route for optical materials, since these crystals were synthesized at lower temperature (140 °C) in a short time (10 min). Besides that, MH method allowed the formation of microcrystals with irregular cube-like shape. The results obtained indicate the presence of an intense PL emission at 613 nm related to f–f characteristic transitions of the Eu³⁺ ion, which are strong dependent of Eu³⁺ content into CaTiO₃ lattice. The monitoring of different concentrations of the Eu content into CaTiO₃ lattice is very important for understanding the nature of the lattice modifiers as well as the structural defects into the orthorhombic structure.

In the literature, some others rare-earth ions (Pr³⁺, Nd³⁺, Sm³⁺) have been employed in the A-site (Ca²⁺ ions) substitution into CaTiO₃ lattice to improve its optical properties [16–18]. Derén et al. [19] have synthesized CaTiO₃:Eu³⁺ nanocrystals (40 nm) by the sol–gel technique. A strong green up-conversion luminescence was verified after a continuous excitation at 980 nm (4I₀/₂ → 4I₁₁/₂). The obtained results show that this material is a good infrared converter, allowing its use in high definition electronic devices.

However, in this paper, we report for the first time the obtention of calcium copper titanate (Ca₁−xCux)TiO₃ microcrystals with (x = 0, 0.01 and 0.02) by MH method at 140 °C for 30 min. These microcrystals were structurally and morphologically characterized by X-ray diffraction (XRD), Rietveld refinement, X-ray absorption near-edge structure spectroscopy (XANES), micro-Raman (MR) spectroscopy and field emission scanning electron microscopy (FE-SEM). Finally, their optical properties were investigated by ultraviolet–visible (UV–vis) absorption and PL measurements.

2. Experimental details

2.1. Synthesis of (Ca₁−xCux)TiO₃ microcrystals

(Ca₁−xCux)TiO₃ microcrystals with different molar ratio (x = 0, 0.01 and 0.02) labeled as CTO, CCTO1 and CCTO2, respectively, were synthesized by the MH method. In the synthesis, titanium (IV) isopropoxide, [Ti(OC₃H₇)₄] (97%, Aldrich), calcium carbonate, CaCO₃ (99.9%, J.T. Baker), copper (II) nitrate hemipentahydrate, Cu(NO₃)₂·2.5H₂O (99.99%, Aldrich) and potassium hydroxide KOH (99%, Merck) were used as starting materials. The experimental procedure is described as follow: CaCO₃ was dissolved in 25 mL of deionized water giving rise to a transparent solution, following by addition of 0.01 mol of the [Ti(OC₃H₇)₄] under constant stirring. In a similar way, stoichiometric quantities (1.0 and 2.0% M) of Cu(NO₃)₂·2.5H₂O were dissolved into 25 mL of deionized water and added to the system. The resulting solution was mixed with 50 mL (6 M - KOH solution), which acts as a mineralizer. This procedure promoted the formation of nanocrystalline titanate oxide [TiO(OH)₂], as well as calcium hydroxide Ca(OH)₂ and copper hydroxide Cu(OH)₂ into the reactional mixture. In order to prevent the formation of calcium carbonate as a second phase, nitrogen gas was constantly bubbled to the system. In the sequence, this mixture was transferred to a Teflon autoclave, which was finally sealed and placed in the MH system using 2.45 GHz microwave radiation with maximum power of 800 W [20]. The MH conditions were kept at 140 °C for 30 min, using a heating rate fixed at 10 °C min⁻¹. Finalized the MH processing, the autoclave was naturally cooled at room temperature. Thus, the solid product was washed with water deionized for several times until neutral pH, and then, dried at 75 °C for 12 h.

2.2. Characterizations

The CTO, CCTO1 and CCTO2 microcrystals were structurally characterized by X-ray diffraction (XRD) in Rietveld routine using a Rigaku-DMax/2500PC (Japan) with Cu-Kα radiation (λ = 1.5406 Å) and in the 2θ range from 10° to 130° with a scanning rate of 0.02° min⁻¹. The MR spectra were obtained using a 488 nm line of a Nd:YAG laser, keeping its maximum output power at 25 mW. The XANES (X-ray absorption near edge structure) spectra were measured at the titanium (Ti) and calcium (Ca) K-edge using the D08B-XAFS2 beam line at the Brazilian Synchrotron Light Laboratory (LNLS). The Ti and Ca K-edge XANES spectra were collected in samples deposited on polymeric membranes, in transmission mode at room temperature with a Si(111) channel-cut monochromator. The spectra were measured from 30 eV below to 150 eV above the edge, with an energy step of 0.3 eV near the edge region. The
analysis of the XANES spectra were performed using IFEFFIT package [21]. Ultraviolet-visible absorption spectra of the (Ca1-xCux)TiO3 microcrystals were performed using Cary 5G equipment. Crystals morphologies were verified using a Scanning Electron Microscope (Jeol JSM-6460LV microscope). PL was measured with a 139 Thermal Jarrel-Ash Monospec 27 monochromator and a Hamamatsu R446 photomultiplier. The 350 nm exciting wavelength of a krypton ion laser (Coherent Innova) was used, keeping a nominal output power of 200 mW. All the measurements were performed at room temperature.

3. Results and discussion

3.1. XRD patterns and Rietveld refinement analyses

The polycrystalline nature of (Ca1-xCux)TiO3 microcrystals was evaluated by XRD patterns and Rietveld refinement analyses. Fig. 1 shows the XRD patterns of CTO(a), CCTO1(b) and CCTO2(c) microcrystals synthesized at 140 °C for 30 min. As it can be observed in the Fig. 1(a–c), CTO, CCTO1 and CCTO2 microcrystals present well-defined diffraction peaks correspondent to a CaTiO3 perovskite-type orthorhombic structure, indicating that these crystals present a structural order at long-range (Fig. 1). All the XRD patterns are in agreement with its respective Inorganic Crystal Structure Database (ICSD) N° 62-149. The Rietveld refinement method was performed to evaluate the effect of copper into CaTiO3 lattice in the CTO, CCTO1 and CCTO2 crystals (Fig. 2(a–d)).

The lattice parameters, unit cell volume and atomic positions were obtained from the Topas Academic program (version 4.1) [22] and the results of diffraction peak profiles were better adjusted as described by Cheary et al. [23]. The structural refinement results for (Ca1-xCux)TiO3 crystals presented at Fig. 2(a–c) indicated that these crystals crystallized in an orthorhombic structure with space group Pbnm, point group symmetry D_{16}^{2}h and four molecular formula per unit cell (Z = 4) [24]. These results show a good relation between the observed XRD patterns and the theoretical ones, as shown by a line (Y_{obs} - Y_{cal}) at Fig. 2(a–c). Moreover, no presence of secondary phases were observed, indicating that the Cu atoms

| Table 1 |

<table>
<thead>
<tr>
<th>Lattice parameter</th>
<th>(Ca1-xCux)TiO3</th>
<th>CTO</th>
<th>CCTO1</th>
<th>CCTO2</th>
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<tr>
<td>a(Å)</td>
<td>5.3796</td>
<td>5.4035(2)</td>
<td>5.4016(2)</td>
<td>5.4030(2)</td>
</tr>
<tr>
<td>b(Å)</td>
<td>5.4426</td>
<td>5.4878(2)</td>
<td>5.4787(2)</td>
<td>5.4895(2)</td>
</tr>
<tr>
<td>c(Å)</td>
<td>7.6401</td>
<td>7.6626(2)</td>
<td>7.6586(2)</td>
<td>7.6595(3)</td>
</tr>
<tr>
<td>V(Å³)</td>
<td>223.68</td>
<td>227.2(1)</td>
<td>226.65(1)</td>
<td>227.18(2)</td>
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<tr>
<td>θ[Ti–O–Ti]</td>
<td>156.7</td>
<td>152.1</td>
<td>152.1</td>
<td>151.7</td>
</tr>
<tr>
<td>Rwp(%)</td>
<td>7.94</td>
<td>6.92</td>
<td>14.46</td>
<td>6.76</td>
</tr>
<tr>
<td>Rbragg (%)</td>
<td>1.60</td>
<td>6.92</td>
<td>2.70</td>
<td>1.30</td>
</tr>
<tr>
<td>χ²</td>
<td>1.37</td>
<td>1.30</td>
<td>1.30</td>
<td>1.30</td>
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</table>

<table>
<thead>
<tr>
<th>Atoms</th>
<th>Atomic coordinates (x; y; z)</th>
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<td>Ca</td>
<td>−0.0067; 0.036; 1/4</td>
</tr>
<tr>
<td>Ti</td>
<td>0; ½; 0</td>
</tr>
<tr>
<td>O1</td>
<td>0.071; 0.484; 1/4</td>
</tr>
<tr>
<td>O2</td>
<td>0.708; 0.2888; 0.0371</td>
</tr>
</tbody>
</table>
were incorporated in the lattice [25]. All the structural refinement data for the analyzed CCTO crystals are presented in Table 1.

Fig. 2(d), presents the change in the lattice parameters (a, b and c) as a function of copper content in (Ca$_{1-x}$Cu$_x$)TiO$_3$ crystals. As can be seen in this figure, the lattice parameters in CTO, CCTO1 and CCTO2 present small deviations as indicated by the error bars. In CaTiO$_3$ crystal, the b lattice parameter value presents a significant change, which probably can be influenced by the microwave assisted hydrothermal method employed in the synthesis. For (Ca$_{1-x}$Cu$_x$)TiO$_3$ microcrystals, it is noticed a reduction in the b lattice parameter value as the concentration of copper increases to 0.01, followed by an enhance of its value for further increase of Cu to 0.02. Probably, this behavior can be associated to the replacement of Ca sites (ionic bond with radial orientation) into the perovskite structure by the Cu atoms (covalent bond with directional orientation).

3.2. Schematic representation of CaTiO$_3$ unit cell

From the lattice parameters and atomic positions obtained from the Rietveld refinement data, it was possible to model a schematic representation of a perovskite-type orthorhombic CaTiO$_3$ unit cell, using the Visualization for Electronic and Structural Analysis (VESTA) program version 2.1.6 for Windows [26], that is illustrated at Fig. 3.

In this representation, the Ca atoms are coordinated to twelve oxygen atoms forming [CaO$_{12}$] clusters with cubic structure, configuration, while the Ti atoms are coordinated to six oxygen atoms forming [TiO$_6$] clusters with octahedral configuration. In the CaTiO$_3$ matrix, it is also possible to observe that the adjacent [TiO$_6$] clusters are displaced from their symmetric center, and present angles between the [TiO$_6$] planes of approximately 152.1, 152.1 and 151.7°. According to Moreira et al. [27], these angles of approximately (154° and 158°) can create structural defects into CaTiO$_3$ lattice, which can be responsible for their PL properties.

3.3. Micro-Raman spectroscopy analyses

Fig. 4(a–c) illustrates the micro-Raman spectra in range from 80 to 750 cm$^\text{-1}$ of the CTO, CCTO1 and CCTO2 microcrystals prepared by MH method.

According to the literature [28,29], the MR spectroscopy is considered a powerful tool in order to determine the degree of structural defects or asymmetric–symmetric into the CaTiO$_3$ lattice.

According to group theory calculations [30-32], the CaTiO$_3$ with perovskite-type orthorhombic structure and space group Pbnm with four clusters per unit cell exhibit 24 Raman-active modes, which are represented by Equation (1) below:

$$I_{\text{(Raman)}} = 7A_g + 5B_{1g} + 7B_{2g} + 5B_{3g}$$  

(1)

The observation of the Raman-active modes in the MR spectrum arises from the stretching, torsional and bending vibrations of the metal–oxygen bonds in the CaTiO$_3$ perovskite-type crystalline structure. However, small changes in polarizability into orthorhombic CaTiO$_3$ lattice [33] caused by the MH method, can improve the interaction between the ions and also promote the overlapping of some Raman active modes with modes of low intensity. Thus, only nine Raman active modes P$_1$, P$_2$, P$_3$, P$_4$, P$_5$, P$_6$, P$_7$, P$_8$ and P$_9$ were detected from the 24 Raman-active modes in the MR spectra of (Ca$_{1-x}$Cu$_x$)TiO$_3$ crystals. The MR spectra of these crystals as well as the Raman peak positions are identified at Fig. 4(a–c) and listed in Table 2, respectively.

The Raman peak P$_1$ is ascribed to the vibration mode of CaTiO$_3$ orthorhombic lattice [34]. The Raman peaks P$_2$, P$_3$, P$_4$, P$_5$, P$_6$ and P$_9$ are

![Fig. 3. Schematic representation for the CaTiO$_3$ unit cell with orthorhombic structure and illustrations of distorted [CaO$_{12}$] clusters and tilted [TiO$_6$] clusters.](image)

![Fig. 4. Micro-Raman spectra of (a) CTO, (b) CCTO1, and (c) CCTO2 microcrystals. The vertical dashed lines indicate the positions and relative intensities of Raman-active peaks and inset shows the symmetric stretching of the O–Ti–O bonds presents in tilted [TiO$_6$]–a–[TiO$_6$] clusters and symmetric stretching of O–Ti–O– bonds.](image)

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Vibration modes</th>
<th>(Ca$_{1-x}$Cu$_x$)TiO$_3$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>0</td>
</tr>
<tr>
<td>P$_1$</td>
<td>CaTiO$_3$ lattice</td>
<td>122</td>
</tr>
<tr>
<td>P$_2$</td>
<td></td>
<td>181</td>
</tr>
<tr>
<td>P$_3$</td>
<td></td>
<td>227</td>
</tr>
<tr>
<td>P$_4$</td>
<td>O–Ti–O bending mode</td>
<td>245</td>
</tr>
<tr>
<td>P$_5$</td>
<td></td>
<td>296</td>
</tr>
<tr>
<td>P$_6$</td>
<td></td>
<td>344</td>
</tr>
<tr>
<td>P$_7$</td>
<td>TiO$_3$ torsional mode</td>
<td>464</td>
</tr>
<tr>
<td>P$_8$</td>
<td></td>
<td>536</td>
</tr>
<tr>
<td>P$_9$</td>
<td>Ti–O symmetric stretching</td>
<td>714</td>
</tr>
</tbody>
</table>
related to O–Ti–O bending vibration modes or caused by the tilting phenomenon between the [TiO₆]–x–[TiO₆] clusters [35] (Inset Fig. 4). The P7 and P8 Raman peaks are attributed to the torsional modes, while the peak P9 is assigned to the Ti–O symmetric stretching vibration mode [36].

As the concentration of Cu²⁺ increases up to \( x = 0.02 \) in the CaTiO₃ lattice (Fig. 4(a–c)), it is possible to observe that the Raman active modes situated at 714, 693 and 723 cm\(^{-1}\) (P9) for the CTO (Fig. 4(a)), CCTO1 (Fig. 4(b)) and CCTO2 (Fig. 4(c)) microcrystals, respectively, present a more evident shift with increase of Cu content into CaTiO₃ lattice. The shifts observed on the characteristic positions of Raman peaks (Table 2), comparing to the pure CaTiO₃ can be related to the symmetry breaking of the [CaO₁₂] clusters caused by the introduction of copper in the A-site into the CaTiO₃ matrix. This symmetry breaking is caused by the covalent nature of the Cu–O linkages, which is able to change the electronic density of the [CaO₁₂] and [TiO₆] clusters [37], since its clusters are interconnected into the CaTiO₃ matrix. Besides that, this effect produces structural defects such as distortions and/or strains in the matrix that can modify the rotational modes of the \( \sim O \sim Ti \sim O \) bonds in the octahedral [TiO₆] clusters. Table 2 shows a comparative between the Raman modes obtained in this work for the CTO, CCTO1 and CCTO2 microcrystals with those reported in the literature [38,39].

As can be observed in this table, the Raman positions presented in this work are close to the reported by the literature and the small deviations are influenced by the distortions and defects into lattice due to MH method employed in the synthesis of the CTO, CCTO1 and CCTO2 microcrystals.

3.4. X-ray absorption near edge structure spectroscopy analyses

The XANES analyses were usually performed as a semi-quantitative technique to get information about changes in the coordination of titanates lattice formers as well as the lattice modifiers [11,31,32]. Fig. 5(a) presents a normalized Ti K-edge XANES spectra of CTO, CCTO1 and CCTO2 microcrystals prepared by MH method, respectively.

In these spectra, it was observed a small peak situated at around 4970.8 eV (\( \sim \)), which is attributed to a transition of the 1s electron to an unfilled d level. This forbidden electronic dipole transition is normally allowed by the mixture of p orbitals from surrounding oxygen atoms into the unfilled d states of titanium atoms [39]. Farges et al. [40] have reported that the intensity and energy of this peak in titanates is associated with the coordination number of the Ti atoms (4, 5, and 6) with the oxygen atoms. As can be seen at Fig. 5(a), the pre-edge peak observed for \((\text{Ca}_1-x\text{Cu}_x)\text{TiO}_3\) is characteristic of a six-coordination of the octahedral [TiO₆] clusters, which is observed in well-crystallized titanates [41,42]. Besides that theoretical and experimental studies showed that for the perovskite type materials the higher intensity of this peak indicates that the local environment of Ti is non-centrosymmetric, i.e., is distorted from its symmetric center [27,29].

Concerning the main pre-edge peak (\( \sim \)) of the \((\text{Ca}_1-x\text{Cu}_x)\text{TiO}_3\) crystals illustrate in details on Fig. 5(b), it is possible to verify that the pre-edge peak of the \((\text{Ca}_1-x\text{Cu}_x)\text{TiO}_3\) crystals increase in the intensity value as the concentration of copper increases from \( x = 0 \) to 0.02 (inset in Fig. 5(b)). From local point of view, the analysis of the XANES at the Ti K-edge indicated the local polarization of
behavior is accompanied by dislocation of the $[\text{TiO}_6]-[\text{TiO}_6]$ adjacent clusters from its symmetric center [45,46].

The obtained results show that the local defects into the orthorhombic structure, caused by the changes in $\alpha$-angles are strongly related to the formation of $[\text{TiO}_6]_o$ $\leftrightarrow$ $[\text{TiO}_6]_d$ clusters ($o =$ ordered, $d =$ disordered) in the $(\text{Ca}_{1-x}\text{Cu}_x)\text{TiO}_3$ microcrystals. Thus, the distortion between these complex clusters causes a polarization and/or difference in charge density in the structure [47,48], which is able to promote a charge transfer from the $[\text{TiO}_6]_o \rightarrow [\text{TiO}_6]^x$. These complex clusters can also create the $(h^+)$ holes $\leftrightarrow$ electron (e$^-$) pair or $[\text{TiO}_6]_d \leftrightarrow [\text{TiO}_6]^x$ clusters in the CTO, CCTO1 and CCTO2 systems. The charge transference in $(\text{Ca}_{1-x}\text{Cu}_x)\text{TiO}_3$ crystals is also represented by Kröger–Vink notation [49] by means of clusters notations in Equation (2):

$$[\text{TiO}_6]^x + [\text{TiO}_6]_d \rightarrow [\text{TiO}_6]_o + [\text{TiO}_6]^x$$  (2)

Based on the obtained results we propose that PL emission is affected not only by the structural defects in the network former, but also in the network modifier. So, this phenomenon was studied by means of Ca K-edge XANES experiments. Fig. 6(a) illustrates the pre-edge region (●) situated at around 4.040 eV and the XANES spectra of the CaTiO$_3$ and $(\text{Ca}_{1-x}\text{Cu}_x)\text{TiO}_3$ microcrystals presents a similar profile as reported by our research group [31,32].

As it can be seen in the inset of Fig. 6(b), the intensity of the pre-edge region (●) for the CTO, CCTO1 and CCTO2 also varies with the amount of copper added to these systems. As there is an interconnection of $[\text{TiO}_6]$ and $[\text{CaO}_{12}]$ clusters in the perovskite structure, it was possible to conclude that the distortions on the $[\text{TiO}_6]$ clusters caused by the $[\text{CuO}_{12}]$ clusters, can promote the deformation of the Ca–O bonds. Therefore, we can attribute this behavior as the increase in the number of distorted $[\text{CaO}_{12}]$ clusters into the CaTiO$_3$ orthorhombic structure [50]. Another important fact to be considered is that the disorder–degree of these $[\text{CaO}_{12}]$ complex clusters is strongly dependent of Ca/Cu ratio in the $(\text{Ca}_{1-x}\text{Cu}_x)\text{TiO}_3$ systems.

The local defects into the perovskite structure caused by the disorder into the lattice modifier are associated to the charge transfer from the $[\text{CaO}_{12}]^x \leftrightarrow [\text{CaO}_{12}]_o$ complex clusters. Also, the proposed model for the lattice former can be extended for the network modifiers, and is represented by Kröger–Vink notation [49] by means of clusters notations in Equation (3):

$$[\text{CaO}_{12}]_o \leftrightarrow [\text{CaO}_{12}]^x$$  (3)
\[ \frac{1}{2} \text{CaO}_{12}^{x} + \frac{1}{2} \text{CaO}_{12}^{d} \rightarrow \frac{1}{2} \text{CaO}_{12}^{y} + \frac{1}{2} \text{CaO}_{12}^{z} \]  

The obtained results reported through the Ti-K edge XANES and Ca K-edge XANES analyses showed a good agreement with those observed through the micro-Raman analyses (Fig. 4), which also confirms that the presence of \( \text{[TiO}_6^{4-} \text{]}_{d} \) and \( \text{[CaO}_{12}^{z} \text{]}_{d} \) complex clusters as concentration of copper increases in the CTO, CCTO1 and CCTO2 systems are able to create structural defects, such as: distortions and/or strains into the CaTiO\(_3\) matrix, which can influence its optical properties.

### 3.5. UV–vis absorption spectroscopy analyses

Fig. 7(a–c) shows the UV–vis absorbance spectra of CTO, CCTO1 and CCTO2 crystals synthesized at 140 °C for 30 min in MH system.

In this paper, the optical band gap energy \( (E_{\text{gap}}) \) was estimated by the method proposed by Kubelka–Munk [51]. This method allows the obtention of \( E_{\text{gap}} \) values with best accuracy [52]. The light-scattering phenomena causes some problems with turbid or colloidal samples. Besides that, this effect can lead to substantial energy losses. Thus, the diffuse reflectance spectroscopy is more accurate than the transmission spectroscopy, since it is possible to extract information on the optical properties and we can apply for both crystalline powders and amorphous thin films oxides. In this case, the Kubelka–Munk equation at any wavelength is given by Equation (4) below:

\[
F(R_\infty) = \frac{1 - R_\infty}{2R_\infty} = \frac{k}{s} 
\]  

where, \( F(R_\infty) \) is the Kubelka–Munk function or is the diffuse reflectance of the layer relative to a non- or low-absorbing
standard. In our case the MgO was used to get the term 
\( R_\infty = \frac{R_{\text{sample}}}{R_{\text{MgO}}} \), \( k \) is the molar absorption coefficient of the 
(\( \text{Ca}_{1-x}\text{Cu}_x\text{TiO}_3 \)) crystals and \( s \) is the scattering coefficient.

In the parabolic band structure, the \( E_{\text{gap}} \), and absorption coefficient (\( \alpha \)) of a semiconductor oxide [53] are related through the well known Equation (5):

\[
a\nu = C_1 (R_\infty (\nu - E_{\text{gap}})^n
\]

where \( \alpha \) is the linear absorption coefficient of the material, \( \nu \) is the photon energy, \( C_1 \) is a proportionality constant, \( E_{\text{gap}} \) is the optical band gap and \( n \) is a constant associated to the different types of electronic transitions (\( n = \frac{1}{2} \) for direct allowed, \( n = 2 \) for indirect allowed, \( n = 3/2 \) for direct forbidden and \( n = 3 \) for indirect forbidden).

The literature [27] describes that the band gap energy is direct when the electronic transitions occur from the maximum-energy states (near or inside) the valence band (VB) to minimum-energy states (below or inside) the conduction band (CB), in a same regions in the Brillouin zone. Therefore, the presence of different \( E_{\text{gap}} \) values calculated from the UV–vis absorption spectra indicates the existence of intermediary energy levels between the valence and conduction band [54].

For CaTiO3 crystals, the electronic transitions occurs inside the [TiO6] octahedral clusters, since the 2p orbitals of oxygen atoms in valence band and the 3d orbitals of the titanium atoms can also be associated to the conduction band (Fig. 7(a)), which can be perturbed or non-uniformly distributed in the Brillouin zone. However, for the (\( \text{Ca}_{1-x}\text{Cu}_x\text{TiO}_3 \)) microcrystals (Fig. 7(b) and (c)) the 3d orbitals of the copper atoms will be associated to the conduction band [55], so a decrease of the optical gap is observed. Moreover, structural defects such as distortions and/or strains in the CaTiO3 lattice caused by the introduction of copper in these systems are able to induce the symmetry break of the [TiO6] and [CaO12] leading to an appearance of intermediary levels between the valence and conduction bands. Thus, an increase in the \( E_{\text{gap}} \) value is observed for the CCTO2 crystal (Fig. 7(c)).

### 3.6. Photoluminescence analyses: emission spectra studies

To a better understanding the optical properties of the CTO, CCTO1 and CCTO2 crystals, the PL spectra measurements were performed at room temperature, using an excitation of a krypton laser source at 350 nm. The obtained results are presented in Fig. 8.

According to the literature [30–32], the PL properties of the distorted CaTiO3 microcrystals are related to defects into the orthorhombic lattice. As it can be observed in Fig. 8, the pure CaTiO3 crystals have a high PL emission at room temperature with maximum PL emission at 496 nm. Moreover, these CaTiO3 crystals present a low PL emission with a shoulder at around 771 nm (infrared region). As the substitution of Ca by Cu increases in the (\( \text{Ca}_{1-x}\text{Cu}_x\text{TiO}_3 \)) crystals (CTO and CCTO1), it is noticed that PL emission appear only in the visible region of the spectra (green region).

The CTO, CCTO1 and CCTO2 crystals presented a broad band emission typical of systems which the relaxation processes occur by different paths, involving intermediary levels in the band gap. Thus, the decomposition of these broad bands was used to get the information of which electronic transitions group is influencing the PL response (Fig. 9(a–c)). The decomposition was performed using the PeakFit [56] Program (version 4.05), and the Gaussian function was used successfully to fit the PL peaks and tuning parameters, including the peak positions and its corresponding areas (Fig. 9(a–c)).

In this work, the PL curves can be composed by three components: The violet component (with a maximum around of 438 nm), the blue component (with a maximum around 488 nm) and the green one (with a maximum around of 551 nm). Analyzing the evolution of the PL emission of the CTO, CCTO1 and CCTO2 crystals prepared by MH method (Fig. 9(a–c)) it is notice that all samples exhibit a PL emission with maximum situated at 550 nm (green emission). Moreover, the percentage area of this component increases with the concentration of copper. This observation confirmed that the PL response is directly ascribed to localized states in the band gap due to structural defects in the (\( \text{Ca}_{1-x}\text{Cu}_x\text{TiO}_3 \)) crystalline structure. The green emission (less energetic) is accompanied by a reduction in the \( E_{\text{gap}} \) for CCTO2 crystals, which is
related to the insert of deep defects between the valence and conduction bands [57]. Moreover, we have observed a low concentration of shallow defects in violet–blue region in PL spectra for all (Ca\(_{1-x}\)Cu\(_x\))\(\text{TiO}_3\) crystals.

Based on the XANES obtained results, we believe that the symmetry breaking of the [CaO\(_{12}\)] and [TiO\(_6\)] clusters caused by the introduction of copper in the lattice, causes some modifications charge density of the [CaO\(_{12}\)] and [TiO\(_6\)] clusters, which makes more favorable the charge transference process from the [TiO\(_6\)]\(^{2-}\) to [CaO\(_{12}\)]\(^{2-}\) and from the [CaO\(_{12}\)]\(^{2-}\) to [CaO\(_{12}\)]\(^{2-}\). The process charge transfer in the (Ca\(_{1-x}\)Cu\(_x\))\(\text{TiO}_3\) crystals can facilitates the radiative recombination, that is favorable to intense the PL emission process.

3.7. Field emission scanning electron microscopy analyses

Fig. 10 illustrates the FE-SEM images of the: (a) CTO, (b) CCTO1, and (c) CCTO2 microcrystals, respectively.

From these FE-SEM images shown in the Fig. 10(a–c) were verified that the crystals are agglomerate and polydisperse. These microcrystals exhibit a shape as irregular cubes in agreement with the literature [15,27]. Some of these cube-like (Ca\(_{1-x}\)Cu\(_x\))\(\text{TiO}_3\) microcrystals are small, regular, very faceted and present a smooth surface that may be associated to the microwave irradiation exposure.

A possible growth mechanism for the microcrystals was proposed to explain in details the effect of microwave and synthesizes conductions on the shape of these microcrystals (Fig. 11).

In the synthesis of the (Ca\(_{1-x}\)Cu\(_x\))\(\text{TiO}_3\) microcrystals using basic conditions (KOH [6 M]), initially, occurs the hydrolysis of Ca\(^{2+}\), Cu\(^{2+}\) and Ti\(^{4+}\) ions giving rise to the Ca(OH)\(_2\), Cu(OH)\(_2\) and TiO(OH)\(_2\) precipitates (Fig. 11(a)). At pH = 14, there is an excess of OH\(^-\) ions in the reactive mixture. Besides that, in this pH range, the Cu species does not react directly with the Ti species, so, only the (Ca\(_{1-x}\)Cu\(_x\)) TiO\(_3\) species is formed in the end of the MH method [58]. The microwave radiation interacts with the permanent dipole of the liquid phase (water) inside the Teflon autoclave camera. This interaction leads to a vibration on the charged particles or molecules, resulting in a rapid heating of the chemical solution, promoting, consequently, the dissociation of the as formed Ca(OH)\(_2\), Cu(OH)\(_2\) and TiO(OH)\(_2\) particles into Ca\(^{2+}\), Cu\(^{2+}\), Ti\(^{4+}\) and OH\(^-\) ions. These hydroxyls group are located in the particles surfaces which are connected through H-bonds. The heating promoted by these vibrations leads to a break of these interplanar H-bonds and consequently accelerates the dehydration rate. As consequence, this mechanism contributes to a rapid transformation process of Ca(OH)\(_2\), Cu(OH)\(_2\) and TiO(OH)\(_2\) to (Ca\(_{1-x}\)Cu\(_x\))\(\text{TiO}_3\) micro-cubes (Fig. 11(b)). Moreover, the hydroxyls radiation and the excess of the hydroxyls in the reactive media is able to accelerate the solid particles to higher speed leading to an increase of the interparticle collisions, inducing the effective coalescence of these particles at the point of collision. These mechanisms are responsible for the fast nucleation of the (Ca\(_{1-x}\)Cu\(_x\))\(\text{TiO}_3\) small particles, as well as the small crystals dissolve and it deposits onto larger crystals. This growth mechanism is known as Ostwald Ripening.

From the FE-SEM images illustrated in the Fig. 10(a–c), it is possible to observe that the aggregation process is favored in the (100) and (010) planes [59]. The formation of the Cu(OH)\(_2\) is very important in this process, because it can modify the electrostatic interactions between these ions promoting the initial formation of (Ca\(_{1-x}\)Cu\(_x\))\(\text{TiO}_3\) plates (Fig. 11(b)). Moreover, the self-assemble of these plates is favored in some energetic crystallographic planes. Therefore, the micro-cubes will grow from aggregation and self-assemble of these plates along the (100) and (010) directions [60]. As the concentration of Cu\(^{2+}\) increases to 0.02, the presence of copper ions in the reactive media promotes the increase of the electrostatic interaction between the ions. As a consequence, the plates are dissolved in the reational media followed by the condensation in the (100) and (010) directions forming irregular cubes that grow in these directions (Fig. 11(b,c)).

We believe that the irregularities and aggregation of cube-like (Ca\(_{1-x}\)Cu\(_x\))\(\text{TiO}_3\) microcrystals were caused by the fast nucleation of the first small plates crystals and by the high collision rates between small particles. The schematic representation of the growth mechanism of the (Ca\(_{1-x}\)Cu\(_x\))\(\text{TiO}_3\) particles by the MH proceeding is exposed at Fig. 11(c).

4. Conclusions

In summary, irregular cube-like (Ca\(_{1-x}\)Cu\(_x\))\(\text{TiO}_3\) microcrystals were prepared by MH method in a short time (30 min) and a low temperature (140 °C). This method is very promising in the synthesis of other titanates with interesting PL properties to possible applications in optical devices. XRD patterns and Rietveld refinement data indicated that these microcrystals crystallize in an orthorhombic structure. XANES spectra and micro-Raman confirms the presence of Cu in the CTO, CCTO1 and CCTO2 systems can induce a local polarization in the [CaO\(_{12}\)] and [TiO\(_6\)] clusters which is associated to the covalent nature of Cu\(^{2+}\) ion. Moreover, XANES analyses indicated that the increase of Cu concentration favors the
presence of TiO$_6^{2-}$/TiO$_5^{4-}$ and [CaO$_2$]$_n$/[CaO]$_n$ complex clusters into lattice. UV–vis spectra showed a tendency for a reduction in $E_{\text{gap}}$ values of crystalline CTO, CTO1 and CTO2 microcrystals, which can be associated to introduction of 3d orbitals of Cu. The TiO$_2$ powder presented an intense PL blue-emission and low emission with a shoulder at around 771 nm (infrared emission). A reduction in the intensity PL emission as well as a shift for green-emission was noted with Cu increase up to x = 0.01. FEG-SEM images showed that the (Ca$_1-x$Cu$_x$)TiO$_2$ crystals are composed by aggregated and polydisperse cubes. Finally, we have suggested from FEG-SEM images that Ostwald-ripening and self-assemble mechanisms can be responsible by growth process of these microcrystals.

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