SrZrO$_3$ powders obtained by chemical method: Synthesis, characterization and optical absorption behaviour

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Abstract

Strontium zirconate (SrZrO$_3$) powders have been synthesized by the polymeric precursor method after heat treatment at different temperatures for 2 h in oxygen atmosphere. The decomposition of precursor powder was followed by thermogravimetric analysis, X-ray diffraction (XRD) and Fourier transform Raman (FT-Raman). The UV-visible absorption spectroscopy measurements suggested the presence of intermediary energy levels in the band gap of structurally disordered powders. XRD, Rietveld refinement and FT-Raman revealed that the powders are free of secondary phases and crystallizes in the orthorhombic structure.

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1. Introduction

SrZrO$_3$ (SZO) powder was initially obtained by conventional solid-state reaction of SrCO$_3$ and ZrO$_2$ at 1473 K for 48 h, with intermittent grinding [1]. The SZO powders obtained for this method presents several problems like inhomogeneity, impurity contamination and coarser powder with nonuniform size and distribution. To minimize such type of problems, wet chemical methods such as sol–gel [2], co-precipitation [3] and hydrothermal methods [4] have been employed to synthesize SZO powders with desired stoichiometry, physical and chemical characteristics. However, some problems still persist in these methods, such as inhomogeneous compositional distribution [5], difficulty in controlling the degree of hydrolysis [6] and the use of highly concentrated alkaline solutions in hydrothermal treatment, which can lead to formation of impure phases like SrCO$_3$ [7]. According to Potdar et al. [3], SZO fine powders can be obtained by the pyrolysis of a strontium zirconyl oxalate precursor, as follows: (a) dehydration, (b) decomposition of oxalate and (c) decomposition of carbonate to strontium zirconate. Carbon dioxide is found to be trapped in the solid during the decomposition of the oxalate [8] heat treated in air at temperatures as low as 1173 K. The heterogeneous equilibria [9] make the formation of strontium zirconyl oxalate precursor rather complicated. Some other methods [10,11] have also been applied to optimize the oxalate precursor route by adding some other external solvents.

Several properties and applications for these perovskites include: dielectric [12], luminescent [13], refractories [14], heterogeneous catalysis [15] and protonic conductivity [16]. However, few studies of structural evolution and optical absorption behaviour have been reported in literature. In this
paper, we report the synthesis of SZO powders prepared by the polymeric precursor method and characterization at room temperature using X-ray diffraction, Rietveld refinement, Fourier transform Raman spectroscopy and UV—vis absorption spectroscopy.

2. Experimental details

2.1. Synthesis

SZO powders were synthesized by the polymeric precursor method. Strontium nitrate, Sr(NO₃)₂ (99.9% Aldrich), zirconium n-propoxide, [Zr(OC₃H₇)₄] (99.9% J.T. Baker) and citric acid, C₆H₈O₇ (99.5% Mallinckrodt) were used as raw materials. Zr(OC₃H₇)₄ was quickly added in aqueous solution of citric acid for reduction of the hydrolysis reaction of alkoxide in air environment. The clear and homogenous zirconium citrate is formed under constant stirring at 363 K for several hours. In the following step was realized the gravimetric procedure for correction and determination of the stoichiometric value of the mass of ZrO₂ in grams of zirconium citrate. Sr(NO₃)₂ was dissolved in citrate solution and then a stoichiometric quantity of Zr citrate was added to it. Ammonium hydroxide, NH₄OH (35% NH₃—Synth), was added to adjust the pH of the solution (pH 7—8) and to prevent precipitation of strontium citrate, which is favored in an acid solution. After homogenization of Sr²⁺ cations, C₂H₆O₂ was added to promote the polyesterification reaction [17]. The citric acid:metal molar ratio was fixed at 3:1, and the citric acid:ethylene glycol mass ratio was fixed at 60:40 to promote citrate polymerization by polyesterification reaction [18,19]. The obtained polymeric resin was then placed in a conventional furnace and heated at 623 K for 4 h, causing it to pulverize into powder. The precursor powders were heat treated at different temperatures, in the range of 623—1523 K for 2 h in a tube furnace under oxygen atmosphere, in order to verify the structural evolution.

2.2. Characterizations

The thermal effect on the material was investigated by thermogravimetric analysis (TGA) in the apparatus, STA 409, Netzsch, Germany, in oxygen atmosphere of flow (30 cm³/min) using a constant heating rate of 283 K/min from room temperature up to 1525 K. The crystalline phase of the SZO powders was analyzed by X-ray diffraction (XRD) patterns recorded on a Rigaku-DMax 2500PC, Japan with Cu Kα radiation in the 2θ range from 5 to 75 degree in a continuous scan with 0.02°/min. For the Rietveld analysis the measurements were performed in a scan step mode with 2θ varying from 10° to 110°, angular step of 0.02° and exposure time of 2 s. Fourier transform Raman spectroscopy (FT-Raman) was performed on Bruker-RFS 100, Germany. A 1064 nm Nd:YAG laser was used to obtain the Raman spectra as excitation source with its power kept at 95 mW. Ultraviolet—visible (UV—vis) spectroscopy for the spectra of the optical absorbance for disordered and crystalline SZO powders was taken using Cary 5G equipment. All measurements were taken at room temperature.

3. Results and discussion

3.1. Thermal analysis

Fig. 1 shows the thermal decomposition behaviour of the SZO precursor powders studied by thermal gravimetry analysis (TGA).

In these experiments, the precursor powders were heat treated at 623 K for 4 h. In this temperature, we observed a high structural disorder. The TGA curve suggests two stages of weight loss. The first stage between 300 and 645 K, presents a weight loss of approximately 10%, due to the decomposition of residual organic materials such as ethylene glycol and citric acid. The weight loss of around 26% between 645 and 1063 corresponds to the decomposition of organic compounds not decomposed in the first stage. Both stages led to strong weight loss due the decomposition of residual solvent and decomposition of organic compounds present in precursor powders. From 1063 K no weight loss was observed, suggesting the formation of a stable oxide, due to SZO perovskite oxides’ present thermal stability at highest temperatures [20].

3.2. X-ray diffraction analysis

Fig. 2(a—c) presents the XRD patterns of SZO powders heat treated in a tube furnace in the temperature range from 623 to 1523 K for 2 h under oxygen atmosphere.

Fig. 2(a) indicates no diffraction peaks of SZO powders heat treated from 623 to 773 K for 2 h indicating high structural disorder degree of these powders. From 848 K until 1523 K a progressive increase of structural order is observed with the rise of thermal treatment temperature (see Fig. 2(c)). All SZO powders crystallize in an orthorhombic structure according to literature [21—23] and the respective
This structural order was analyzed comparing the average lattice parameters $a$, $b$, and $c$ values with those reported in the JCPDS cards listed in Table 1.

All the reflections of the X-ray patterns were identified as belonging to the SZO phase in agreement with JCPDS card no. 44-0161.

Increasing the temperature leads to formation of SZO phase at 948 K. For the SZO phase, experimental lattice parameters were calculated using the least square refinement from the UNITCELL-97 program with the respective error bars.

Lattice parameters of orthorhombic structure present few deviations as indicated by error bars. Increasing the temperature leads to formation of SZO phase at 948 K. For the SZO phase, experimental lattice parameters were calculated using the least square refinement from the UNITCELL-97 program with the respective error bars.
powders heat treated at 1443 and 1523 K we observe few deviations caused by three phase transitions at high temperatures. This may cause several changes in the lattice parameters, especially when the SZO powder crystallizes in an orthorhombic structure at room temperature. The orthorhombic phase is stable in the temperature range of room temperature to about 960 K. At room temperature, SZO presents an orthorhombic structure with space group \( \text{Pnma} \) [22]. As previously discussed, Matsuda et al. [26] had investigated the structural phase transitions in SZO showing three phase transitions as follows: orthorhombic (\( \text{Pnma} \)) \( \rightarrow \) orthorhombic (\( \text{Cmcm} \)) at 995 K \( \rightarrow \) tetragonal (\( \text{i4/mcm} \)) at 1105 K \( \rightarrow \) cubic (\( \text{Pm3m} \)) at 1440 K.

### 3.3. Rietveld refinement analysis

The Rietveld analysis [27] was carried out on X-ray patterns of crystalline SZO powder treated at 1523 K for 2 h (Fig. 4).

These analyses were accomplished by using the fullprof package [28], assuming \( \text{Pbnm} \) space group for orthorhombic distorted perovskite structure. We have used a pseudo-Voigt function described by Finger et al. [29], to fit 26 parameters to the data point: one scale factor, one zero shifting, four background, three cell parameters, five shape and width of the peaks, one global thermal factor, two asymmetric factors, and two Sr, two Zr, and five oxygen positional parameters. In such perovskite structure atoms are placed at the following crystalline sites: the Sr and O(1) at \( 4c(x,y,1/4) \), Zr at \( 4b(0,0,0) \), and O(2) at \( 8d(x,y,z) \). A typical example of such analyses is shown in Fig. 4, which presents the experimental and calculated X-ray patterns obtained through these refinements of the SZO phase. The strain anisotropy broadening was corrected by the phenomenological model described by Stephens [30]. The reliability parameters obtained through this refinement are \( \text{Chi}^2 = 3.56 \), \( R_{wp} = 8.35 \) and \( R_{\text{Bragg}} = 5.540 \). The values of the structural parameters obtained through the refinement are listed in Table 2.

### 3.4. Crystalline \( \text{SrZrO}_3 \) unit cell

Fig. 5 illustrates the orthorhombic unit cell of perovskite structure of SZO.

The SZO unit cell is distorted due to a tilted \([\text{ZrO}_6]\) cluster octahedra. The Sr atoms in the interstices present approximately 12 coordination configuration. The XCrystDen [31] program was used to build the SZO crystalline structure.

### 3.5. Raman spectroscopy analysis

At room temperature, SZO presents an orthorhombic structure with a \( \text{ZrO}_6 \) octahedra tilted in a unit cell as shown in Fig. 5. SZO presents 24 Raman active modes, represented by \( 7A_g, 5B_{1g}, 7B_{2g} \) and \( 5B_{3g} \). Fig. 6 presents the Raman spectra...
Fig. 6. Room temperature depolarized Raman spectra of SZO powders heat treated (a) from 623 to 723 K, (b) from 748 to 848 K, (c) from 873 to 973 K, (d) from 1123 to 1523 K for 2 h in oxygen atmosphere and (e) in detail, Raman peaks for SZO powder heat treated at 1523 K for 2 h.

Table 3
Data obtained by Raman spectra analysis of SZO powders in comparison with the SZO, prepared for different methods reported in literature

<table>
<thead>
<tr>
<th>Method</th>
<th>$T$ (K)</th>
<th>$t$ (h)</th>
<th>$A_x$</th>
<th>$A_y$</th>
<th>$B_{2g}$</th>
<th>$B_{3g}$</th>
<th>$B_{2e}$</th>
<th>$A_x$</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>PPM</td>
<td>1523</td>
<td>2</td>
<td>83.6</td>
<td>102.8</td>
<td>116.4</td>
<td>131.8</td>
<td>145.3</td>
<td>168.4</td>
<td>This work</td>
</tr>
<tr>
<td>FZ</td>
<td>1541</td>
<td>15</td>
<td>96</td>
<td>107</td>
<td>117</td>
<td>133</td>
<td>146</td>
<td>169</td>
<td>[32]</td>
</tr>
<tr>
<td>SG</td>
<td>1923</td>
<td>24</td>
<td>92</td>
<td>105</td>
<td>115</td>
<td>–</td>
<td>–</td>
<td>142</td>
<td>163</td>
</tr>
</tbody>
</table>

$T$ = temperature; $t$ = time; $A_n$ = kind of symmetry; $P_n$ = peak number (cm$^{-1}$); PPM = polymeric precursor method; SG = sol–gel; FZ = floating zone and Ref. = reference.
in the 85–175 cm\(^{-1}\) range of the SZO powders heat treated at different temperatures. In the 85–175 cm\(^{-1}\) range seven Raman modes or peaks are observed whose assignments were analyzed using the \(D_{2h}\) symmetry. Twenty four Raman active modes were noted, although only seven Raman modes in the range of interest will be presented. All seven peaks are characteristic of SZO powders confirming the orthorhombic structure in agreement

![Graphs showing absorbance spectra and evolution of optical band gap with temperature](image)

**Fig. 7.** UV–vis absorbance spectra for the SZO powders heat treated at different temperatures for 2 h in oxygen atmosphere: (a) 748 and 773 K, (b) 973 K, (c) from 1123 to 1423 K, (d) 1523 K. (e) Evolution of the optical band gap with the increase of temperature, for the respective tails. The vertical bars denote standard errors of the mean.
with literature [32–34]. Fig. 6(a) shows Raman spectra of SZO powders heat treated from 623 to 723 K. No Raman active modes were noted due the high structural disorder degree at short range. Fig. 6(b) shows the Raman active modes in SZO powders heat treated at 748 K. The peak located at 83.6 cm⁻¹ is closer to the calculated mode frequencies at 85.8 cm⁻¹ by Kamishima et al. [32]. The second peak located at 145.3 cm⁻¹ is observed when the SZO powder is heat treated at 798 K due to its symmetry B₂g. The arrows pointed in Fig. 6(b) represent the Raman modes in formation process near of 168.4 cm⁻¹ for SZO powders heat treated at 823 and 848 K. Fig. 6(d) shows Raman spectra for SZO powders heat treated from 1123 to 1523 K for 2 h. The Raman peaks are well defined due to the enhancement of structural order degree. Fig. 6(e) presents SZO powder heat treated at 1523 K for 2 h, showing the Raman spectra more defined and represented by a dashed line.

Table 3 presents the Raman peak showed in Fig. 6(e), compared with the relative position of SZO prepared by different methods reported in literature.

Table 3. Raman peaks of the SZO powders prepared by different methods. The Raman peaks of the SZO powders prepared by different methods are compared with those reported by Kamishima et al. [32] and Fujimori et al. [33]. These differences in Raman peaks’ positions are due to differences in preparation method, average crystal size and structural order degree of crystal.

<table>
<thead>
<tr>
<th>Method</th>
<th>Temperature (K)</th>
<th>Time</th>
<th>Optical gap (eV)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>PPM 748</td>
<td>2 h</td>
<td>4.49</td>
<td></td>
<td>This work</td>
</tr>
<tr>
<td>PPM 773</td>
<td>2 h</td>
<td>4.91</td>
<td></td>
<td>This work</td>
</tr>
<tr>
<td>PPM 973</td>
<td>2 h</td>
<td>4.96</td>
<td></td>
<td>This work</td>
</tr>
<tr>
<td>PPM 1123</td>
<td>2 h</td>
<td>5.02</td>
<td></td>
<td>This work</td>
</tr>
<tr>
<td>PPM 1223</td>
<td>2 h</td>
<td>5.04</td>
<td></td>
<td>This work</td>
</tr>
<tr>
<td>PPM 1423</td>
<td>2 h</td>
<td>5.11</td>
<td></td>
<td>This work</td>
</tr>
<tr>
<td>PPM 1523</td>
<td>2 h</td>
<td>5.22</td>
<td></td>
<td>This work</td>
</tr>
<tr>
<td>FZ</td>
<td>—</td>
<td>—</td>
<td>5.41</td>
<td>[36]</td>
</tr>
<tr>
<td>SGC 973</td>
<td>1 h</td>
<td>5.20</td>
<td></td>
<td>[37]</td>
</tr>
<tr>
<td>PLD 673</td>
<td>5 min</td>
<td>5.70</td>
<td></td>
<td>[38]</td>
</tr>
<tr>
<td>SG</td>
<td>5 min</td>
<td>4.63</td>
<td></td>
<td>[39]</td>
</tr>
<tr>
<td>MOD 873</td>
<td>—</td>
<td>5.50</td>
<td></td>
<td>[40]</td>
</tr>
</tbody>
</table>

UV—vis absorption spectroscopy analysis

The optical energy band gap is related to the absorbance and to the photon energy by Eq. (1):

\[ h\nu \alpha \propto \left( h\nu - E_g^{opt} \right)^2 \]

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

The optical band gap energy is related to the absorbance and the photon energy by Wood and Tauc [35]. In the disordered SZO powders, the absorbance measurements suggest a nonuniform band gap structure with a tail of localized states.

The optical band values obtained for the several tails of UV—vis spectra are shown in Fig. 7 and presented in Table 4.

The exponential optical absorption edge and the optical band gap are controlled by the structural order—disorder degree in the SZO powders. The increase of band gap can be ascribed to the reduction of defects or impurities that give rise to intermediary energy levels in the band gap region of structurally disordered SZO powders. The progressive treatment promotes a reduction in structural disorder and increase the inclination of dashed line or tail, reducing deviations in the optical gap value.

The SZO powders heat treated at 748 and 773 K for 2 h in oxygen atmosphere showed a similar spectral dependence to that found in amorphous semiconductors such as silicon and insulators (see Fig. 7(a)). These powders are structurally disordered as confirmed by the optical gap value presented in Table 4 and XRD patterns (see Fig. 2(a)). An evolution of optical band value for the SZO powders heat treated from 973 to 1523 K for 2 h (see Fig. 7(b—d) and Table 3), showed the disappearance of intermediate levels due to the reduction of the structural disorder.

Table 4 compares the optical gap values of SZO prepared by polymeric precursor method with SZO prepared by different methods, reported in literature.

The optical band gap is dependent on the preparation method and similar to reported by Zhang et al. [37] for SZO powder heat treated at 1523 K for 2 h. The increase of band gap with the structural evolution of SZO powders can be used to evaluate the order—disorder degree in the SZO lattice. Differences in the optical band gap values with other preparation methods reported in Table 4, can be related to the form of SZO such as crystals, bulk or thin films.

4. Conclusions

SZO powders free of secondary phases and with orthorhombic structure was obtained from the polymeric precursor method. Rietveld analysis confirms the orthorhombic phase with space group \( \text{Pbmn} \). Less variations in the lattice parameters were observed in crystalline SZO powders heat treated at 1123 and 1223 K for 2 h. XRD patterns suggest that the crystallization of SZO powders starts at 848 K while Raman analysis reveals that SZO powders treated at 748 K present a beginning of structural order at short range. UV—vis spectra shows the presence of localized levels in the band gap of disordered SZO powders and these levels are reduced with the increase of structural order.

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