Photoluminescent behavior of SrZrO$_3$/SrTiO$_3$ multilayer thin films

M.L. Moreira$^a$, J. Andrés$^b$, V.M. Longo$^c$, M.S. Li$^d$, J.A. Varela$^c$, E. Longo$^c$

$^a$LIEC, Departamento de Química, Universidade Federal de São Carlos, C. Postal 676, Rod. Washington Luís, Km 235, 13565-905 São Carlos, SP, Brazil
$^b$Departamento de Química Física y Analítica, Universitat Jaume I, 12071 Castello, Spain
$^c$LIEC, Departamento de Fisico-Quimica, Instituto de Quimica, Universidade Estadual Paulista, C. Postal 355, R. Francisco Degni, s/n, Bairro Quitandinha, 14801-907 Araquara, SP, Brazil
$^d$Instituto de Física, Universidade de São Paulo, C. Postal 369, 13560-970 São Carlos, SP, Brazil

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**A B S T R A C T**

A detailed investigation was made into the origin of photoluminescence in an alternate multilayer system of SrZrO$_3$ (SZO) and SrTiO$_3$ (STO) thin films. XRD and room-temperature PL studies revealed a high consistency with respect to improved crystallization at elevated temperatures. The photoluminescence behaviour of SZO/STO multilayered system consists in the superposition of independent photoluminescence emissions of both STO and SZO films. Based on the present results and on previous experimental and theoretical data, we propose that the origin of the photoluminescence emission results from structural disorder generated by the presence of distortions in the ideal constituent clusters of these materials.

**1. Introduction**

Alternating lattice-matched perovskite superlattices or ultra-thin films have been investigated extensively in the search for new functionalities and behavior related to a broad range of materials properties [1–3]. For this reason, perovskite titanates have attracted much attention [4–8] and special attention has been focused on perovskites grown on SrTiO$_3$ (STO) [9–11]. STO and SrZrO$_3$ (SZO) are among the most extensively studied and widely used perovskite-type materials, and their combination, SZO/STO, has been the subject of many studies due to the exceptional properties that are not originally present in individual superlattice component materials. These properties are at the crux of technological interest [12], and experimental results are accompanied, in many cases, by theoretical calculations aimed at better understanding their physical and chemical origins [9–13]. However, few studies have focused on the investigation of photoluminescent (PL) properties as a function of temperature. Such investigations would be of considerable importance in order to shed light on the potential of these materials for optical, electronic and catalytic applications.

Within the framework of a more extended project [14–18], the purpose of this work is to elucidate the PL behaviour of SZO and STO thin films and of the SZO/STO multilayer system, and to evaluate newly synthesized luminescent materials. To this end, X-ray diffraction was used to characterize the evolution of the crystalline nature of these systems, while field emission scanning electron microscopy was employed to analyze the films’ morphology. PL depends on electronic excitations. Therefore a necessary complement to spectroscopic studies concerning lattice excitations, yielding structural information of a completely different nature from that obtained by diffraction-based techniques, since the latter detects long-range order while the former yields information on local surroundings. The present results allied to previous studies allow us to propose a structural order-disorder model to explain our PL measurements.

In the past decades, thin films of several oxides have been prepared by different synthesis methods such as sputtering, pulsed laser deposition, and molecular beam epitaxy. However, the preparation of these materials usually requires complex procedures, sophisticated equipment and rigorous experimental conditions. Thus, recent years have seen the development of new synthesis methods to minimize these problems, particularly an alternative route based on the deposition of a chemical solution, called the complex polymerization route [18], which has been used successfully to grow thin films of several oxides. STO and SZO have dissimilar structures. STO has a cubic perovskite structure at room temperature and a cubic tetragonal phase transition at 105 K, while increasing temperatures transform the structure of the SZO phase, causing it to change from orthorhombic (Pnma) to orthorhombic (Cmcm) at 970 K.

**2. Synthesis method and characterization techniques**

SZO and STO thin films were prepared by the complex polymerization method, involving the addition of metallic alkoxides to a citric acid solution to produce a metallic citrate complex. Titanium isopropoxide and zirconium butoxide (Aldrich) were used for STO and SZO, respectively. A stoichiometric amount of strontium car-
bonate (Mallinkrodt) was then added. Ammonium hydroxide NH₄OH, 30% NH₃ (Mallinkrodt), was added to adjust the pH 7–8 in the SZO solution to prevent the precipitation of strontium citrate, which is not necessary in the synthesis of STO compound. After homogenization of the Sr²⁺ cations in the solution, ethylene glycol was added in a ratio of 60:40 to citric acid promote the polymerization reaction. The viscosity was adjusted to 15 MPa by controlling the water content using a Brookfield viscosimeter. Using a Chemat Technology KW-4B spin-coater operating at 7000 rpm for 25 s, the polymeric resins were then deposited onto quartz and Si (1 1 1) substrates to avoid the superposition of wide backgrounds that commonly occurs with pure quartz substrate. The films were heat-treated at 350, 450, 550 and 650 °C for 2 h in air atmosphere. Each of the four deposited layers was fully heat-treated before the deposition of the next layer.

The samples were characterized by X-ray diffraction (XRD, Rigaku PC-Max2500) using Cu Kα radiation. Data were collected from 20° to 60° in the 2θ range, and the microstructure of the films was characterized by field emission scanning electron microscopy (FE-SEM, Zeiss Supra™ 35). Photoluminescence spectra of the thin films were taken with a Thermal Jarrel-Ash Monospec 27 monochromator and a Hamamatsu R446 photomultiplier. The 350.7 nm exciting wavelength of a krypton ion laser source (Coherent Innova) was used, with the nominal output power of the laser kept at 200 mW at room temperature. The STO, SZO and multilayered STO/SZO thin films were subjected to UV–vis absorption using a Cary 5G spectrometer in transmittance mode to determine the band gap (BG) values. To gain a better understanding of the PL properties, the PL curves were analyzed by PcaFir deconvolution software [19].

3. Results and discussion

Fig. 1a and c depicts the X-ray diffraction patterns of the STO and SZO thin films deposited on Si (1 1 1) substrates at different temperatures. An analysis of the XRD data for the films annealed at 350 and 450 °C indicated the complete absence of diffraction peaks. This finding confirms that, at these temperatures, both films presented a disordered structure, indicating nonstructured or quasi-amorphous material. The first diffractions peaks corresponding to quasi-crystalline tauronite (STO) and SZO phase appeared at 550 °C. The samples heat-treated at 650 °C were crystalline and the corresponding diffraction peaks were indexed to the Pnma orthorhombic structure for STO and to the Pnma orthorhombic structure for SZO, in accordance with JCPDS card numbers 35-0734 and 44-0161, respectively.

The surface FE-SEM image of STO thin film depicted in Fig. 1b suggests a nonuniformly distributed particle size of around 32 nm due to the typical coalescence behaviour of STO nanoparticles growing in nanostructured thin films. The spherical-like nanoparticles joined to form nanostructured agglomerates, which grew by adhesion, decreasing the value of surface energy. Fig. 1d shows uniform SZO nanoparticles with a spherical morphology and diameters of around 17 nm, displaying no indication of coalescence process.

The XRD results for the SZO/STO samples presented in Fig. 1e at 350 and 450 °C correspond to a quasi-amorphous condition, while the samples treated at 550 and 650 °C presented diffraction peaks of both STO and SZO phases associated with a quasi-crystalline structure. It is important to note that the low intensity diffractions of SZO at (2 2 1) (1 1 2) and that of STO thin films at (1 0 5) were not visible in the X-ray patterns of the SZO/STO multilayered quasi-crystalline system. This may have been due to the relatively lower intensity diffraction peak resulting from the grain size and thickness of the alternate layers of STO and SZO thin films. In addition, no peaks were recorded for the Sr(Ti,Zr)O₃ solid solution phase. These findings indicate that the proposed methodology allows for the deposition of multilayer heterostructures without diffusion at the interfaces of adjacent SZO-STO layers as depicted in Fig. 1f.

The band gap (BG) values of individual STO and SZO and of SZO/STO multilayered systems are listed in Table 1. An analysis of the results reveals: (i) that the band gap energy is much higher than the excitation energy (3.54 eV, 350 nm) required to record PL spectra [20]. This seems to indicate that the presence of localized levels within the band gap by reason of the direct electron transition between the valence band and the conduction band is not allowed. (ii) The predominant effect of SZO over STO in terms of BG values for the SZO/STO system, i.e., the BG value of the SZO/STO system is closer to STO than to SZO. However, the difference between the BG values of the SZO/STO and STO systems increases from 0.09, 0.15, 0.20, and 0.94 eV, while the difference between the BG values of the SZO/STO and SZO systems follows the sequence 0.99, 0.58, 0.48 and 1.06 eV, starting from 350, 450, 550, and 650 °C, respectively.

Fig. 2 depicts the PL spectra for STO and SZO individual thin films as well as the SZO/STO multilayered system as a function of temperature. PL intensity decreased significantly with increasing temperature, while no PL emission was observed in the thin films annealed at 650 °C. The PL profile is typical of a multiphoton process, i.e., emission that occurs by several paths and involves numerous states within the forbidden band gap. In addition, the peak positions display a similar behavior in all the samples, indicating that the peak position of the emission band shifts to a longer wavelength with as the temperature increases.

To discuss the PL profile, the luminescence spectra were decomposed into three peaks and fitted to a symmetric Gaussian function. Fig. 3 depicts typical peak-resolution results, showing that three Gaussian curves represent the overall luminescence of the different materials. These bands indicate that the first maximum occurred at 2.75 eV (blue component), followed by two others at 2.35 (green component) and 2.03 eV (yellow component) in all the thin films under study (see Supplementary material S1). An analysis of the results points to the following tendencies: (i) in the STO and SZO/STO systems, the green and yellow components represent the largest contributions, but the participation of the former decreases as the temperature increases while the latter shows the opposite tendency. In SZO, the green component makes the largest contribution, and its value is maintained as a function of temperature. The blue band decreases as the temperature increases, while the yellow band shows the opposite behavior. (ii) The PL emission of STO/SZO indicates a synergic effect, i.e., it is a superposition of individual STO and SZO spectra, as can be seen from the SZO/STO experimental response, representing the sum of individual SZO, STO emissions depicted in both experimental and theoretical SZO/STO profiles. These results reinforce the synergic concept of SZO and STO PL emissions owing to the stronger contribution of the blue component emitted by the SZO layer and the green-yellow component emitted by the STO layer. (iii) Another important point to mention is the fact that the split-up of maximum emission energy between STO-350 °C and SZO-350 °C thin films is 0.25 eV, while that of STO-550 °C and SZO-550 °C thin films is lower than 0.1 eV. In this case, based on the maximum emission profile of STO and SZO wide bands, it can be stated that increasing the processing temperature leads to more significant changes in the PL emission of SZO than of STO thin films. Hence, the states inside the forbidden band gap are more strongly affected by increases in the heat treatment temperature applied to the SZO system [14], as indicated in Table 1. This seems to indicate a situation of low crystallinity films, in other words, there is a transition from quasi-amorphous thin films (annealed at 350 °C) to quasi-crystalline (annealed at 550 °C) thin films. The term quasi-crystal-
It is well established that both BG values and PL measurements are associated with the presence of intermediary energy levels within the band gap of materials. These energy levels depend on the degree of structural disorder in the lattice. An increasing structural organization in the lattice reduces these intermediary energy levels, thereby increasing the BG value. Therefore, the optical BG and PL behaviour are not only controlled by the materials structure but are also affected by the degree of disorder resulting from the distorted crystalline structure, which dictates the PL properties. The wide range of PL spectra can therefore be ascribed to a broadening of the energy bands. The highly coinciding trends in the UV–vis spectra and PL results demonstrate the strong potential of the optical properties in probing the microstructure of nanomaterials. This fact was mentioned recently by Yan et al. with respect to their work on ZnO crystals. Even for quasi-crystalline films, it refers to situations which show the same weak XRD diffractions patterns associated with the same structural distortions that allow for the existence of PL emissions. Thus, the PL results provided further evidence that the crystallinity improved with rising temperatures.

Table 1
Band gap values (eV) of single, STO and SZO, and multilayered SZO/STO thin films.

<table>
<thead>
<tr>
<th>System</th>
<th>350 °C</th>
<th>450 °C</th>
<th>550 °C</th>
<th>650 °C</th>
<th>Ref. [32]</th>
<th>Ref. [33]</th>
</tr>
</thead>
<tbody>
<tr>
<td>STO</td>
<td>3.86</td>
<td>3.89</td>
<td>3.98</td>
<td>3.67</td>
<td>3.20</td>
<td>–</td>
</tr>
<tr>
<td>STO/SZO</td>
<td>3.95</td>
<td>4.04</td>
<td>4.18</td>
<td>4.61</td>
<td>–</td>
<td>5.21</td>
</tr>
<tr>
<td>SZO</td>
<td>4.94</td>
<td>5.62</td>
<td>5.66</td>
<td>5.67</td>
<td>–</td>
<td>5.12</td>
</tr>
</tbody>
</table>

Fig. 1. X-ray diffraction (a, c, e) and FE-SEM image of SrTiO₃ (b) SrZrO₃ (d) and SrZrO₃/SrTiO₃ (f) in multilayered thin films annealed at 650 °C for 2 h.
annealed at 550 °C, these species supply the necessary condition for the existence of PL emission. However, as the heat-treatment time increases, the lattice tends to relax its structural stresses and the complex vacancies tend to disappear, leading to the rapid decline of PL, as illustrated in Fig. 2, causing the system to assume a more ordered structure. Fig. 4 contains a schematic representation of multilayered deposition by superposition of SZO orthorhombic layers and STO cubic layers, as well as a band model to explain the excitation process and the PL spectra. After excitation, $h\nu$, the conduction band is populated due to a rapid transition from the valence band, and there is a subsequent recombination of the discrete energy levels in the conduction band. Finally, the photoluminescence, $h\nu'$, is produced.

The origin of the PL emission has been investigated in our group and we have now reached a consensus that room temperature PL emission of quasi-amorphous ABO$_3$ materials originates mainly from their structural disorder [14–16,23]. Such structural disorder will result in a nonuniform band gap structure in which electrons...
or holes may be trapped [15,24–26]. From the seminal works of Blasse et al. [27,28], it is well recognized that the polyhedral groups consisting of both transition metal and oxygen ions are responsible for PL properties in titanates, niobates and tungstates. In our case, these polyhedral groups are the polyhedral constituents of $\text{ABO}_3$ perovskite-based materials, i.e., the ideal octahedral, $\text{BO}_6$, and dodecahedral $\text{AO}_{12}$ clusters, as indicated in Fig. 5. In the case of titanates, a different coordination forms the clusters: pyramidal, $\text{TiO}_5$, and octahedral, $\text{TiO}_6$, and their presence and the various manners of linkage of these clusters are the crux of PL properties. Therefore, it is clear that PL is controlled by both the structure and the degree of disorder of materials. The concept of constituent clusters has also been proposed by Takahashi et al. [29–31] to explain the origin of PL in suzukite $\text{BaTiSi}_2\text{O}_7$.

Based on experimental and theoretical studies of PL in powders of different perovskite materials prepared by the polymeric precursor method, we have demonstrated that the structural distortions likely originate from two kinds of $\text{B}$ coordination, i.e., fivefold, $\text{BO}_5$, and sixfold, $\text{BO}_6$, oxygen coordination, as well as $\text{AO}_{11}$ and $\text{AO}_{12}$ [15,24–26]. The coexistence of these clusters produces a charge imbalance that encourages the trapping of holes in the aforementioned localized states. During the crystallization process, the displacement of oxygen related to Ti, Zr and Sr is able to modulate different species of trapped holes, the $\text{V}_d^-$, $\text{V}_t$ and $\text{V}_c$ species, around $[\text{TiO}_5]$, $[\text{ZrO}_5]$ or $[\text{SrO}_{11}]$ clusters, giving rise to complex clusters vacancies [14–17]. Thus, photoluminescence may be attributed to the radiative recombination between trapped electrons and holes in tail gap states [32]. From a structural and electronic standpoint, the optical transition involved in PL measurements is due to a reorganization of electronic charges in distorted $[\text{TiO}_5]$, $[\text{ZrO}_5]$ and $[\text{SrO}_{11}]$ clusters. Fig. 5 depicts the constituent polyhedra of both $\text{SZO}$ and $\text{STO}$ systems, showing the ideal and ordered clusters $[\text{TiO}_6]$, $[\text{ZrO}_6]$ and $[\text{SrO}_{12}]$. Their distortions that form the distorted (disordered) cluster $[\text{TiO}_5]$, $[\text{ZrO}_5]$ and $[\text{SrO}_{11}]$ and the manner in which they are linked are at the root of their PL properties. Distorted clusters yield a local lattice distortion that is propagated throughout the material, shifting the surrounding clusters away from their ideal positions. Thus, distorted clusters must move for these properties to occur, changing the electronic distribution throughout the network of these polar clusters, and this electronic structure dictates the materials optical properties. However, these movements can be induced within the crystal lattice by irradiation during PL measurements and this anisotropic cooperative movement leads to the PL property.

4. Conclusions

In summary, this Letter offers a detailed report of PL results and a systematic analysis of $\text{STO}$ and $\text{SZO}$ individual thin films and $\text{SZO}$/ $\text{STO}$ multilayered thin films. Both XRD patterns and PL emission offer evidence of the remaining order (crystalline) and disorder (amorphous) in the material. Our XRD analysis of the sample treated at 350 and 450 °C shows that quasi-amorphous phase was formed, while the initial crystallization of both $\text{STO}$ and $\text{SZO}$ occurred after heat treatment at 550 and 650 °C. The PL profile normally represents a typical multiphonon process, which, in the case discussed here, was a composition of numerous states within the forbidden band gap of $\text{SZO}$ and $\text{STO}$ band structures and a synergistic effect of $\text{SZO}$ and $\text{STO}$ systems, which provided an interesting PL spectra for $\text{SZO}/\text{STO}$ thin films. A structural model based on the presence of distorted $[\text{TiO}_5]$, $[\text{ZrO}_5]$ or $[\text{SrO}_{11}]$ clusters was proposed to explain the origin of PL spectra. The present results offer a guideline for thin film synthesis when PL properties are present, suggesting a potential innovative property generated from multi-layer heterostructured systems for optical applications.

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Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.cplett.2009.03.021.
References