New methodology for a faster synthesis of SrSnO$_3$ by the modified Pechini method

(Nova metodologia para síntese rápida de SrSnO$_3$ pelo método Pechini modificado)

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Abstract

SrSnO$_3$, a perovskite-type complex oxide, was synthesized by the modified Pechini method using two different precursors, tin chloride and metallic tin. The first one is already traditional in the literature and it claims about 30 days, only for the cleaning of tin citrate aiming at the elimination of the chloride. The second route was developed by our research group and saves time, taking 6 h to complete the synthesis of the resin. The results show that SrSnO$_3$ obtained from the metallic tin show a higher short range order, leading to a band gap value higher than those reported in the literature, besides a meaningful reduction in the formation of SrCO$_3$, as compared to the one obtained from tin chloride.
Keywords: perovskite, stannate, chemical synthesis.

Resumo

SrSnO$_3$, um óxido complexo tipo perovskita, foi sintetizado pelo método Pechini modificado usando dois precursores diferentes, cloreto de estanho e estanho metálico. O primeiro já é tradicional na literatura levando cerca de 30 dias, apenas para limpeza do citrato de estanho com objetivo de eliminar o cloreto. A segunda rota foi desenvolvida pelo nosso grupo de pesquisa e reduz o tempo, levando 6 h para completar a síntese da resina. Os resultados mostram que SrSnO$_3$ obtidos do estanho metálico mostram um aumento da ordem de curto alcance, que conduz a um valor de intervalo de banda mais elevada do que os relatados na literatura, para além de uma redução significativa na formação do SrSnO$_3$, quando comparado com o obtido a partir do cloreto de estanho.
Palavras-chave: *perovskita, estanato, síntese química.*

INTRODUCTION

Perovskite-type compounds, with the formula ABO$_3$, have a versatile structure capable of generating a large family of solids. In their lattice, the A cation (alkaline, alkaline-earth metals or lanthanides) with big size is 12-fold coordinated, while B (transition metals, mainly) is smaller with 6-fold coordination by the oxygen anions [1-3]. These compounds were initially studied for their exceptional physical properties such as ferroelectricity, piezoelectricity, pyroelectricity and magnetic effects [3].

Stannates with perovskite structure (MSnO$_3$, M = Ca, Sr, Ba) have interesting technological applications, for example as thermally stable capacitors, lithium batteries, catalysts, pigments and sensors [4-8]. Strontium stannate, SrSnO$_3$, present a structure distortion due to the octahedral tilt stimulated by the Sr^{2+} cation in the lattice. SrSnO$_3$ exhibits phase transition from orthorhombic to tetragonal or cubic according to the cation substitution, the calcination temperature and the method of synthesis [9, 10]. Stannate

perovskites can be obtained by different methods of synthesis, such as hydrothermal, sol-gel, electrospinning, solid state reaction and polymeric precursor method. Many papers reporting the synthesis of tin compounds by chemical methods are normally supported in the use of chlorides as precursors [11, 14-18]. For synthesis based on the Pechini method [12-14, 19, 20], tin citrate is usually precipitated from the solution being washed several times for elimination of the chloride. This process is the highest drawback of using chloride salts as precursors, as elimination does not occur easily with a high consumption of distilled water that could be seen as an environmental impact. Even when procedure is carefully done, the presence of residual chloride can even occur. When SnSO$_4$ was used as precursor, residual sulfate was observed at the end of the synthesis [21].

This work presents a new synthesis route utilizing metallic tin as precursor for the synthesis of SrSnO$_3$ by the modified Pechini method, aiming at reducing the synthesis time and amount of residues and avoiding the presence of residual contaminants.

EXPERIMENTAL

The reagents used were $SnCl_2.2H_2O$ 99.9% from J. T. Baker, citric acid ($C_6H_8O_7.H_2O$) 99.5% from Cargill, metallic tin 99.0%, nitric acid (HNO_3) 65% and ethylene glycol ($C_2H_6O_2$) 99.5%, all three from Vetec.

Perovskite $SrSnO_3$ was synthesized by two different routes, both based on the modified Pechini method. In both routes, a 3:1 citric acid to metal molar ratio was used besides a 40:60 ethylene glycol:citric acid mass ratio.
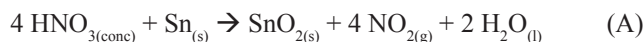
Sample 1 (named SNCL) was synthesized in two steps using tin(II) chloride dihydrated, as precursor. The first step consisted in the synthesis of tin citrate and the second one in the preparation of the resin, elsewhere described [22]. In the first step, after precipitation, the tin citrate underwent a series of washings in order to eliminate chloride ions, summing up a period of 30 days, leading to an elevated consumption of distilled water. Sample 2 (SN) was synthesized from metallic tin using only one step. 0.5 g Sn was dissolved in 100 mL of dilute HNO_3 at about 10 °C and chelated with citric acid, using the same molar ratio of the first route. Since the nitric acid is highly oxidant, an accurate control of the solution concentration and of system temperature was necessary, avoiding the formation subproducts. Considering the pKa values of citric acid (pKa$_1$ = 3.09, pKa$_2$ = 4.75), the solution pH was adjusted to 4 by the addition of NH_4OH, unlike synthesis starting from $SnCl_2$ when pH below 2 was used. Stoichiometric strontium citrate solution was added to the system, under stirring at 60 °C. Afterwards, ethylene glycol was added for the material polymerization, being the system submitted to heating at the 90-110 °C temperature range.

The resins from both synthesis routes were heat treated at 300 °C for 2 h and de-agglomerated. After milling, both polymeric precursors were sieved at 100 mesh and heat treated in an oxygen atmosphere at 300 °C for 7 h, with a heating rate of 1°C.min^{-1}. Finally, the powders were submitted to calcination in air atmosphere at 800 °C for 4 h.

The samples were characterized by X-ray diffraction (XRD) in a LabX-6000 Shimadzu diffractometer, with Cuk$_\alpha$ radiation. The analyses at the infrared region were recorded in a Shimadzu IRPrestige-21 spectrophotometer in the 400-2000 cm^{-1} region, using KBr pellets. The micro-Raman spectra were obtained in an inVia Renishaw spectrophotometer using an Ar laser of 10 mW, wavelength of 514 nm. The UV-VIS spectra were obtained in a Shimadzu UV-2550 spectrophotometer in the 190-1000 nm region.

RESULTS AND DISCUSSION

Literature data [23] report that the reaction of metallic tin with concentrated nitric acid produces a white precipitate composed of tin (IV) oxide in a very exothermic reaction. However reaction with well diluted nitric acid at low temperatures leads to the formation of aqueous tin nitrate. The other precursors of the synthesis can be added into this solution so that the whole process is done in only one step.

$$4\ HNO_{3(conc)} + Sn_{(s)} \rightarrow SnO_{2(s)} + 4\ NO_{2(g)} + 2\ H_2O_{(l)} \quad\quad (A)$$

$$10\ HNO_{3(diluted)} + 4\ Sn_{(s)} \rightarrow 4\ Sn(NO_3)_{2(aq)} + NH_4NO_{3(aq)} + 3\ H_2O_{(l)} \quad (B)$$

The synthesis of $SrSnO_3$ using $SnCl_2$ as precursor is usually performed in two distinct reaction steps [22]. The first one aims at obtaining the tin citrate, with several washings for elimination of the chloride. In the second step, tin citrate is dissolved in concentrated nitric acid followed by addition of strontium citrate and ethylene glycol. This step is very sensitive to the presence of excess of water.

The XRD patterns of the $SrSnO_3$ samples are displayed in Fig. 1, with indexation according to the JCPDS file 77-1798 for the orthorhombic $SrSnO_3$ (unit cell volume 262.6 Å^3).
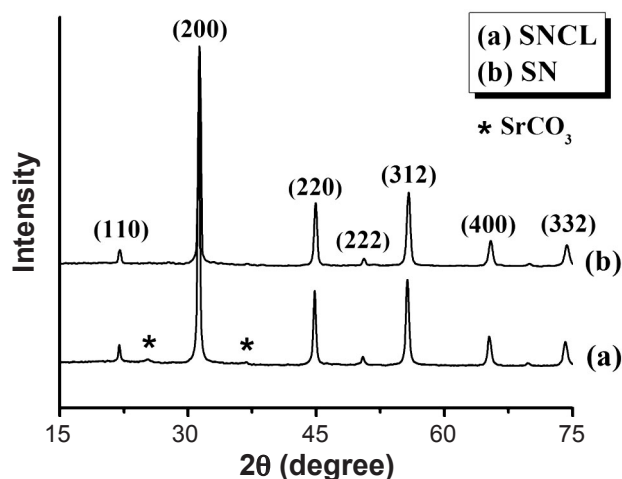

Figure 1: XRD patterns for the strontium stannate, $SrSnO_3$, synthesized by two different routes.
[Figura 1: Difratogramas de raios X de estanato de estrôncio, $SrSnO_3$, sintetizado por duas rotas diferentes.]

The long-range order of the $SrSnO_3$ samples was evaluated based on the FWHM values of the peak (200). These FWHM values were 0.26° and 0.23° whereas the unit cell volumes were 261 Å^3 and 264 Å^3, for the samples SNCL and SN, respectively. These results point out that the change of the precursor and of the synthesis route practically do not alter the long-range order of the perovskite structure. On the other hand, the formation of strontium carbonate is favored for the SNCL sample.

At pH values smaller than 3.09 (pKa$_1$), the dissociation of R-COOH groups of the citric acid is not favored, and thus the formation of chelates with metal ions is difficult. Otherwise, at pH values higher than 6.40 (pKa$_3$), higher amounts of R-COO$^-$ would be present in solution, inhibiting the esterification reaction between the metal citrate (COOH) and ethylene glycol (R-OH) [14]. In both cases stoichiometric control provided by the modified Pechini method would be underprivileged.

The process initiating from de tin chloride imply in pH values lower than pKa$_1$ (3.09), making the metallic

ion chelation more difficult. As a consequence, the Sr^{2+} ions would be free to react with the CO_2 formed during the calcination of the organic polymer. This reaction could explain the higher amount of carbonate residues in the materials prepared from tin chloride.

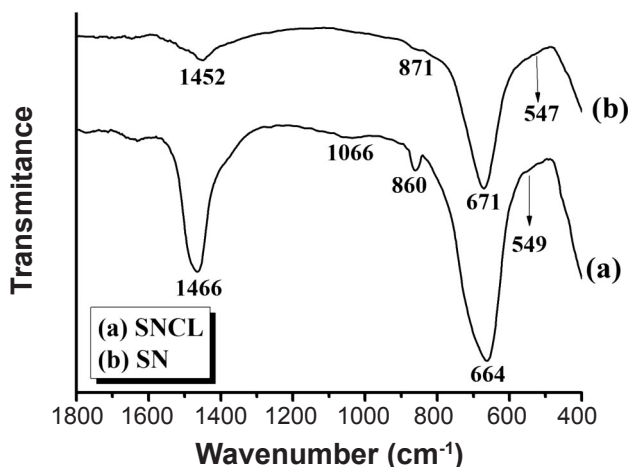Fig. 2 presents the infrared spectra of strontium stannate samples.

Figure 2: Infrared spectra of strontium stannate, $SrSnO_3$, synthesized by two different routes.
[Figura 2: Espectros de infravermelho do estanato de estrôncio, $SrSnO_3$, sintetizado por duas rotas diferentes.]

The vibrational modes for the (SnO_3^{2-}) groups are displayed as intense bands in the regions of 400 cm^{-1} and 600 cm^{-1}, while the bands related to the Sn-O bond stretching are observed at around 675 cm^{-1} with the formation of shoulder between 510 and 550 cm^{-1} [22, 24]. In the present work such bands were observed at 664 cm^{-1} and 549 cm^{-1}, for sample SNCL and at 671 cm^{-1} and 547 cm^{-1} for SN sample. In the SNCL sample infrared spectrum the bands at 1466 cm^{-1}, 1066 cm^{-1} and 860 cm^{-1} were attributed to vibration of carbonate groups [26]. For the infrared spectrum of the SN sample, these bands were observed at 1452 cm^{-1} and 871 cm^{-1}, with a markedly smaller intensity.

The orthorhombic crystalline structure of $SrSnO_3$

displays the *Pbnm* spatial group and thus presents 24 Raman-active vibrational modes. The irreducible representations for the Raman-active vibrational modes are $\Gamma_{Raman} = 7A_g + 5B_{1g} + 7B_{2g} + 5B_{3g}$ [25]. From all the Raman-active modes, some of them cannot be observed due to overlapping and/or low polarization. Fig. 3 illustrates the Raman spectra, at the 100-1000 cm^{-1} region, for the $SrSnO_3$ samples while the attributions of the bands are presented in Table I. The broad and weak bands at higher frequencies can be attributed to second-order scatterings resulting of the superposition of different combinations of modes [25-27].

The peaks assigned to strontium carbonate are observed at 148, 183, 248 and 701 cm^{-1} [28]. Superposition among some of these peaks and the perovskite ones occurs. In spite of this, the highest intensity of the peak at 147 cm^{-1} in comparison to the other peaks assigned to perovskite, for the sample SNCL, indicates the presence of carbonate. This secondary phase is confirmed by the peaks or shoulders at 180, 242 and 700 cm^{-1}. This result is in agreement with
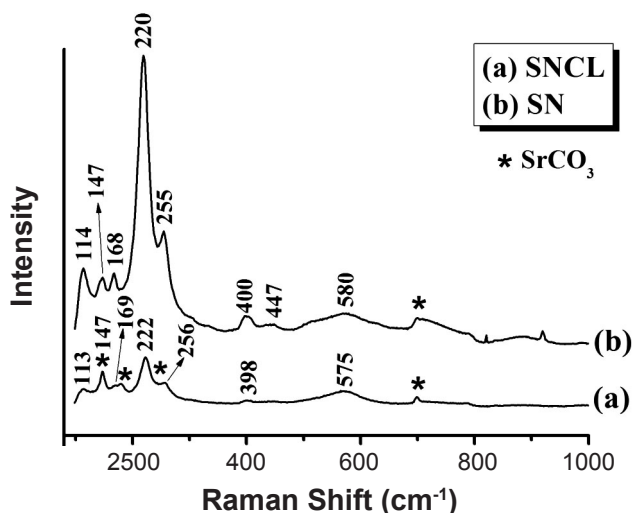

Figure 3: Raman spectra of strontium stannate, $SrSnO_3$, synthesized by two different routes.
[Figura 3: Espectros Raman do estanato de estrôncio, $SrSnO_3$, sintetizado por duas rotas diferentes.]

Table I - Frequency values of the peaks and FWHM's of the Raman bands for the $SrSnO_3$ samples.
[Tabela I - Valores de freqüência dos picos e largura à meia altura das bandas Raman das amostras de $SrSnO_3$.]

mode	Γ	frequency (cm^{-1})				FWHM (cm^{-1})	
		Ref. [25]	Ref. [26]	SNCL	SN	SNCL	SN
Sr-SnO_3	B_{2g}	113	119	113	114	-	-
	B_{2g}	147	150	147	147	-	-
	A_g	166	168	169	168	-	-
Sn-O-Sn	A_g	223	220	222	220	23.9	20.1
O-Sn-O	A_g	256	257	256	255	-	-
Sn-O_3	A_g	390	403	398(wk)	400	-	-
	-	-	-	596	575	580	-

wk - weak

the infrared spectra and indicates that a higher amount of carbonate is formed when SnCl$_2$ is used as precursor

The FWHM values of the Raman peaks, Table I, point out a decrease in the width for the band near to 220 cm^{-1} (Sn-O-Sn) suggesting that the SrSnO$_3$ synthesis method based on metallic Sn displayed a higher order among the octahedra. Moreover, the Raman spectrum of the SrSnO$_3$ synthesized by the metallic tin route displayed bands with higher intensity than the SrSnO$_3$ synthesized by the tin chloride route. It should be emphasized that this spectra was very similar to the theoretical one [25]. These observations indicate that a higher symmetry was attained for the SN sample.

The absorption spectra in the UV-vis region of SrSnO$_3$ obtained by both synthesis routes are shown in Fig. 4. The region of highest energy absorption was observed between 200-350 nm. According to literature, bands at about 200 and 280 nm refer to the ligand metal charge transfer (LMCT) O^{2-} ↔ Sn^{4+} with ions in an octahedral environment [29]. In the present work, LMCT bands were identified at 204 nm and 238 nm (equivalent to 6.08 and 5.21 eV) for the SN sample and at 209 nm and 255 nm (equivalent to 5.93 and 4.86 eV) for the SNCL sample indicating that a displacement occurred.

The energy band gap (Eg) was calculated using the method described in [30]. The values found were 3.7 eV and 4.3 eV for SNCL and SN, respectively. Values equal to 4.1 eV were observed for SrSnO$_3$ synthesized by solid state reaction [31] and by microwave assisted hydrothermal method [9, 32]. In this work, SrSnO$_3$ obtained by the modified Pechini method using Sn as precursor showed Eg value slightly higher than that described. It can also be observed that low intensity transitions at lower energy regions are observed for the SNCL sample. These observations indicate a higher short-range order for the SN sample being in agreement with the Raman spectra.

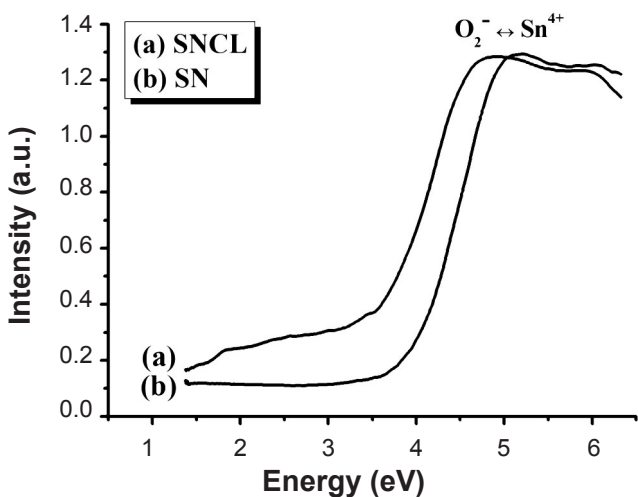It was reported that the presence of halides is one of

the factors that may justify a smaller organization to short-range derivatives of tin chloride [33]. Another aspect that may influence the short-range order is the control of the hydrogenionic potential of the solution. As stated before, the low pH used in the synthesis of SNCL sample makes chelation more difficult. As a consequence, segregation may occur, leading to a less homogeneous cation distribution in the polymeric resin. As a consequence a higher short-range disorder takes place in the final powder.

CONCLUSIONS

SrSnO$_3$ was successfully synthesized, using metallic tin (Sn) as precursor, with a meaningful reduction in the synthesis time and forming much less residues. This new methodology can also be applied to other methods of chemical syntheses which require the solubilization of Sn. The perovskite obtained using metallic tin as precursor presented a higher short-range order and smaller amount of carbonate, indicating that the proposed procedure (using Sn as precursor) is better than the traditional one (using chlorides).

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Figure 4: UV-VIS optical absorption spectra of strontium stannate, SrSnO$_3$, synthesized by two different routes.
[Figura: Espectros de absorção óptica UV-VIS do estanato de estrôncio, SrSnO$_3$, sintetizado por duas rotas diferentes.]

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