J Therm Anal Calorim (2011) 106:513–517
DOI 10.1007/s10973-011-1526-5

Influence of Cu(II) in the $SrSnO_3$ crystallization

**D. Melo · R. M. M. Marinho · F. T. G. Vieira ·
S. J. G. Lima · E. Longo · A. G. Souza ·
A. S. Maia · I. M. G. Santos**

CBRATEC7 Conference Special Issue

Abstract Perovskite type oxides have been intensively studied due to their interesting optical, electrical, and catalytic properties. Among perovskites the alkaline earth stannates stand out, being strontium stannates ($SrSnO_3$) the most important material in ceramic technology among them due to their wide application as dielectric component. $SrSnO_3$ has also been applied as stable capacitor and humidity sensor. In the present work, $SrSnO_3$:Cu was synthesized by polymeric precursor method and heat treated at 700, 800, and 900 °C for 4 h. After that, the material was characterized by thermal analysis (TG/DTA), X-ray diffraction (XRD), infrared spectroscopy, and UV–vis spectroscopy. Results indicated three thermal decomposition steps and confirmed the presence of strontium carbonate and Cu^{2+} reduction to Cu^{+} at higher dopant amounts. XRD patterns indicated that the perovskite crystallization started at 700 °C with strontiatite ($SrCO_3$) and cassiterite (SnO_2) as intermediate phases, disappearing at higher temperatures. The amount of secondary phase was reduced with the increase in the Cu concentration.

Keywords Strontium stannate · Copper · TG/DTA · Polymeric precursor method and perovskite

Introduction

Ceramic oxides with perovskite structure (ABO_3) have been widely studied by the scientific community due to its excellent optical, electrical, magnetic, and catalytic properties [1]. These properties depend on the B cation characteristics, on the partial or total substitution of A and/or B cation and on the preparation method [2, 3]. The possibility of controlling such properties is directly related to the flexibility of this structure to accommodate cations of different sizes and oxidation states, besides cationic and anionic vacancies [4].

Among perovskite, alkaline earth stannates ($ASnO_3$) stand out, due to applications as thermally stable capacitors, gas sensors, including CO, NO_x and H_2O, and catalysts for reduction in the amount of pollutants as NO_x [5, 6]. One of the most important stannates is strontium stannate ($SrSnO_3$) that presents the orthorhombic perovskite structure (Pbnm space group) at room temperature with high degree of pseudo cubic symmetry [7].

Copper-doped perovskites have been widely studied as catalysts due to its activity in a high variety of reactions for NO transformation. The copper ion with low coordination is considered as an active site for NO reduction reactions indicating that copper neighborhood is of high importance for catalytic activity [8].

In this work, $Sr_{1-x}Cu_xSnO_3$ samples were synthesized by the polymeric precursor method in order to evaluate the influence of copper in the structural, thermal, and optical properties of the perovskite. The used method has advantages in relation to other ones as low cost, high

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D. Melo · R. M. M. Marinho · F. T. G. Vieira ·
A. G. Souza · A. S. Maia · I. M. G. Santos (✉)
Laboratório de Combustíveis e Materiais - INCTMN,
UFPB, João Pessoa, PB, Brazil
e-mail: ieda@quimica.ufpb.br

D. Melo
e-mail: dannielym@yahoo.com.br

S. J. G. Lima
LSR, Depto de Engenharia Mecânica/CT, UFPB,
João Pessoa, PB, Brazil

E. Longo
LIEC - CMDMC – INCTMN, Instituto de Química,
UNESP, Araraquara, SP, Brazil

homogeneity, relatively low temperatures of synthesis, good stoichiometric control, and good morphological control [9]. This method has been widely used by our research group in the synthesis of materials with different structures and applications [10, 11].

Experimental

Tin citrate was used in the preparation of $Sr_{1-x}Cu_xSnO_3$ ($x = 1$, 5, and 10%) precursor using the methodology already described in literature [11]. After preparation of the tin citrate, aqueous solutions of citric acid the strontium or cupper salts were prepared and slowly added to tin citrate solution at about 60 °C. Ethylene glycol was added at the end of the synthesis. A molar ratio of 3:1 of citric acid:-metal was used to guarantee the complete chelation of the metallic cations and ethylene glycol was used with a mass ratio of 60:40 of citric acid:ethylene glycol. The reagents used in the synthesis of perovskite are listed in Table 1.

The resin was heat treated at 300 °C for 2 h to obtain the powder precursors. These materials were milled in alcoholic media in an atritor Mill for 4 h and than heat treated in oxygen atmosphere at 300 °C for 7 h. After this first heat treatment, the precursors were characterized by thermogravimetry (TG) and differential thermal analysis (DTA). The curves were obtained using a SHIMADZU-DTG-60 thermal analyzer with 10.0 ± 0.5 mg of sample in alumina crucibles, with a synthetic air flow of 100 mL min^{-1} in. Heating was done with a rate of 10 °C min up to 1200 °C.

The precursors with lower amount of carbon were heat treated between 700 and 900 °C for 4 h. Characterization was done by X-ray diffraction in a Siemens D-5000diffractometer, in a 2θ range between 15° and 75° with Cu Kα radiation. Infrared spectra were obtained in a Bomem Mb102 spetrofotometer, in the range from 2000 to 400 cm^{-1}, using samples pressed with KBr. The UV–visible spectra of all samples were recorded using a SHIMADZU-UV-2550 UV–vis Spectrometer, in the 190–900 nm range.

Results and discussion

Figure 1a and b shows the TG and DTA curves of the $SrSnO_3$:Cu precursors.

TG curves (Fig. 1a) showed three thermal decomposition steps, except for sample with 10% of copper that presented four steps. The first step was assigned to the elimination of water and gases adsorbed on the material surface with an endothermic step in DTA curves at about 75 °C. The second mass loss step was associated to an exothermic peak in DTA curves between 300 and 600 °C being assigned to the combustion of the organic material characteristic of the polymeric precursor method. According to Souza et al. [7], this combustion is related to the presence of esters as identified by infrared spectroscopy. The third mass loss step was assigned to the carbonate decomposition, with endothermic peaks near 730 °C for all systems. For the systems with 5 and 10% of copper the decomposition of residual carbonate was observed at approximately 830 and 910 °C, respectively (Fig. 1c, d). Samples with 5 and 10% of copper presented another mass loss step at about 1000 °C associated to endothermic peaks in DTA curves, being assigned to Cu(II) reduction. A broad endothermic peak near 1090 °C was also observed in DTA curves, probably due to a structural rearrangement among SnO_6 polyhedra in orthorhombic perovskite structure, as already observed by Alves et al. [11]. For samples with 5 and 10% of copper, this broad band was superposed to the endothermic peak assigned to reduction.

The characterization of the materials after calcination is presented in Figs. 2, 3, and 4.

According to the infrared spectra (Fig. 2), high intensity bands were observed being assigned to SnO_3^{2-} vibrations around 400 and 670 cm^{-1}. A shoulder between 515 and 560 cm^{-1} assigned to SnO_3^{2-} was also observed [12, 13]. At 700 °C, SnO_3^{2-} band at about 670 cm^{-1} had a lower definition for samples with higher copper amount indicating that doping led to a higher short range disorder. At higher temperatures, this band was well defined for all samples.

Table 1 Precursors used in the synthesis of $SrSnO_3$:Cu perovskites

Reagents	Chemical formula	MM/g mol^{-1}	Purity/%	Manufacturer
Citric acid	$C_6H_8O_7 \cdot H_2O$	192.13	99.5	Cargill
Ethylene glycol	$HO \cdot CH_2 \cdot CH_2 \cdot OH$	62.07	99.0	Vetec
Cupper nitrate	$Cu(NO_3)_2 \cdot 3H_2O$	241.60	99.0	Vetec
Strontium nitrate	$Sr(NO_3)_2$	211.63	99.0	Vetec
Nitric acid	HNO_3	62.997	65.0	Dinâmica
Tin chloride	$SnCl_2 \cdot 2H_2O$	225.65	99.9	Mallinkrodt
Amonium hydroxide	NH_4OH	35.04	99.0	Vetec

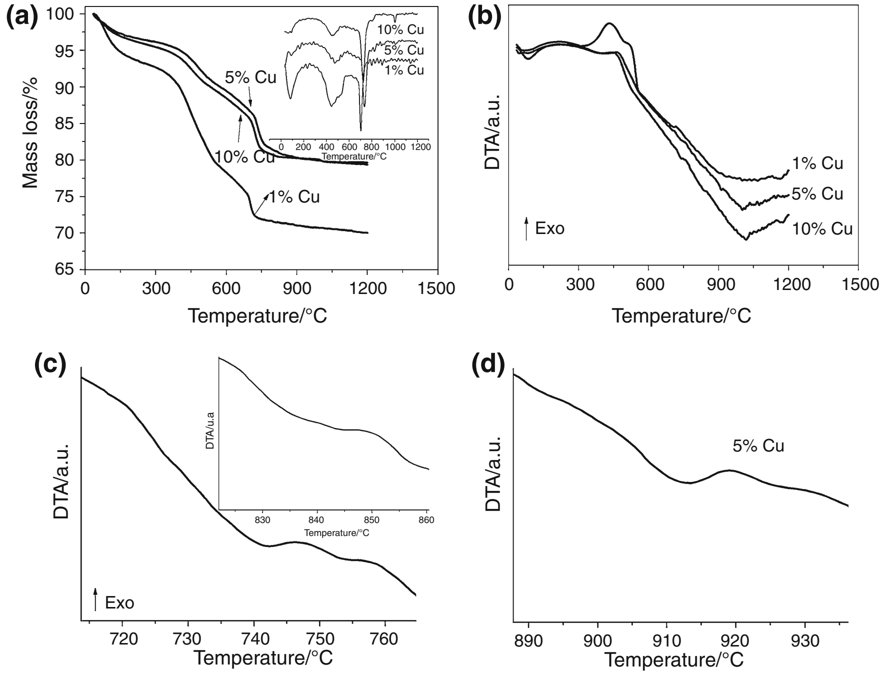


Fig. 1 **a** TG and **b** DTA curves of the powder precursors of the samples $SrSnO_3$:Cu. **c** and **d** Detail of DTA curves, showing the endothermic peaks assigned to carbonate decomposition

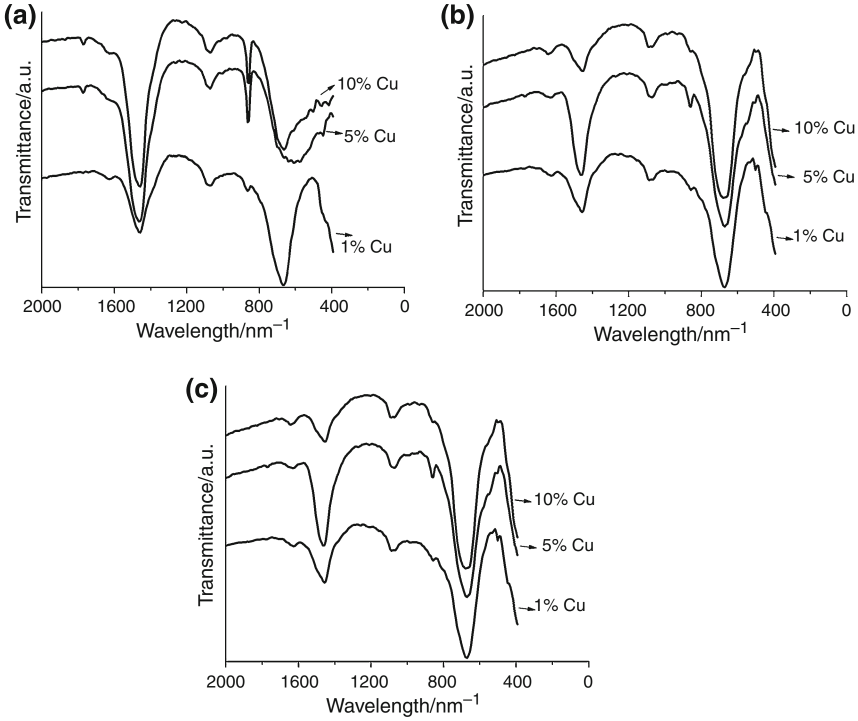


Fig. 2 Infrared spectra of $SrSnO_3$:Cu heat treated at different temperatures. **a** 700 °C, **b** 800 °C, and **c** 900 °C

Bands assigned to the presence of water (1626 cm^{-1}) and carbonates (~860, 1080, and 1470 cm^{-1}) were also observed, confirming TG/DTA results [7, 14]. With temperature increase, a decrease in the intensity of carbonate bands was observed, except for the one at 1080 cm^{-1}, indicating the presence of hydroxyl groups on the powder surface. At 900 °C, carbonate bands had a low intensity, confirming that the third mass loss observed in TG/DTA curves (around 700 °C) was due to carbonate elimination.

XRD patterns (Fig. 3) indicated that all samples crystallized with orthorhombic perovskite structure. At 700 °C, secondary phases were observed for sample doped with 1% of copper, indicating the presence of cassiterite (tetragonal SnO_2) and strontium carbonate ($SrCO_3$). It could also be

Fig. 3 XRD patterns of $SrSnO_3$:Cu samples. **a** 700 °C, **b** 800 °C, and **c** 900 °C. *Asterisks* $SrCO_3$, *plus sign* SnO_2, *hash* $SrSnO_3$

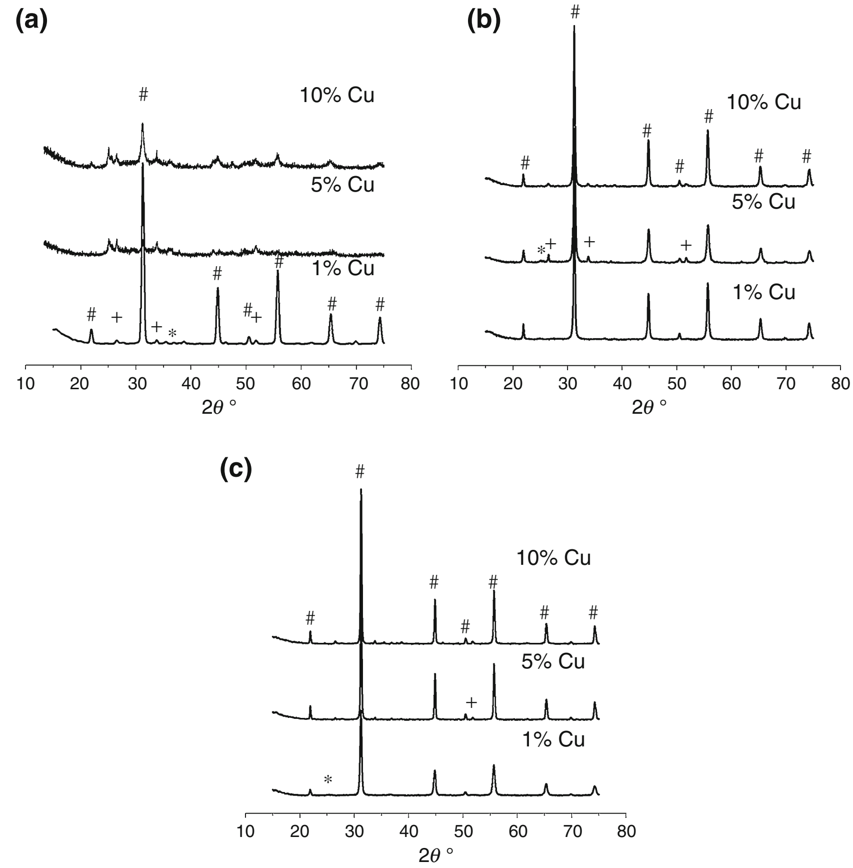
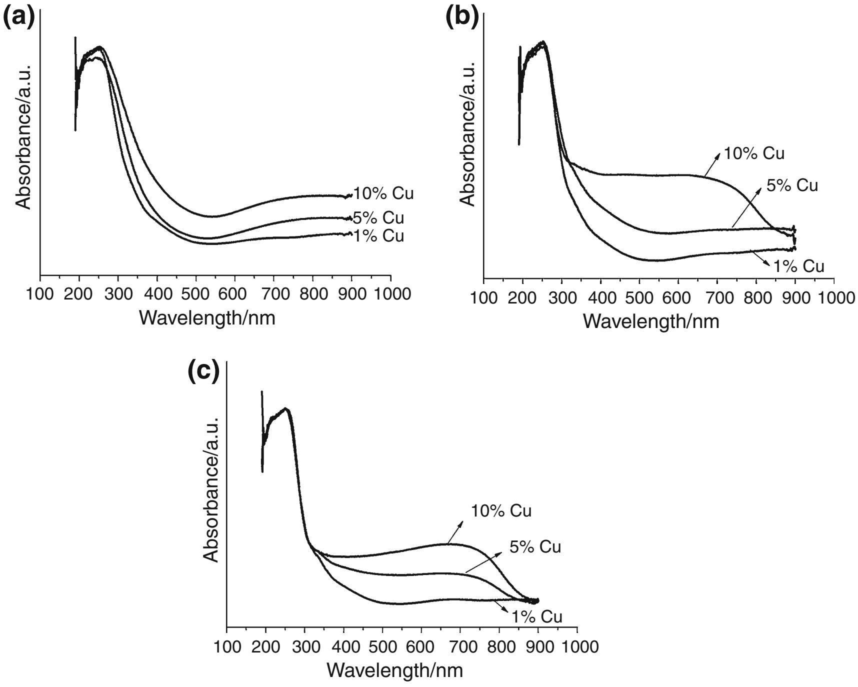


Fig. 4 UV–vis spectra of $SrSnO_3$:Cu samples. **a** 700 °C, **b** 800 °C, and **c** 900 °C



observed that increase in copper amount made long range ordering more difficult, with peaks of lower intensities. These results were in agreement with infrared spectra that showed a higher short range disorder for these samples. At higher temperatures, high intensity peaks were observed, indicating that all samples had a high long range order. A decrease in the intensity of peaks assigned to strontium carbonate was also observed as in TG curves and in infrared spectra.

UV–vis spectra (Fig. 4) showed absorption bands near 250 nm assigned to ligand metal charge transfer of $O^{2-} \rightarrow Sn^{4+}$ in octahedral environment [15]. The bands at 340 and 440 nm were assigned to the ligand metal charge transfer of $O^{2-} \rightarrow Cu^{+}$ as already observed for Cu_2O [16], while bands at 650 and 800 nm were related to the ligand metal charge transfer of $O^{2-} \rightarrow Cu^{2+}$ as showed for CuO [16]. For samples doped with 1% of copper, the absorption bands at 340 and 440 nm had a low intensity indicating that a low concentration of Cu(I) was present. A higher amount of this cation was observed for samples with 5% of copper after calcination at 900 °C and for samples with 10% of copper calcined at 800 and 900 °C. For these samples one band at 500 nm was also observed being assigned to Cu(I) [17]. These results indicate that the endothermic peak in DTA curve was assigned to Cu(II) reduction, as previously stated.

Conclusions

The polymeric precursor method was efficient in the synthesis of the $SrSnO_3$:Cu perovskites. Assignment of TG/DTA events could be confirmed by other techniques. The increase in the copper concentration made decomposition of strontium carbonate easier at temperatures above 700 °C. On the other hand, it also led to a higher short and long range disorder, especially when calcination was done at 700 °C. Copper reduction was observed by an endothermic peak in DTA curve and could be confirmed by UV vis spectroscopy that showed higher amounts of Cu(I) for samples with higher copper amount and higher heat treatment temperatures.

Acknowledgements The authors acknowledge Coordination of Improvement of Higher Education Personnel (CAPES), National Institutes of Science and Technology/National Council for Scientific and Technological Development (INCT/CNPq/MCT), Research and Projects Financing (FINEP/MCT) and Petrobras for the financial support of this work.

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