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INFLUENCE OF THE PRECURSOR SALTS IN THE SYNTHESIS OF $CaSnO_3$ BY THE POLYMERIC PRECURSOR METHOD

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$CaSnO_3$ was synthesized by the polymeric precursor method, using different precursor salts as $(CH_3COO)_2Ca\cdot H_2O$, $Ca(NO_3)_2\cdot 4H_2O$, $CaCl_2\cdot 2H_2O$ and $CaCO_3$, leading to different results. Powder precursor was characterized using thermal analysis. Depending on the precursor different thermal behaviors were obtained. Results also indicate the formation of carbonates, confirmed by IR spectra. After calcination and characterization by XRD, the formation of perovskite as single phase was only identified when calcium acetate was used as precursor. For other precursors, tin oxide was observed as secondary phase.

Keywords: *Pechini method, perovskite, stannate, thermal analysis*

Introduction

Alkaline earth stannate perovskites have attracted considerable attention in recent years due to their promising applications in a wide range field, including dielectric ceramics, sensors, battery electrodes, etc. [1]. $CaSnO_3$, for example, is a semiconductor of great interest due its high dielectric potential.

There are different synthesis methods to obtain a semiconductor material, the peroxide precursor [2], the hydrothermal [3], the sol–gel [4], the polymeric precursor method [5], etc. The temperature of thermal treatment is an important factor, varying according to the synthesis method. Many times, the use of a high temperature is necessary to obtain crystalline single phase materials, as in the case of peroxide precursor, which is based on the solid-state reaction method.

$CaSnO_3$ with an orthorhombic perovskite structure is normally synthesized by solid state reaction between $CaCO_3$ and SnO_2 at temperatures above 1250°C [6]. The synthesis by the polymer precursor method leads to a lower thermal treatment temperature, besides a higher chemical homogeneity, leading to different properties. Besides the lower thermal treatment temperature, another great advantage of the polymeric precursor method in relation to other chemical synthesis methods is its low cost, once the reagents used in larger amounts are relatively cheap [7].

The polymeric precursor method consists in the chelation of metallic cations throughout a polymer chain obtained from an esterification reaction between metallic citrate and ethylene glycol [5, 8–10].

The precursor salts have an important influence on the $CaSnO_3$ synthesis when the polymeric precursor method is used. This occurs because different chemical properties may change the characteristic of the solution and consequently, the phases present at the end of the synthesis.

The present work aims to evaluate the influence of precursor salts on the synthesis of $CaSnO_3$ by the polymeric precursor method.

Experimental

The reagents used in the synthesis of $CaSnO_3$ by the polymeric precursor method are listed in Table 1.

Calcium citrate was prepared by the addition of citric acid to distilled water at 70°C, followed by the slow addition of calcium precursor, up to its complete dissolution. Tin citrate was also separately prepared from $SnCl_2\cdot 2H_2O$. 3:1 citric acid to metal molar ratio was used in both citrates.

In a beaker, calcium citrate was added to tin citrate under stirring. Finally, ethylene glycol was added to the solution, to achieve 40:60 ethylene glycol:citric acid mass ratio. The temperature was raised to ~100°C to promote the esterification reaction and the formation of the polymeric resin.

This resin was heat treated in an oven at 350°C, leading to the formation of the powder precursors.

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Table 1 Characteristics of the used reagents

Reagents	Chemical formula	Purity/%	Supplier
Citric acid – CA	$C_6H_8O_7{\cdot}H_2O$	99.5	Cargill
Ethylene glycol – EG	$HO{\cdot}CH_2{\cdot}CH_2{\cdot}OH$	99.0	Avocado
Calcium acetate	$(CH_3COO)_2Ca{\cdot}H_2O$	99.0	Vetec
Calcium nitrate	$Ca(NO_3)_2{\cdot}4H_2O$	99.0	Vetec
Calcium chloride	$CaCl_2{\cdot}2H_2O$	74–78	Reagen
Calcium carbonate	$CaCO_3$	99.0	Vetec
Nitric acid	HNO_3	65.0	Dinâmica
Chloride tin dihydrate	$SnCl_2{\cdot}2H_2O$	99.973	J. T. Backer

These precursors were powdered, passing through a 120 mesh sieve. A second heat treatment was performed at 700°C for 2 h.

TG and DTA curves of the powder precursors were recorded by the help of a SDT 2960 thermal analyzer (TA Instruments). Samples were heated at 10°C min^{-1} up to 900°C, in air with a flow rate of 100 mL min^{-1}. About 10 mg of material was weighed into alumina pans.

X-ray diffraction patterns (XRD) were obtained using a Siemens D-5000 diffractometer, with CuK_α radiation. Infrared spectra (IR) were recorded by means of a Bomem MB 102 spectrometer, using KBr pellets.

Results and discussion

TG/DTG and DTA results of the different powder precursors are presented in Figs 1 and 2 and Table 2. Three or four steps of thermal decomposition were recorded on TG curves, depending on the calcium salt used. The first step was related to the loss of water and the evolution of some gases adsorbed on the surface of the powder precursors. The effects between 300 and 500°C were assigned to the decomposition of the organic matter. These events are related to an exothermic peak in the DTA curve indicating that combustion reactions occur. The endothermic peaks associated to mass loss at about 700°C were assigned to carbonate decomposition. The use of calcium acetate as precursor led to the highest amount of carbonate. When calcium chloride was used, an endothermic peak at 630°C was observed, related to a small mass loss. As carbonate decomposition was observed (Fig. 2b) at higher temperatures, this event may be assigned to a reduction process, probably the $Sn^{4+}\rightarrow Sn^{2+}$ transition. Three exothermic peaks were observed between 645 and 755°C. When calcium carbonate or nitrate was used exothermic peaks were also observed at 778 and 776°C, respectively. These peaks are probably related to carbon combustion indicating that chloride nitrate and carbonate may lead to the formation of more stable carbon compounds as already observed in literature [11].

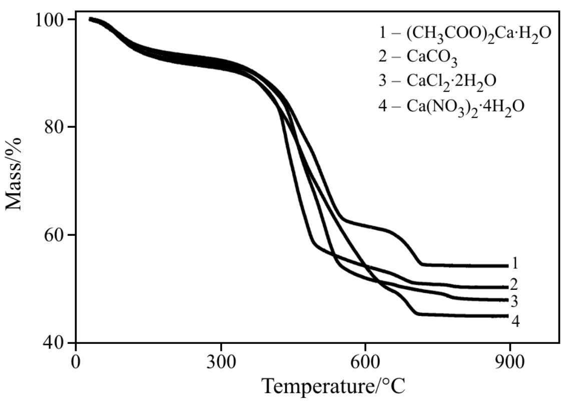

Fig. 1 TG curves of the powder precursors obtained using different salts

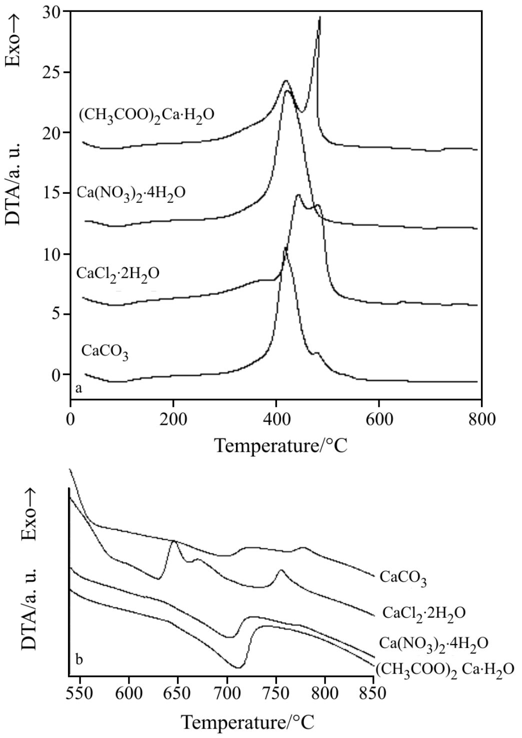

Fig. 2 a – DTA curves of the powder precursors obtained using different salts; b – part of DTA curves at higher temperatures

Table 2 Temperature and mass losses determined from TG and DTA curves

Precursor	Step	T_{range}/°C	Mass loss/%	DTG T_{peak}/°C	DTA T_{peak}/°C
$(CH_3COO)_2Ca{\cdot}H_2O$	1	75–128	4		–
	2	419–485	31	457	419, 486 (exo)
	3	485–754	7	512	711 (endo)
$CaCO_3$	1	90–43	4	436, 482	419, 445* (exo) 697 (endo), 778 (exo)
	2	417–478	32		
	3	695–790	3		
$CaCl_2{\cdot}2H_2O$	1	88–128	4	453, 513	–
	2	442–630	37		441, 484 (exo)
	3	645–794	2		630 (endo), 646, 670 and 755 (all exo)
$Ca(NO_3)_2{\cdot}4H_2O$	1	88–138	5		–
	2	421–646	42	465	420 (exo)
	3	421–807	4	516	702 (endo), 776 (exo)

*shoulder

Infrared spectra of the oxide powders prepared using different Ca^{2+} salts, thermally treated at 700°C for 2 h (Fig. 3) presented bands assigned to $CaSnO_3$ around 639 and 462 cm^{-1} and bands assigned to carbonates around 893, 1090 and 1420 cm^{-1}. These results confirmed the TG/DTA ones, indicating that the endothermic decomposition steps were due to the carbonate decomposition (Figs 1 and 2). Bands assigned to the COO stretching mode for a unidentate complex were also observed from 1630 to 1643 cm^{-1} [12]. These complexes are related to the small exothermic peaks above 700°C observed in DTA curves (Fig. 2b).

Different positions of the Me–O band were observed when different calcium precursors were used. The band position was 633, 663, 644 and 648 cm^{-1}, for nitrate, chloride, carbonate and acetate salts, respectively.

XRD patterns of the oxide powders prepared using different Ca^{2+} salts, thermally treated at 700°C for 2 h, are presented in Figs 4a and b. When calcium acetate was used, calcium carbonate and calcium oxide were observed as secondary phases. In order to observe the influence of calcium carbonate in the formation of secondary phases, carbon was previously eliminated in an oxygen atmosphere, at 250°C for 12 h. In this case, a single phase material was obtained. Acetate ion is similar to the organic material already present in the resin. This way, it leads to less changes in the polymeric resin.

When calcium nitrate is used, Ca_2SnO_4 is detected as secondary phase. The structure of Ca_2SnO_4 consists of SnO_6 octahedra which are linked by edges and the Ca^{2+} which are surrounded by seven oxygen

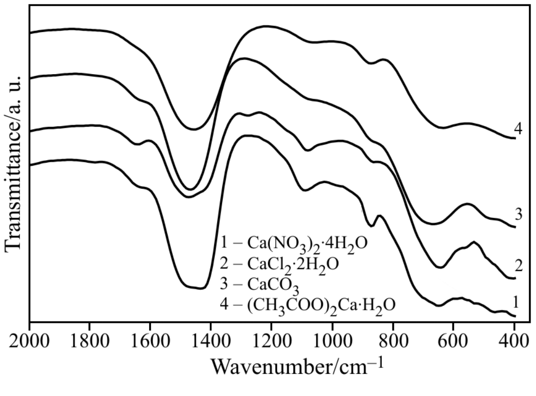

Fig. 3 Infrared spectra of the oxide powders prepared using different Ca^{2+} salts, thermally treated at 700°C for 2 h

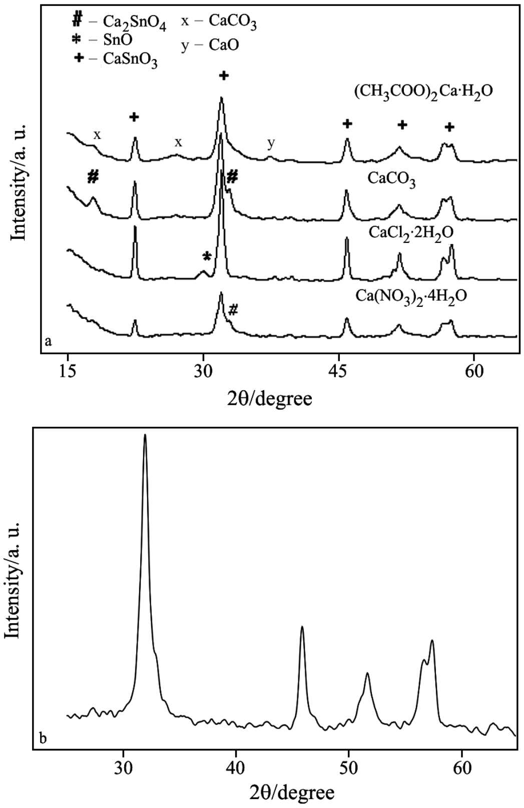

Fig. 4 a – XRD patterns of oxide powders prepared after heat treatment at 700°C for 2 h; b – XRD pattern of the oxide powder, obtained using calcium acetate, with previous carbon elimination

ions in an arrangement of low symmetry [13]. The formation of this secondary phase may be related to calcium coordination in the polymeric resin, making perovskite formation more difficult. In perovskite Ca^{2+} has a 12-fold coordination.

Calcium carbonate is a precursor successfully applied in the synthesis of $CaSnO_3$ by sol–gel method [6] and by solid-state reaction (the traditional ceramic method). In the synthesis by the polymeric precursor method, aqueous media is used, making the use of $CaCO_3$ difficult due to its low solubility. Furthermore the excess of carbon, which is only completely eliminated at about 800°C (Figs 1 and 2) makes crystallization more difficult. As a consequence, Ca_2SnO_4 is observed as secondary phase.

In spite of its high solubility, calcium chloride did not lead to a single phase material. Chlorine is rather difficult to eliminate at low temperatures. At higher temperatures its elimination occurs according to Eq. (1) leading to tin reduction Eq. (2). In spite of this a high degree of crystallinity was observed.

$$2Cl^{-} \rightarrow Cl_2(g)+2e^{-} \quad (1)$$

$$Sn^{4+}+2e^{-} \rightarrow Sn^{2+} \quad (2)$$

Tin reduction makes perovskite crystallization more difficult. Due to this process, tin oxide is observed as a secondary phase. As observed in other precursors an excess of carbon is also present contributing to the formation of secondary phase.

The unit cell volume of $CaSnO_3$ was calculated using a Rede 93 Program [14] and FWHM (full width to half maximum) was calculated using Peak Fit v4 Program. Results are presented in Table 3. Comparison with theoretical value of unit cell volume (246.1702 Å) reported in JCPDS card (31-0312) indicates few deviations. When calcium carbonate is used a higher unit cell volume and a higher long range disorder (higher FWHM value) are obtained indicating that more defects are present in the structure. As a consequence this precursor led to the highest amount of secondary phase. The opposite behavior was observed for calcium acetate and calcium chloride, which presented small unit cell volumes and also a low long range disorder.

Table 3 Unit cell volume of $CaSnO_3$ and FWHM synthesized using different precursors

Precursor	Unit cell volume/Å^3	FWHM/degree
$Ca(NO_3)_2 \cdot 4H_2O$	246.1758	0.334
$CaCl_2 \cdot 2H_2O$	246.1699	0.287
$CaCO_3$	247.6091	0.435
$(CH_3COO)_2Ca \cdot H_2O$	246.0505	0.292

Conclusions

$CaSnO_3$ was successfully synthesized by the polymeric precursor method at low temperature. XRD analysis indicated that the use of calcium acetate as precursor led to a single phase material when carbon is previously eliminated. This is due to the high amount of calcium carbonate formed during calcination. DTA analysis indicates that calcium chloride and calcium carbonate make carbon elimination more difficult. In these cases, secondary phases are observed. Calcium chloride also leads to tin reduction leading to SnO precipitation.

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