(Sr,Tm)ZrO₃ powders prepared by the polymeric precursor method: Synthesis, optical properties and morphological characteristics

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(Sr₂₋₀.₉₅(Tm₀.₀₅)ZrO₃ (STZO) powders were prepared by the polymeric precursor method and heat treated at different temperatures for 2 h under oxygen flow. These powders were analyzed by X-ray diffraction (XRD), Ultraviolet–visible (UV–vis) absorption spectroscopy, photoluminescence (PL) measurements, field-emission gun-scanning electron microscopy (FEG-SEM) and energy dispersive X-ray spectrometry (EDXS). XRD patterns revealed that the powders crystallize in an orthorhombic structure without the presence of secondary phases. UV–vis absorption spectra suggest that the STZO powders heat treated at low temperatures present intermediary energy levels within the band gap as consequence of structural defects in the lattice. PL measurements indicated the presence of broad, broad/narrow and narrow bands in STZO powders. The broad bands were associated to the asymmetric STZO structure and/or p–d transitions while, the narrow bands were ascribed to f–f transitions arising from thulium ions. A simple model was proposed in order to explain the PL behavior of these powders. FEG-SEM micrographs showed that these powders are composed by several microparticles with irregular morphologies and agglomerated nature. EDXS data were used for analyses of chemical compositional of powders.

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1. Introduction

At room temperature, the ceramic oxides with perovskite-type structure are characterized by the general formula ABO₃ (A = Ca, Sr, Ba; B = Ti, Zr). These materials have received special attention of several researchers due to its technological importance [1–6]. In particular, the zirconates (CaZrO₃ [7,8], SrZrO₃ [8–11] and BaZrO₃ [12,13]) when doped with acceptor ions (B = Ga³⁺, Sc³⁺, In³⁺, Lu³⁺, Y³⁺ and Gd³⁺) present a protonic conduction at high temperatures. This property has been widely employed in different industrial applications, including: fuel cells, electrolysis and hydrogen separation [14]. Moreover, the zirconates are attractive materials in metallurgy and nuclear energy fields because of its chemical stability, high melting point and high corrosion resistance in alkaline vapors and melts [15,16]. Recently, SrZrO₃ have been especially investigated due to its excellent luminescent properties at room temperature [17–19]. In recent years, the literature has reported some works on the luminescent properties of rare earth-doped zirconates [20–23]. Zhang et al. [20] investigated the photoluminescence (PL) properties of Eu³⁺-doped SrZrO₃ nanocrystals formed by the combustion method. Rérot et al. [21] observed a broad PL band centered at 430 nm for the SrZrO₃:Ce nanoparticles prepared by the combustion method with the target of medical imaging. Lu et al. [22] argued that the PL properties in Eu³⁺-doped BaZrO₃ microcrystals are dependent of its shapes. In another work, Liu and Wang [23] verified that the PL emission intensity of BaZrO₃:Eu³⁺ phosphor powders increases with Eu³⁺ content up to approximately 2 mol%.

Thulium (Tm³⁺) ions have been extensively used as doping in some inorganic compounds for different purposes. For instance, the up-conversion process was observed in Tm³⁺-doped LiNbO₃ when excited by 800 nm wavelength. PL emissions verified at 371 nm and 455 nm were assigned to 1D₂ and 1G₄ absorption bands, which can be strongly affected by the Tm³⁺ concentration [24]. PL measurements of Tm³⁺-doped KLu(WO₄)₂ single crystals were performed to characterize the laser emission channels in this host. This material is widely promising in the development of multi-Watt diode laser pumped thulium laser [25]. Luminescent properties of Tm³⁺-doped ZrO₂ nanocrystals obtained by the Pechini sol–gel complex method were investigated through the host structure, phases and Tm³⁺ concentration [26]. When excited by 257 nm wavelength, a blue PL emission centered at around 475 nm was observed in Y₃Gd₂₋ₓVO₄ₓ:Tm³⁺ phosphors. This PL behavior was ascribed to 1G₄ → 3H₄ transition of Tm³⁺ [27]. RE₂O₃:Tm³⁺ (RE = Gd³⁺, Y³⁺) phosphors prepared by the combustion method exhibited a blue PL emission at around 452 nm, due to 1D₂ → 3H₄ transition. High luminescent intensities were verified for the 0.5 mol Tm³⁺-doped Gd₂O₃ nanoparticles [28]. Recently, Zhang et al.
2. Experimental

2.1. Synthesis of (Sr0.995Tm0.005)ZrO3 powders

STZO powders were synthesized by the PPM [30]. In this synthesis, strontium nitrate, Sr(NO3)2 (99.9% Aldrich), thulium oxide, Tm2O3 (99.0% Merck), zirconium n-propoxide, [Zr(O(C2H5)2)]4 (99.9% Aldrich), ethylene glycol, C2H4O2 (99% J.T. Baker) and citric acid, C6H8O7 (99.5% Synth) were used as raw materials. The typical experimental procedure is described as follows: (a) In the first stage, Zr(O(C2H5)2)4 was quickly added in citric acid aqueous solution to avoid hydrolysis reaction between alkoxide and air environment. (b) Clear and homogenous zirconium citrate was formed under constant stirring at 90 °C for several hours. (c) The gravimetric procedure was performed for the correction and determination of the stoichiometric value correspondent to the ZrO2 mass (grams) contained into the zirconium citrate. (d) A stoichiometric quantity of Sr(NO3)2 was dissolved into the zirconium citrate solution. (e) In the second stage, the thulium solution was prepared through the dissolution of Tm2O3 in nitric acid. (f) This solution was added into the strontium–zirconium citrate solution. (g) After solution homogenization, C2H4O2 was added into the solution heated at 110 °C in order to promote the citrate polymerization by the polyesterification reaction [31]. (h) The citric acid/metal molar ratio was fixed at 4/1 and citric acid/ethylene glycol mass ratio was fixed at 60/40 wt% [32,33]. After polyesterification reaction, the resulting polymeric resin was then placed in a conventional furnace and heat treated at 350 °C for 2 h to promote the pulverization and decomposition of organic compounds arising from citric acid and ethylene glycol. (i) Finally, the obtained precursor powders were heat treated at different temperatures in the range from 400 °C to 700 °C for 2 h in a tube furnace under oxygen flow. Fig. 1 shows a flowchart on the preparation stages of STZO powders by the PPM.

2.2. Characterizations of (Sr0.995Tm0.005)ZrO3 powders

STZO powders were characterized by X-ray powder diffraction (XRD) using a DMax/2500PC diffractometer (Rigaku, Japan). XRD patterns were obtained using Cu-Kα radiation in the 2θ range from 10° to 75° and step size of 0.02°/min. Ultraviolet–visible (UV–vis) spectra were taken using a Cary 5G (Varian, USA) equipment in total reflection mode. Photoluminescence (PL) measurements were taken using a U1000 Jobin–Yvon double monochromator coupled to a cooled GaAs photomultiplier with a conventional photon counting system. The 488 nm excitation wavelength of an argon ion laser was used, keeping its maximum output power at 30 mW. A cylindrical lens was used to avoid sample overheating. The slit width utilized was 100 μm. UV–vis and PL spectra were taken three times for each sample in order to ensure the reliability of the measurements. The microstructure of STZO powders was verified using a FEG-SEM (Supra 35-VP, Carl Zeiss, Germany). The compositional analyses of STZO powders were performed using a scanning electron microscope (DSM 940, Carl Zeiss, Germany) equipped with an EDXS spectrometer (Oxford Instruments, UK). All measurements were performed at room temperature.

3. Results and discussion

3.1. X-ray diffraction analyses

Fig. 2 shows the XRD patterns of STZO powders heat treated in the range from 400 °C to 700 °C for 2 h under oxygen flow. XRD patterns were employed to verify the structural evolution at long-range during the crystallization process of STZO powders with the increase of temperature. In Fig. 2a, it was not observed diffraction peaks ascribed to STZO phase, probably due to the presence of structural defects in these powders. STZO powders heat treated at 725 °C present a wide diffraction peak (at around 30°) associated to the initial structural organization process of the lattice (Fig. 2b). XRD patterns of the powders heat treated at 600 °C indicated a reduction of the structural defects in the lattice. Moreover, all diffraction peaks can be indexed to the orthorhombic structure of the strontium zirconate (SrZrO3) (SZO) phase, in agreement with the reported in the literature [34,35] and respective “ICSD” (Inorganic Crystal Structure Database) card No 00-0650 [36] (Fig. 2c). Therefore, this result is an indicative of the Tm3+-doped SZO phase.
Fig. 3 shows a, b and c lattice parameter values as a function of heat treatment temperature. As it can be seen in this figure, lattice parameter values present small deviations as indicated by the error bars. Possibly, it was...
caused by small distortions on the STZO lattice due to the differences between the ion radius of Sr2+ and Tm3+ [37,38].

The experimental lattice parameter values were calculated using the least square refinement from the UNITCELL-97 program [39]. The structure was analyzed through a comparative between the lattice parameters values obtained in this work with those reported in the literature by different methods and with the respective ICSD card, as listed in Table 1.

In this table, it was verified that the STZO powders formed by the PPM requires a reduced heat treatment temperature and low processing time compared to the other conventional synthesis methods. The lattice parameter values are in agreement with the reported in the literature [40–43] and ICSD card No 00-0650 [36] for the SZO phase. The lattice parameters of STZO phase have not been reported in the literature yet. Thus, the lattice parameters of SZO phase were taken as standard. Also, it was observed that the increase of temperature leads to the lattice parameter values very close to the ICSD card No 00-0650 [36]. In this case, the increase of heat treatment temperature promotes an increase of structural organization of the STZO lattice.

3.2. Unit cell representation for the (Sr0.995Tm0.005)ZrO3

Fig. 4a and b show a schematic representation of two unit cells in order to explain the structural organization evolution of STZO powders prepared by the PPM. These crystallographic structures were modeled using the Diamond Crystal and Molecular Structure Visualization (Version 3.1 for Windows) softwares by means of the atomic coordinates reported in the literature [41,43,44].

Fig. 4a shows the schematic representation a symmetric STZO unit cell with perovskite-type orthorhombic structure and Pnmm space group (no 62). In this unit cell, Zr atoms are surrounded by six oxygens ([ZrO6] clusters) in an octahedral configuration, while Sr atoms situated in the vertices from the unit cell are bonded with twelve oxygens in a dodecahedral configuration. These octahedrons are tilted into this distorted orthorhombic structure. Fig. 4b illustrates an asymmetric STZO unit cell formed by the simultaneous presence of [ZrO2]-[ZrO6] clusters. In this model, one Zr atom was displaced along the [001] direction (z-axis) to represent the two Zr environments, i.e., [ZrO3-V5] clusters with pyramidal-type configuration V5 = V5 and [ZrO5] octahedral-type configuration. Therefore, these proposed models can be extended to n-clusters in a random distribution into the lattice. The formation of [ZrO2] clusters, where the Zr atoms coordinated with five oxygens has been reported in the literature by means of extended X-ray absorption fine structure measurements [45].

The defects observed in this unit cell are associated to the oxygen vacancies, which present three different charge states: (a) neutral (V5) – capture up to two electrons, (b) singly ionized (V5) – capture only one electron and (c) double ionized (V5) – it is not able to trap electrons. Double charged oxygen vacancies (V5) are considered to be the most mobile charge carriers in a material with perovskite-type structure, which play an important role in the conduction mechanism. Therefore, the replacement of trivalent Tm3+ ions into sites normally occupied by divalent Sr2+ ions leads to negative charge compensation into the SZO lattice, in agreement with the following equations:

\[
\text{SrO}_{12}^{2-} + 3\text{SrO}_{11} \rightarrow \text{SrO}_{11} + \text{SrO}_{12}^{0}
\]

This model suggests that the increase of heat treatment temperature reduces the defects or asymmetry in the STZO lattice, creating electron-captured oxygen vacancies. The proposed equations are in agreement with the Kröger–Vink notation by means of complex clusters [46,47]. In this system, the complex clusters with (V5, V5 and V5) stabilize the lattice defects via charge compensation.

For the network formers:

\[
\text{SrO}_{12}^{2-} + 3\text{SrO}_{11} \rightarrow \text{SrO}_{11} + \text{SrO}_{12}^{0}
\]

In this structure, [SrO11-V5] [TmO5] and [ZrO3-V5] complex clusters are electron donor species, [SrO12] and [ZrO5-V5] complex clusters are electron acceptor species; [SrO11-V5] [TmO5] and [ZrO3-V5] complex clusters are electron donor–acceptor species. The presence of [SrO12] and [ZrO3-V5] with [SrO11-V5] [TmO5] and [ZrO3-V5] complex clusters results in a stabilization of the defects by the charge compensation.

3.3. Ultraviolet–visible absorption spectroscopy analyses

Fig. 5a–e show the UV–vis absorbance spectra of STZO powders heat treated at different temperatures for 2 h under oxygen flow. The obtained optical band values as a function of heat treatment temperature are shown in Fig. 5f.

According to Wood and Tauc [48], the optical band gap is associated to the absorbance and photon energy by the following equation:

\[
E_{\text{gap}} = \frac{\hbar}{h} \times (\frac{\nu}{E_{\text{gap}}})^{2}
\]

where \(\alpha\) is the absorbance, \(h\) is the Planck constant, \(\nu\) is the frequency and \(E_{\text{gap}}\) is the optical band gap.

In this case, the optical band gap energy \(E_{\text{gap}}\) of STZO powders was evaluated extrapolating the linear portion of the curve or tail. In Fig. 5a–e, it was verified that the powders heat treated from 525°C to 575°C have characteristic absorption spectra of amorphous semiconductors (silicon and insulators), while the heat treated from 600°C to 700°C present typical absorption spectra of crystalline materials. The spectra behavior shows that the \(E_{\text{gap}}\) dependent of heat treatment temperature. This result indicates that the exponential optical absorption edge and optical band gap are controlled by the degree of structural defects into the lat-
tice. Thus, the increase of optical band gap value with the heat treatment temperature promotes a reduction of the intermediary energy levels, as consequence of the structural organization in the lattice. This behavior can be described through a linear function of $E_{\text{gap}}$ as a function of heat treatment temperature (Fig. 5f).

Table 2 shows a comparative between $E_{\text{gap}}$ values of STZO prepared by the PPM method with those reported in the literature for the SZO powders prepared by different methods [49–52]. The $E_{\text{gap}}$ values of STZO powders were not reported in the literature yet. Therefore, the $E_{\text{gap}}$ values of SZO phase were used in the comparative of Table 2.

In this table, it was verified that the $E_{\text{gap}}$ of SZO can be influenced by the formation methods. Moreover, the differences verified for the $E_{\text{gap}}$ between SZO and STZO can be arising from the replacement of Sr by Tm atoms into the SZO structure. Also, it was observed that the increase of heat treatment temperature leads to an increase of $E_{\text{gap}}$ for the STZO powders. Hence, the optical band gap evolution with the temperature can be used as a tool in order to determine the degree of structural defects or asymmetric–symmetric into the STZO lattice.

### 3.4. Photoluminescence analyses: emission spectra studies

Fig. 6 shows the photoluminescence (PL) spectra at room temperature of STZO powders heat treated at different temperatures for 2 h under oxygen flow.

In Fig. 6a, it was verified an intense and broad PL emission with the maximum situated at around 590 nm (yellow emission) for the STZO powders heat treated from 400 °C to 500 °C. Similar spectra were also observed for the SZO as reported in Ref. [19]. In this work, the nature of the PL emission was explained by the presence of structural defects, additional intermediary energy levels within the band gap and trapping electrons near from the valence band.

As it can be seen in Fig. 6a, PL profile of STZO powders suggests an emission mechanism by multilevel process, i.e., a system in which the relaxation occurs by means of several paths, involving the participation of numerous energy states within the band gap of the material. Probably, this behavior is caused by the structural defects in the lattice, which are able to create additional energy levels within the band gap, in agreement with XRD and UV–vis results (Figs. 2a,b and 5a–c). PL is a powerful tool for investigating...
the energy levels of materials. Due to its sensitivity, it often highlights features that absorption measurements would rarely define. In particular, PL is of fundamental importance in determining a class of energy levels that are invisible to absorption measurements [53]. Therefore, the present work opens a possibility to explain the PL behavior and optical properties through the addition of rare earths into the SZO lattice. PL spectra of STZO powders heat treated from 525 °C to 575 °C also suggest the presence of

Fig. 5. UV–vis absorbance spectra of STZO powders heat treated at (a) 525 °C, (b) 550 °C, (c) 575 °C and 600 °C, (d) 625 °C and 650 °C, (e) 675 °C and 700 °C for 2 h under oxygen flow and (f) optical band gap values as a function of heat treatment temperature, where \( r \) = correlation coefficient and the vertical bars show the standard mean error.
Table 2
Comparative results between optical band gap values of STZO obtained in this work with those reported in the literature for the SZO formed by different methods.

<table>
<thead>
<tr>
<th>Method employed</th>
<th>Temperature (°C)</th>
<th>Time (min)</th>
<th>Optical band gap (eV)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>MOD</td>
<td>600</td>
<td>–</td>
<td>5.50</td>
<td>[49]</td>
</tr>
<tr>
<td>SG</td>
<td>500</td>
<td>5</td>
<td>4.63</td>
<td>[50]</td>
</tr>
<tr>
<td>PLD</td>
<td>400</td>
<td>5</td>
<td>5.70</td>
<td>[51]</td>
</tr>
<tr>
<td>FZ</td>
<td>–</td>
<td>5</td>
<td>5.41</td>
<td>[52]</td>
</tr>
<tr>
<td>PPM</td>
<td>525</td>
<td>120</td>
<td>4.05</td>
<td>[5]</td>
</tr>
<tr>
<td>PPM</td>
<td>550</td>
<td>120</td>
<td>4.42</td>
<td>[5]</td>
</tr>
<tr>
<td>PPM</td>
<td>575</td>
<td>120</td>
<td>4.73</td>
<td>[5]</td>
</tr>
<tr>
<td>PPM</td>
<td>600</td>
<td>120</td>
<td>4.67</td>
<td>[5]</td>
</tr>
<tr>
<td>PPM</td>
<td>625</td>
<td>120</td>
<td>4.73</td>
<td>[5]</td>
</tr>
<tr>
<td>PPM</td>
<td>650</td>
<td>120</td>
<td>4.86</td>
<td>[5]</td>
</tr>
<tr>
<td>PPM</td>
<td>675</td>
<td>120</td>
<td>5.02</td>
<td>[5]</td>
</tr>
<tr>
<td>PPM</td>
<td>700</td>
<td>120</td>
<td>5.12</td>
<td>[5]</td>
</tr>
</tbody>
</table>

MOD = metallo-organic decomposition; SG = sol–gel; PLD = pulsed laser deposition; FZ = floating zone; PPM = polymeric precursor method; ￦ = this work and Ref. = reference.

Structural defects, as shown in Fig. 6b. These powders present a broad PL emission related to the electronic transition from oxygen 2p states (near the valence band) to zirconium 4d states (below the conduction band), i.e. p–d transitions. As represented in the model shown in Fig. 4b, STZO structure has structural defects associated to the oxygen vacancies. Probably, in this orthorhombic structure occurs a charge-transference process from \( \frac{1}{2} \) \( \text{ZrO}_5 \cdot V_0^+ \) to \( \frac{1}{2} \) \( \text{ZrO}_6 \) and/or \( \text{SrO}_1 \cdot V_0^+ \) to \( \text{SrO}_1 \cdot V_0^+ \) or \( \text{TmO}_2 \cdot V_0^+ \) to \( \text{TmO}_2 \cdot V_0^+ \) complex clusters, resulting in the formation of hole (h) polarons and electron (e') known as Jahn–Teller bipolarons [54]. We believe that these complex oxygen vacancies induce to the formation of new energy levels within the band gap, which can be mainly composed by strontium, thulium and zirconium-complex oxygen vacancy centers. The increase of heat treatment temperature favors the structural organization of the STZO phase due to the reduction of defects, as described by the Eq. (9) and Fig. 4a.

\[
[\text{ZrO}_2 \cdot V_0^+] + \frac{1}{2} \text{O}_2 \rightarrow [\text{ZrO}_6].
\]
In Fig. 6b, it was also observed the presence of two narrow bands (475 and 487 nm) ascribed to f–f transitions of Tm3+. In this case, the electron population is excited from ground state to 1G4 level within a band gap of 4.50 eV. The emission of photons occurs by the decay process of electrons from 1G4 to 3H6 energy level [55,56].

As it can be seen in Fig. 6c, STZO powders heat treated at 600 °C do not presents a broad PL emission arising from p–d transitions. However, it was verified the presence of a second band formed by two peaks (650 and 657 nm) ascribed to f–f transitions of Tm3+, related with the decay process from 1G4 to 3F4 energy level. The increase of heat treatment temperature at 625 °C leads to a third not well-defined emission band situated around 801 nm arising from 3H4–3H6 transition. Güell et al. [57] verified all transitions of Tm3+ in Tm3+-doped K2FeCl6 single crystals formed by the top-seeded-solution growth slow-cooling method. These transitions were observed due to the high degree of crystallinity of these crystals. In Fig. 6c, it was not verified the weak 1D2–3F2 transitions at around 753 nm. Possibly, it was caused by the high degree of crystallinity of STZO powders heat treated at 700 °C (Fig. 6c). The literature has reported on the wide band in excitation spectra of different rare earth-doped materials, such as: Tm3+-doped CaZrO3, Eu3+-doped BaZrO3, Eu3+-doped CaZrO3 and Eu3+-doped Sr2SnO4 powders [29,58,59]. In these materials, the excitation process is caused by the charge-transfer state (CTS) band, where an electron is transferred from oxygen 2p orbital to empty 4f orbital of rare earth, which may be ascribed as ligand-to-M (M = Tm3+, Eu3+) charge-transfer transitions (LMCT) [29,60]. Fig. 6d shows a schematic representation of the energy levels for the f–f transitions arising from Tm3+. The arrows indicate the number of f–f transitions verified for the STZO powders heat treated at 700 °C for 2 h under oxygen flow, including: 1G4–3H6, 1G4–3F4 and 3H4–3H6, more details are found in the Refs. [61,62].

3.5. Proposed model for explain the photoluminescence behavior of STZO powders

Fig. 7 shows a proposed model for the explanation of the PL behavior at room temperature of STZO powders excited by 488 nm wavelength. Fig. 7a illustrates the laser employed in the excitation process of STZO powders heat treated at 575 °C for 2 h under oxygen flow. The use of different wavelengths is able to promote the excitation of electrons localized in different energy levels within the band gap. The Egap value of STZO powders heat treated at 575 °C was 4.50 eV. In this case, it was not possible a band-to-band emission process because the laser’s energy (2.54 eV) is small than the Egap of STZO powders. The broad PL emission observed in these powders can be attributed to the contribution of different energy levels within the band gap. Fig. 7b shows a second stage before excitation process. Thus, the structural defects of STZO powders promoted their formation of localized energy levels within the band gap (4.57 eV) and an inhomogeneous charge distribution into the lattice. During the excitation process, some electrons are promoted from oxygen 2p states (near the valence band) to zirconium 4d states (below the conduction band) through the absorption of photons (hν). This mechanism results in the formation of self-trapped excitons (STEs), i.e. trapping of electrons (e−) by holes (h+) (Fig. 7c). Fig. 7d shows a radiative decay process in which an electron localized in an intermediary energy level (4d states) near from the conduction band decays into an empty state near from the valence band, resulting in the emission of photons (hν) responsible for the PL emission (Fig. 7e). These recombination and decay processes are in agreement with the hypotheses reported in the literature [63,64]. However, it was observed the presence of thulium 4f levels within the band gap. Thus, the broad PL emission is due to the absorption and emission processes of photons between oxygen 2p and zirconium 4d states. The lanthanide crystals have been present as trivalent ion (Tm3+) surrounded by three electrons in the conduction band [65]. Therefore, the narrow band verified at 456 nm corresponds to the Tm3+ intra-4f transitions.

3.6. Morphology characteristics of STZO powders

Fig. 8 shows the FE-SEM micrographs and compositional analyses by EDX of STZO powders heat treated at 400 °C, 575 °C and 700 °C for 2 h under oxygen flow. As it can be seen in Fig. 8a,c,e STZO powders are composed by several microparticles with irregular morphologies, non-uniform particles size distribution and agglomerated nature. The heat treatment performed at 400 °C induced a decomposition process of residual organic compounds arising from citric acid and ethylene glycol during the initial calcination stages. The preformed pores by means of this decomposition were slowly reduced by the micro-particles growth, forming large aggregated regions with irregular shapes (Fig. 8a). At 575 °C, it was observed that the thermal energy favors the diffusion mechanism, leading to the microparticles into a more dense mass (Fig. 8c). The increase of heat treatment temperature at 700 °C resulted in the necking between the grains, as shown in Fig. 8e. According to Leite et al. [66], this mechanism occurs by means of the grain boundary motion due to a reduction in the total grain boundary surface energy. Fig. 8b,d,f shows the compositional analysis obtained by EDX spectra of these powders heat treated at 400 °C, 575 °C and 700 °C for 2 h. These spectra show that the STZO powders are composed only by oxygen, strontium,
zirconium and thulium atoms. The small differences observed on the intensities can be related to the presence of residual organic compounds into the STZO structure.

4. Conclusions

STZO powders were obtained with success by the polymeric precursor method. XRD patterns confirmed that the STZO powders crystallize in an orthorhombic structure and free of secondary phases. These powders exhibited a high degree of crystallinity at heat treated temperatures in the range from 600 °C to 700 °C for 2 h under oxygen flow. UV–vis absorption spectra showed that the increase of optical band gap values is caused by the reduction of intermediary energy levels. The reduction of these intermediary energy levels was ascribed to the increase of structural organization and reduction of structural defects into the STZO lattice. Intense and broad PL emission at room temperature was observed for the powders heat treated from 400 °C to 500 °C. This behavior was attributed to the electronic transition from oxygen 2p to zirconium 4d energy levels. The narrow bands arising from f–f transitions ($^1\text{G}_4 \rightarrow ^3\text{H}_6$, $^1\text{G}_4 \rightarrow ^3\text{F}_4$ and $^1\text{H}_4 \rightarrow ^3\text{H}_6$) of Tm$^{3+}$ were only observed in STZO powders heat treated in the range from 625 °C to 700 °C. FEG-SEM micrographs showed that the powders are composed by several microparticles with irregular morphologies, non-uniform particles size distribution and agglomerated nature. These microstructural characteristics were caused by the diffusion mechanisms and formation of necks between the grains.

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