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Review paper

Intense photoluminescence emission at room temperature in calcium copper titanate powders

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Abstract

A study was undertaken about the structural and photoluminescent properties at room temperature of $CaCu_3Ti_4O_{12}$ (CCTO) powders synthesized by a soft chemical method and heat treated between 300 and 800 °C. The decomposition of precursor powder was followed by thermogravimetric analysis (TG-DTA), X-ray diffraction (XRD), Fourier transform infrared (FT-IR), Fourier transform Raman (FT-Raman) and photoluminescence (PL) measurements. XRD analyses revealed that the powders annealed at 800 °C are becoming ordered and crystallize in the cubic structure. The most intense PL emission was obtained for the sample calcined at 700 °C, which is not highly disordered (300–500 °C) and neither completely ordered (800 °C). From the spectrum it is clearly visible that the lowest wavelength peak is placed around 480 nm and the highest wavelength peak at about 590 nm. The UV/vis absorption spectroscopy measurements showed the presence of intermediate energy levels in the band gap of structurally disordered powders. © 2012 Elsevier Ltd and Techna Group S.r.l. All rights reserved.

Keywords: A. Ceramics; B. Chemical syntheses; B. Powder metallurgy; C. X-ray diffraction

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1. Introduction

Order and disorders of the material are the keys to many unsolved structural problems and unexplained structurerelated properties in solid materials. In particular, structural order-disorder is always present in real materials and may play an important role in technological applications by altering their electronic and optical properties. Therefore, physical principles that govern the structural state of a given perovskite and how that state may change have been for a long time the subject of investigation and debate. Compounds with the perovskite structure, ABO₃, and its derivatives are perhaps the most widely investigated subjects, owing to their significance to both fundamental

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research and the high potential for technological applications because of their diverse physical properties [1-5]. Their electronic structures and photophysical properties have been the goal of many researchers; lots of efforts have been mainly devoted to studying the photoluminescence (PL) emissions of titanates such as $ATiO_3$ (A = Ca, Sr, Ba, Pb) [6-12]. The PL emissions in perovskite materials are considered to be closely related to the crystal structure and they are responsible for the disorders in metal-oxygen polyhedra. In particular, TiO₆ octahedra has significant structural flexibility. Perhaps the most obvious expression of such flexibility is the fact that under ambient conditions many titanates present structures with lower symmetries that can be indeed derived from the cubic aristotype structure (Pm3m symmetry) through the rotation or tilting of regular, rigid octahedra or due to the presence of distorted TiO_6 octahedra [13]. It is significant that although the structure is distorted, the rotation/tilting does not disrupt the corner-sharing connectivity. The tilting of the octahedral framework also plays a key role in determining the properties of oxide perovskites.

The present work focuses on links between the structure and the photoluminescent behavior of CCTO powders. In the framework of a more extensive project [14,15] aimed at the design and synthesis of perovskite-based materials with PL properties, we investigate the role of order and disorders on the structural and photoluminescent behavior of CCTO powders. The main objective is to investigate the impact of structural order and disorders on the PL emission associated with octahedral tilting. This research involves four critical steps: (1) synthesis of the powders; (2) structural characterization of the disorders to clarify their relationships with the orderliness of parental samples; (3) establishing the formation mechanisms of the disorders; and more importantly; (4) revealing the relationships between structural disorders and the properties of PL.

2. Experimental procedure

CCTO powders were prepared by the soft chemical method, as described in the literature [16]. The polymeric resin was placed in a conventional furnace and heat treated at 300 °C for 4 h, forming the precursor powders. These disordered powders were heat treated from 300 to 800 °C for 2 h in a tube furnace under ambient conditions. Thermal effect was investigated by thermogravimetric analysis (TGA) and differential thermal analysis (DTA) in the apparatus STA 409, Netzsch, Germany. Synthetic air flow $(30 \text{ cm}^3/\text{min}^{-1})$ with a constant heating rate of $5 \,^{\circ}\text{C/min}^{-1}$ from room temperature up to 1200 $^{\circ}\text{C}$ was used. The crystalline phase of the CCTO powders was analyzed by X-ray diffraction (XRD) patterns recorded on a Rigaku-DMax 2500PC, Japan, with Cu Ka radiation in the 2θ range from 20° to 80° with $0.03^{\circ}/\text{min}^{-1}$. Fourier transform Raman spectroscopy (FT-Raman) was performed on a Bruker-RFS 100, Germany. A 1064 nm Nd:YAG laser was used as (an) excitation source with its power kept at 70 mW to obtain the Raman spectra. Ultraviolet–visible (UV–vis) spectroscopy for the optical absorbance spectra of ordered/disordered CCTO powders was taken using Cary 5G equipment. PL properties were measured with a Thermal Jarrel-Ash Monospec27 mono-chromator and a Hamamatsu R446 photomultiplier. The excitation source was 350.7 nm wavelength of a krypton ion laser (Coherent Innova), keeping their power at 200 mW. All measurements were performed at room temperature.

3. Results and discussion

Fig. 1 shows the evolution of the XRD patterns of CCTO powders heat treated from 300 to 800 °C for 2 h under ambient conditions. Diffraction peaks are visible in the powders annealed at 450, 500, 600 and 700 °C, indicating that, at these temperatures; the powders are structurally long-range disordered. The presence of CuO, TiO₂ and other unidentified phases are more than evident in this temperature range. XRD patterns revealed that a multiphase CCTO system obtained for different methodologies and heat treated at 800 °C [17-19] are equivalent. CCTO phase is structurally more ordered with the rise of calcination temperature reaching 800 °C. The crystallization process of the structurally disordered CCTO clearly starts at low temperatures as low as 400 °C (see Fig. 1), and is becoming ordered after annealing at 800 °C, which is allowing for its partially indexation in accordance with lattice parameter values obtained from the standard JCPDS No. 75-2188 data. The amount of each phase for this temperature condition will be determined from Rietveld analysis and the results will be presented sooner.

Fig. 2 shows the thermal decomposition behavior of the polymeric resin precursor of CCTO powders analyzed by



Fig. 1. XRD patterns of CCTO powders heat treated from 300 to 800 $^{\circ}$ C for 2 h under ambient condition.



Fig. 2. TG/DTA curves of the polymeric resin precursor of CCTO powders annealed from room temperature to 1200 °C.

TGA and DTA. In these experiments, the decomposition process of the polymeric resin was monitored. The TGA curve shows two main regions, the first one is mostly due to dehydration and evaporation of organic substances, components from 70 to 230 °C. The other large one between 230 and 480 °C seems to be associated with the decomposition and burnout of the organic components. Both stages led to big weight loss due to the decomposition of residual solvent and decomposition of organic compounds present in the precursor powders. The DTA curve presents a small exothermic peak at 325 °C related to the formation of CuO phase. More intensive exothermic peak at around 410 °C may be described as the major process of decomposition of the residual organic compounds to the beginning of the structural order of CCTO phase. Finally, from 490 °C no weight loss was observed, what suggests the formation of ordered or crystalline CCTO phase.

In Fig. 3 the FT-IR spectra of the CCTO powders heat treated from 300 to 800 °C for 2 h under ambient conditions are shown. Typical bands characteristic of oxygen-metal bonds were observed in the $450-640 \text{ cm}^{-1}$ region [20]. The multiple absorption bands appears at 650-780 cm⁻ arising from the v(M-O) and $\delta(O-C=O)$. The absorption at 770 cm⁻¹ will have more contribution from v(Ti–O), whereas the absorption at 635 cm^{-1} have dominance from v (Cu–O) bending. The bridging carbonates groups with the planar (D2h) or twisted (D2d) conformation can exhibit only two absorptions arising from the C-O stretching vibrations (vCO). Independently on the temperature, the samples are free of carbonates (C=O vibration which appears at around 1450 cm^{-1}). This proves, that thermal treatment at low temperature is sufficient to eliminate the organic components and that the resulting phase is indeed a carbon-free transitional inorganic amorphous phase. From a technological point of view, this is a sufficient result since many properties depend on the purity of the raw powders, especially carbonate traces. The band at 2350 cm^{-1} refers to the atmospheric CO2 adsorbed from the environment. The O-H bond tensioning near 3400 cm⁻¹ could be attributed to adsorbed



Fig. 3. FT-IR patterns of CCTO powders heat treated from 300 to 800 $^\circ C$ for 2 h under ambient condition.

water due to the contact of a sample with the environment. In CCTO powders annealed at low temperatures (600 °C and 700 °C) two absorption bands are observed which can be related to the defects in bonding. The first band at 635 cm^{-1} is related to the pyramidal MO_5 (M = Ti), due the presence of bond breakage and/or formation. The bonding formation process, which is reduced by increased temperature and the consequent transformation into MO₆ octahedra, can be related to the second band. The broken bonding can be correlated to the presence of oxygen vacancies Vo between the bonds: $[(O \cdots Ti \cdots O \cdots Ti \cdots V_{O}^{\bullet}) \cdots]$. These two bands are probably the result of co-occurrence of $[MO_5]$ and $[MO_6]$ (M=Ti) clusters. It was observed that the first band was relatively more intense in CCTO powders annealed at 500 °C. After increase of the temperature that two bands merge together and create a wider band. With increasing heattreatment temperature, broad absorption bands at around 770 cm^{-1} , due to the MO₆ stretching mode, suggesting the onset of formation of MO₆ octahedra in the perovskite structure. Due to the resonance with the longitudinal optic (LO) phonon modes, these bands become sharper and narrower, and shift very slightly toward higher wave numbers. This is considered to be a stiffening of a network and a structural rearrangement, which lead to the perovskite phase formation, increasing the crystallinity of the CCTO phase.

Fig. 4 shows the Raman spectra of the CCTO powders heat treated from 300 to 800 °C for 2 h under ambient conditions. For the spectra of a sample thermal treated at 800 °C for 2 h we can point out five evident peaks, all of them associated with CCTO phase: 296, 343, 447, 501, 605 cm⁻¹. These are matching with other reported results for CCTO [21]. Powders heat treated at 700 °C for 2 h present a relevant peak at 447 cm⁻¹, typical of CCTO phase, but the general spectra is significantly poorer than the powder heat treated at 800 °C for 2 h. The Raman line at 296 cm⁻¹ is a weak low frequency peak that is almost certainly associated with the E_g mode [22]. 448 cm⁻¹ and



Fig. 4. Raman spectra of CCTO powders heat treated from 300 to 800 $^{\circ}$ C for 2 h under ambient condition.

511 cm⁻¹ peaks are associated with the Ag symmetry (TiO₆) rotation-like and 575 cm^{-1} of Fg symmetry (O-Ti-O) antitensing. According to the literature [23], the main mode associated to titanium oxide (anatase phase) showed a very intense band at around 143 cm^{-1} . Although high structural disorder degree at short range was noted in the powders heat treated at low temperatures, the spectra showed Raman active modes. A wide Raman active mode of the CCTO powders heat treated at 600 °C, confirmed no structural organization at long range, but structural order at short range. Nevertheless, the Raman spectra obtained from the CCTO powders thermally treated at low temperature evidenced Raman active modes associated to the rutile phase of TiO_2 (610 cm⁻¹) [24]. Besides the main peak of CCTO phase, no significant mode at 249 cm⁻¹ related to CuO phase was evidenced which is in good agreement with XRD results. According to the studies reported by Kolev et al. [7] and Valim et al. [25], the bands near 290, 445 and 510 cm⁻¹ are associated to TiO₆ rotation-like modes, whereas the bands at 574 cm⁻¹ and around 780 cm⁻¹ are characteristic for Ti– O-Ti antitensing and tensing vibrations of TiO₆ octahedra, respectively. Raman active modes associated with calcium titanate or copper oxides, as reported in the literature, are not noticeable in the spectrum [25]. This is in good agreement with the XRD pattern and confirms that CCTO is the main phase with rutile TiO₂ and CuO present only as minor impurities. Raising of the temperature promotes increase of structural order which is due the appearance of well defined Raman peaks (see powders treated at 700 and 800 °C).

Fig. 5 illustrates the UV-vis spectral dependence of absorbance for the ordered-disordered CCTO powders. The maximum absorption was located at around 400 nm with respective band gap values determined from the Kubelka Model [26]. The optical energy band gap is related to the absorbance and to the photon energy by



Fig. 5. UV–vis absorbance spectra of CCTO powders heat treated at (a) 300 and (b) 700 $^\circ C$ for 2 h under ambient condition.

the following:

$$h \nu \alpha \propto \left(h^{\circ} - E_g^{opt}\right)^2 \tag{1}$$

where α is the absorbance, *h* is the Planck constant, *v* is the frequency and E_g^{opt} is the optical band gap [27]. In structurally ordered–disordered CCTO powders, the absorbance measurements suggest a non-uniform band gap structure with a tail of localized states (see Fig. 5a and b). These results are confirmed by the UV–vis spectra, which show the decrease of the Urbach tail with the temperature increase. The reduction in the optical band gap [*E*(gap)] energy of the disordered CCTO can be correlated to the raise of structural defects or localized states inside the band gap. The optical band gap behavior can be associated to the changes in the local atomic structure or lattice, as observed in XRD and Raman results. The obtained values are 1.38 and 1.63 eV which



Fig. 6. PL spectra at room temperature of CCTO powders heat treated from 300 to 800 $^\circ$ C for 2 h under ambient condition.

are quite different to the values reported by Kant et al. (around 200 meV) [28]. This change in the band gap can be ascribed to a reduction of defects in the lattice which decreases the intermediary energy levels due to the reduction of oxygen vacancies located at BO_6^- octahedra. Possibly, this behavior is due to the distortions caused into the [MO₆] octahedra group by differences in the annealing temperature. However, future investigations will be necessary to a better understanding. The disordered powder heat treated at 300 °C (see Fig. 5a) presents a similar spectral dependence as observed in amorphous semiconductors (silicon and insulators). The nature of these exponential optical edges and tails may be associated with localized defect states promoted by the disordered structure. It can be observed that the absorbance spectra indicate that the sample heat treated at a lower temperature displays a more disordered structure. In this sample, a high absorbance values throughout the whole photon energy range, due to the presence of a high amount of secondary phases is evident. However, CCTO powders heat treated at 700 °C showed a typical band (an interband transition) in the high energy region of the absorbance curve for ordered or crystalline materials (see Fig. 5b). The tendency observed shows that the optical band gap depend on the preparation method and heat treatment. Therefore, the development of optical band gap as function of temperature can be used as a means to the evaluation of the structural order-disorder degree of CCTO powders prepared by the soft chemical method.

Fig. 6 shows the PL spectra of CCTO powders heat treated from 300 to 800 °C for 2 h under ambient conditions. CCTO powders heat treated at 700 °C for 2 h present an intense and broad PL with a maximum at around 490 nm in the visible region (orange). PL emission can be lower due to the presence of large amount of defects associated to the disorder in the CCTO lattice. The PL is strongly dependent on the heat treatment conditions

[29,30], showing that high temperatures cause a reduction in the defects or disorder of materials. This disordered material is initially composed of the polymeric precursor, which already presents a slight PL. The intensity of PL emission increases with the elimination of organic matter, as indicated in Fig. 6. This intensity is likely associated with the structure organization level [31], and the charge transfer occurring between calcium, copper and titanium ions. However, it is very important to note that there are electronic levels of the amorphous cluster included in the wide band gap of the crystalline cluster evidencing a charge transfer between (TiO_6) and (TiO_5) centers. In this case, one titanium ion forms an octahedral TiO₆ complex, and the other titanium ion, in a different octahedron, forms an TiO₅ complex plus an oxygen vacancy. If these two different V_O^{••} structures coexist together, the charge of the two holes is compensated by one oxygen vacancy. This suggests, that the formation of an amorphous cluster may introduce electronic levels in the forbidden gap. The octahedral geometry of the crystalline cluster is an advantage for TiO₆ because it minimizes the electrostatic interactions among the six oxygen ligands arranged around the positively charged titanium (Ti (1)) center. The interactions between Ti and O in the (TiO₆) complex are strong, while in the (TiO_5) complex they are weak. This means that the dz^2 and $dx^2 - y^2$ bonding combinations in the crystalline cluster are unstable and in the amorphous cluster are stable. As a consequence, the gap in the crystalline cluster is higher than in the amorphous cluster. The results show that the transfer charge is not only for the network former (TiO_6) , but also for the network modifier (CaO₂ and CuO). Thus, the symmetry of the CaTiO₃ and CuTiO₃ systems is modified intrinsically by the random movement of the calcium and copper atoms, due to their ionic character, associated differently to the titanium, to the ligand defects. The best PL emission was obtained from the structure, that was not completely amorphous (300 °C) neither fully ordered (800 °C). Although crystalline samples are not photoluminescent under excitation by the 488 nm line of an argon ion laser used in this study, similar compounds exhibit luminescence with different light sources [32]. The structural transformations of the CCTO phase occurring from disordered to ordered phases start from the early stage of the polyesterification of the citrate solution containing the titanium, and calcium and cupper ions. The titanium, which is the lattice former, tends ideally to bond with six oxygens, but before it reaches this ideal configuration there exist various coordination numbers for Ti in the structure. When the crystallization is reached, only TiO₆ clusters exist and the PL vanishes, showing, that a complete orderliness is not suitable for a good PL emission. Before the crystallization, the structure is a mixture of TiO_x clusters intercalated by Ca and Cu atoms. The higher the heat treatment temperature, the more frequent the TiO₆ conformation and the more ordered the structure, confirmed by FT-IR and DRX spectra. The PL spectra show, that a complete disorder is not



Fig. 7. Wide band model representation of a simple mechanism to explain the PL behavior of CCTO powders processed by the polymeric precursor method: (a) before excitation, (b) excitation (formation of self-trapped excitons), and (c) after excitation [recombination of electron (e^-) hole (h^{\bullet}) .

favorable for a high PL emission, as the spectrum of the 450 °C sample is much higher than one of the 300 °C sample. According to Pontes et al. [33], if the photoluminescent signal is related to the amorphous structure, as the system is organized, the signal fades away as confirmed by Fig. 6. This conclusion is a good indication that the PL of CCTO powders obtained by the polymeric precursor method, originates from inorganic amorphous phases with photoluminescent properties. Interestingly, as shown, PL measurements of CCTO-based powders thermally treated at 700 °C showed the main band with maximum emission around 590 nm (strong green emission) when excited with a 488 nm wavelength laser. These peaks can be related to TiO₅, CuO₁₁, and CaO₁₁ vacancy clusters. In fact, TiO₆ would be linked to CaO₁₂ and/or CuO₁₂ clusters. According to the literature, the first PL peak at 554 nm indicates that the TiO_5 cluster would be surrounded by four CaO_{12} clusters, whereas the second peak at 800 nm indicates that it would be surrounded by four CuO_{12} clusters [34–36]. The first and second peaks could also be associated with $[CaO_{11} \cdot V_O]$ and $[TiO_5 \cdot V_O]$ and with $[CuO_{11} \cdot V_O]$ and $[TiO_5 \cdot V_0]$ clusters, respectively, in which VO stands for oxygen vacancies [24-26]. These complex defects are deeply inserted into the band gap, leading to PL emission.

A proposed model for wide band PL property is illustrated in Fig. 7 and based on literature data [37]. The most important effects occur before excitation, i.e., before the photon arrives. Structural defects at short and intermediate-range leads to the formation of intermediary energy levels into the band gap and inhomogeneous charge distribution in the unit cell, allowing the trapping of electrons (see Fig. 7a). The conduction band is lower mainly due to the 4d orbitals of titanium atoms. The levels responsible for the reduction of band gap are mainly due to 2p orbitals of oxygen atoms in the valence band, destabilized by the break of the Ti-O bond (see Fig. 7b). The localized levels are energetically distributed so that several photons are able to excite the trapped electrons (see Fig. 7b). After excitation of the photon (see Fig. 7c), occurs the recombination process in which an electron of the conduction band lost its energy and reoccupies the energy levels of an electron (e^{-}) hole (h^{\bullet}) in the valence

band. The recombination and decay process follows the many valid hypotheses presented in the literature [38,39]. The wide-band visible emission, observed in titanates belongs to a universal "green-luminescence", which is a characteristic property of practically all self-activated ABO₃ perovskites [40]. Its origin has been discussed in many papers and the suggested mechanisms include selftrapped excitons [41], donor-acceptor recombination [42], recombination of electron and hole polarons, charge transfer vibronic exciton [43] and transitions in MeO6 complexes [44]. However, our study was concentrated on the wide-band visible emission before photon emission, through a synergic study between experimental data and theoretical results and based on the investigation of Leite et al. [45]. These authors reported, that amorphous lead titanate is formed of Ti-O network and the charge of the lead cation must be compensated by negatively charged "non-bridging" oxygen. These positively charged defects possibly lead to the different valence states in the titanium ion or clusters (Ti^{4+} or TiO_6 and Ti^{3+} or TiO_5).

4. Conclusions

CCTO powders with minor impurities were synthesized by the soft chemical method at 800 °C for 2 h. XRD patterns suggest that the powder crystallization process begins at 500 °C, showing a good crystallinity at 800 °C. Raman analysis revealed that CCTO powders treated at 800 °C are structurally well ordered at short-range. UV-vis spectra revealed the presence of localized energy levels into the band gap of CCTO powders heat treated at 300 and 700 °C, possibly due to the certain structural order-disorder degree in the lattice. The heat treatment promoted an increase of structural order and consequently reduced the localized energy levels into the band gap of CCTO powders heat treated at 800 °C. The decrease in the band gap energy is associated with the localized levels in the band gap and with the charge discontinuities induced by the local disorder, which favors the trapping of electrons and holes to photoluminescent emission. CCTO powders heat treated at 700 °C for 2 h present an intense and broad PL with a maximum at around 490 nm in the visible region showing that high

temperatures cause a reduction in the defects or disorder of materials. The PL behavior at room temperature can be related to order–disorder degree in the lattice of CCTO, which are controlled by $[TiO_5]$ and $[TiO_6]$ clusters.

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