



Influence of synthesis conditions on carbonate entrapment in perovskite SrSnO_3

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ABSTRACT

Strontium stannate (SrSnO_3), a perovskite material, was synthesized by the polymeric precursor method, with different routes to eliminate organic matter. The utilization of pure oxygen for the elimination of organic matter changed the Raman spectra, especially in the low frequency region. Some peaks, which were previously assigned to the perovskite phase, were not noticed when the carbonate amount was lower. On the other hand, the profile of the IR spectra and XRD patterns did not change. These results suggest that carbonate may be present inside the perovskite lattice.

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1. Introduction

Alkaline earth stannates present very interesting properties, as recently shown [1–3]. These perovskites have been successfully synthesized using several synthesis methods, such as the hydrothermal one [4], the peroxide precursors [5], the sol–gel [6], the solid state reaction [2,7] and the polymeric precursors [8–9].

The polymeric precursor method is characterized by the formation of a high amount of organic material, favoring the formation of carbonates, mainly when alkaline–earth elements are present [9,10]. As a consequence, the elimination of this organic material is an important step. In this work, two different routes were used to eliminate this organic material during the synthesis of SrSnO_3 , prior to evaluating the final structure.

2. Experimental

Synthesis of SrSnO_3 is described elsewhere [8–10]. After calcination of the resin at 300 °C to obtain the powder precursors, the precursors were processed using two different routes. The precursor of sample I was calcined in an air atmosphere at 400 °C for 4 h, followed by heating at a rate of 5 °C min⁻¹ up to 700 °C for 4 h. The precursor of sample II was milled in an attritor mill, in alcohol media, at 500 rpm. After sieving and drying, the precursor was calcined in an oxygen atmosphere at 250 °C for 24 h, followed by heat treatment at 10 °C min⁻¹ up to 700 °C for 2 h, in an air atmosphere.

The characterization of the precursors was performed by thermogravimetry (TG) and differential thermal analysis (DTA), using a TA

Instruments SDT 2960 thermal analyzer. Samples of about 10 mg were heated at 10 °C min⁻¹ up to 1200 °C, in an air atmosphere, inside alumina pans, with a flow rate of 100 mL min⁻¹.

The samples were characterized by X-ray diffraction (XRD) using a Siemens D-5000 diffractometer and CuK_α radiation. BET analysis was done in an ASAP 2010 Micromeritics analyzer. The infrared analyses were carried out in a MB 102 Bomem spectrometer, using KBr pellets. The FT-Raman analyses were done in a FRS/100/S Bruker spectrometer, using a Nd:YAG laser.

3. Results and discussion

The TG curves of both powder precursors display three thermal decomposition steps (Fig. 1). The first one is related to the loss of water and gases adsorbed on the surface of the powders. The second step is related to the combustion of the organic matter, and the third one is related to the decomposition of carbonates. Sample II displayed a smaller mass loss than sample I, showing the efficiency of the second route in the partial elimination of organic compounds, even at temperatures as low as 250 °C.

This result is confirmed by DTA curves, which point out the presence of exothermic peaks between 300 and 670 °C. These peaks are related to the combustion of the organic material, corresponding to the second step of the TG curves. The higher intensity of the exothermic peaks in sample I is related to the higher amount of organic material. It can also be noted that the combustion reactions of sample II occur at a higher temperature. This is due to the previous thermal treatment in an oxygen atmosphere, which removed the most reactive organic groups. Higher temperatures were thus needed, compared to sample I, for combustion of the remaining organic matter.

Infrared spectra are presented in Fig. 2. The vibrations of the stannate group (SnO_3^{2-}) are observed as high intensity bands, in the ranges of 300–400 cm⁻¹ and 600–700 cm⁻¹ [11,12]. The stretching vibration of the Sn–O bond is located at about 530 cm⁻¹ [12]. In the present work, these bands are observed at about 671 cm⁻¹, with a shoulder at about 535 cm⁻¹ and another band starting at about 400 cm⁻¹.

Besides the metal–oxygen bands, vibrations assigned to water (1630 cm⁻¹) and carbonates are also observed. According to Nyquist and Kagel, carbonate bands are located at 1320–1530, 1040–1100 and 800–890 cm⁻¹ [13]. In the present work, both samples display bands at around 1445, 1088 and 856 cm⁻¹. Differences in band

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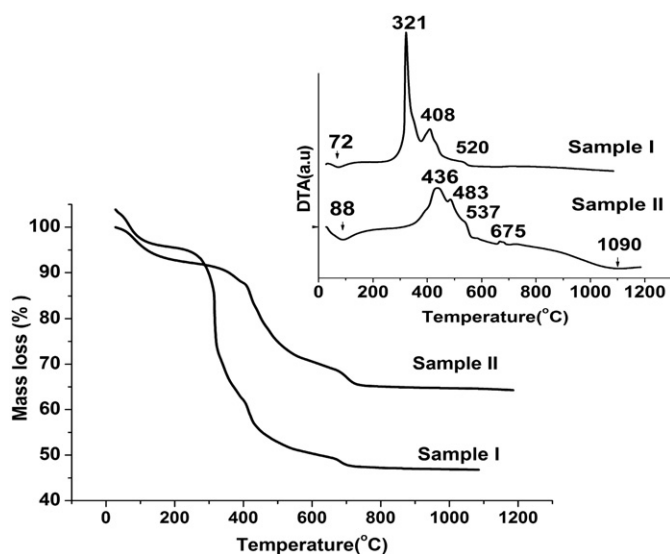


Fig. 1. TG and DTA (inset) curves of the precursor of SrSnO₃ obtained by different routes.

intensities may not be considered because different masses were used for the analysis of each sample, so only qualitative analysis was done.

On the other hand, the Raman spectra for SrSnO₃ samples, synthesized by different routes, display a remarkable difference, especially in the region from 90 to 400 cm⁻¹ (Fig. 3). When most of the carbon is previously eliminated (sample II), it can be observed that the peaks at around 90 and 119 cm⁻¹, related to the Me–SnO₃ vibrations, are either absent or show a low intensity. Drawing from literature data, it may be concluded that these peaks are not assigned to SrCO₃, which has 10 bands at 148, 183, 248, 263, 701, 711, 1073, 1079, 1446 and 1546 cm⁻¹ [14].

The previous carbon elimination leads to a smaller amount of carbonate formation. We believe that such carbonate is trapped inside the perovskite crystalline structure, replacing O²⁻ anions and linked to Sr²⁺, leading to a change in the Raman spectra of the perovskite. It should be stressed that, when the previous carbon elimination is not performed (sample I), the obtained spectrum matches exactly with the literature, in which SrSnO₃ is synthesized by solid state reaction, using strontium carbonate as the starting material [2], or by the Pechini method, without carbon elimination [9].

This kind of result was already found by Kumar et al. [15], who observed the presence of a barium titanium oxycarbonate with stoichiometry close to Ba₂Ti₂O₅CO₃ during BaTiO₃ synthesis by Pechini method.

As a consequence of the carbonate presence inside the SrSnO₃ lattice, higher disorder in the SnO₆ octahedra is noticed in sample I, as indicated by the full width at half-maximum (FWHM) of the Sn–O₃ vibration band (574 cm⁻¹) in the Raman spectra. This measurement has been used to evaluate short-range disorder [16]. In this work, a smaller FWHM value was observed in sample II (54.2 cm⁻¹) than sample I (55.4 cm⁻¹).

Fig. 4 shows the XRD patterns of pure SrSnO₃, submitted to different heat treatment conditions. Samples were identified according to JCPDS 77-1798, which indicates an orthorhombic structure. This result was confirmed by Rietveld calculations for both samples.

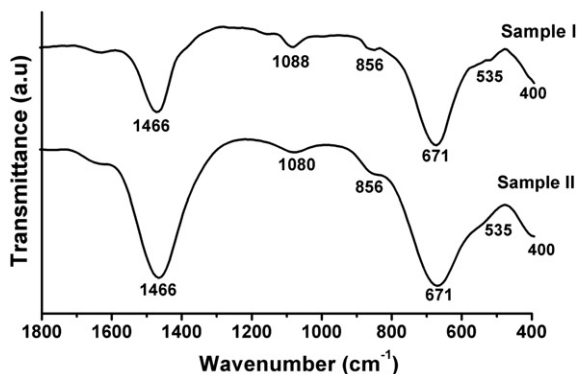


Fig. 2. Infrared spectra of SrSnO₃ calcined at 700 °C, synthesized using different conditions.

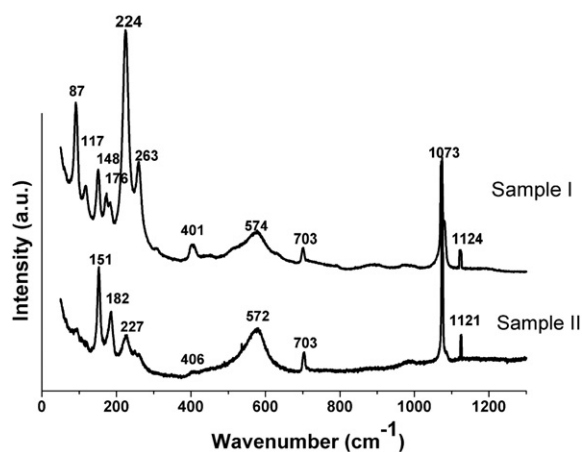


Fig. 3. Raman spectra of SrSnO₃ calcined at 700 °C, synthesized using different conditions.

It was noticed that the sample that was heat treated in air (sample I) displays more intense peaks, indicating a higher crystallinity than the sample that was heat treated in oxygen (sample II). This fact may be related to a local temperature increase due to the combustion process, which is more intense for sample I, as shown in the DTA curves (Fig. 1). This fact is also indicated by BET results. While sample I has a surface area of 7.8 ± 0.1 m²/g (*D*_{BET} = 290 nm), sample II has a surface area of 25 ± 0.4 m²/g (*D*_{BET} = 90 nm) with a meaningful decrease in the particle size. In spite of this, the crystallite size of sample I (14.6 nm) is smaller than sample II (25.3 nm). This result indicates that a higher degree of sintering occurs in the sample without previous carbon elimination.

The FWHM values of the (200) peak indicate more long range disorder for sample I (FWHM = 0.56°) than for sample II (0.34°). As for the Raman spectra, such disorder may be related to the carbonates trapped within the crystalline structure. Moreover, this trapping may also lead to the increase in the unit cell volume of sample I (265.4 Å³) as compared to sample II (263.8 Å³).

4. Conclusions

The use of different conditions for elimination of organic material leads to meaningful changes in the arrangement of atoms in the lattice of SrSnO₃ perovskites. These changes may not be observed in the infrared spectra or in the XRD patterns, which have the same profile. On the other hand, the Raman spectra are very different, especially in the region from 90 to 400 cm⁻¹, which shows the vibrations of the lattice modifier (SrO₁₂). We believe that these changes are due to the entrapment of carbonate molecules inside the crystalline lattice of the SrSnO₃ perovskite, which is bonded to Sr²⁺ ions. As a consequence, higher short and long range disorder is observed, in addition to the increase in the unit cell volume.

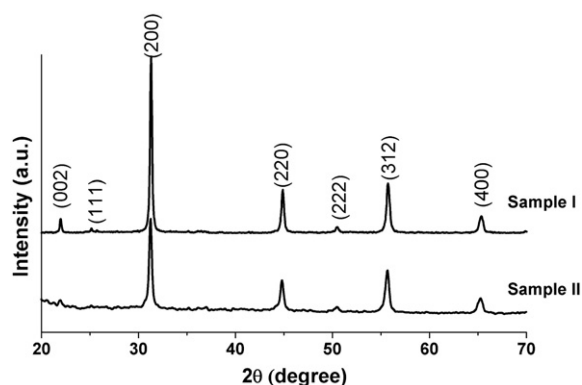


Fig. 4. XRD patterns of SrSnO₃ calcined at 700 °C, synthesized using different conditions.

Acknowledgments

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References

- [1] Zhang W, Tang J, Ye J. *J Mater Res* 2007;22:1859–71.
- [2] Zhang WF, Tang J, Ye J. *Chem Phys Lett* 2006;418:174–8.
- [3] Azad AM, Shyan LLW, Yen PT. *J Alloy Compd* 1999;282:109–24.
- [4] Lu Z, Liu J, Tang J, Li Y. *Inorg Chem Commun* 2004;7:731–3.
- [5] Pfaff G. *Mater Sci Eng B* 1995;33:156–61.
- [6] Sharma N, Shaju KM, Subba Rao GV, Chowdari BVR. *Electrochem Commun* 2002;4:947–52.
- [7] Mountstevens EH, Redfern SAT, Attfield JP. *J Phys-Condens Mater* 2003;15:8315–26.
- [8] Alves MCF, Souza SC, Lima SJG, Longo E, Souza AG, Santos IMG. *J Therm Anal Calorim* 2007;87:763–6.
- [9] Udawatte CP, Kakihana M, Yoshimura M. *Solid State Ion* 2000;128:217–26.
- [10] Souza MAF, Candeia RA, Souza SC, Chaves AC, Lima SJG, Longo E, et al. *Mater Lett* 2005;59:549–53.
- [11] Vegas A, Vallet-Regí M, González-Calbet JM, Alario-Franco MA. *Acta Cryst B* 1986;42:167–72.
- [12] Licheron M, Jouarf G, Hussona E. *J Eur Ceram Soc* 1997;17:1453–7.
- [13] Nyquist R, Kagel R. *Infrared Spectra of Inorganic Compounds*. London: Academic Press; 1971.
- [14] Lin CC, Liu LG. *J Phys Chem Solids* 1997;58:977–87.
- [15] Kumar S, Messing GL, White WB. *J Am Ceram Soc* 1993;76:617–24.
- [16] Pereira LG, Soledade IEB, Ferreira JM, Lima SJG, Fernandes Jr VJ, Araújo AS, et al. *J Alloy Compd* 2008;459:377–85.