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Optimal parameters for synthesizing single phase spinel-type Co_2SnO_4 by sol–gel technique: Structure determination and microstructure evolution

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ABSTRACT

Powder samples of spinel Co_2SnO_4 were successfully synthesized by the sol–gel technique at three different temperatures: 900, 1300 and 1400 °C for 1, 5 and 8 h. XRD patterns and SEM images provided evidence of the structural and morphological evolution during the formation of the spinel phase. Thermal analysis confirmed the reaction pathway in which the spinel is formed by the reaction between SnO_2 (formed from $SnCl_4$) and CoO which in its turn is produced during the decomposition reaction of Co_3O_4 [formed from $Co(NO_3)_2$] into CoO and O_2. Determination of the quantitative phase at each combination of temperature and time as well as the lattice parameters was possible by the Rietveld refinement. The optimal parameters for the complete formation of Co_2SnO_4 are 1400 °C for 5 h. It is worth mentioning that at 1300 °C for 1 h, the percentage of the spinel obtained is considerably high (94.7%).

1. Introduction

In the continual research of ceramic materials for varistor applications, numerous authors have put special interest in the ceramic systems based on tin oxide (SnO_2) exploring different dopants and processing technologies in order to obtain improved electrical properties as well as to gain a deeper understanding of the phenomena involved in the synthesis stage [1–10]. As it has been frequently reported, cobalt oxide (Co_3O_4) has been normally chosen as the preferred dopant to promote densification of SnO_2 ceramics [11–14]. Moreover, it has been described that Co_2SnO_4 compound is usually found in the final microstructure of the ceramic material (as the result of the imperfect reaction between the raw materials), typically segregated near the grain boundaries of tin oxide [12,15,16], though the role it plays on the microstructure and electrical performance of the varistor ceramic has not been explained in detail yet. Furthermore, to the best of the authors' knowledge, there is no established commercial route for the production of Co_2SnO_4, though some researchers have synthesized it as anode material for Li-ion batteries [17–21]. Thus, there are strong reasons for synthesizing Co_2SnO_4 as a single phase. The reported characteristics of Co_2SnO_4 indicate that it has a spinel-structure. The general formula of oxide spinel is AB_2O_4, and the distribution configuration is represented as $^{IV}(A_{1-x}B_x)^{VI}(B_{2-x}A_x)O_4$. Normal spinels have $x = 0$, whereas *inverse* spinels have $x = 1$; any distribution is possible between the extremes [22]. The unit cell contains eight unit formulas, has cubic symmetry, space group *Fd*3*m*, and a cell edge close to 8 Å [23].

Solid state reaction synthesis of Co_2SnO_4 samples has proved to result in poor cycle stability due to larger particle sizes and wider size distributions [21]. Sol–gel method has demonstrated to be an efficient synthesis technique for ceramic oxide compounds due to its potential advantages over the traditional solid-state reaction and co-precipitation methods for achieving a homogeneously mixing of the component cations at atomic scale, lowering the synthesis temperature quite effectively. These advantages were considered when it was decided to follow this route for obtaining Co_2SnO_4.

The results of a previous study on this compound reported a wider range of temperature to obtain the Co_2SnO_4 phase [24]. In the current research, Co_2SnO_4 has been prepared by the sol–gel process to thoroughly study the evolution during the formation of this compound as well as to define the amount of spinel obtained at each condition of temperature and time. At first glance, the percentage of spinel obtained is low but as temperature rises

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to 1400 °C for 5 h, the formation of spinel is complete and therefore higher temperatures are no longer needed. XRD patterns confirmed the formation of the phase as well as the percentage of spinel obtained while SEM results provided evidence of the microstructure evolution.

2. Experimental procedure

The Co_2SnO_4 spinel was synthetized by the sol–gel method using stannic chloride pentahydrate $SnCl_4{\cdot}5H_2O$ (Spectrum, 99.90%) and cobalt nitrate hexahydrate $Co(NO_3)$ $6H_2O$ (Alfa Aesar, 99.74%) as starting materials. Ethylene Glycol CH_2OHCH_2 (CTR, 99.96%) was used as chelating agent. Ethyl alcohol (JT. Baker, 99.6%) and distilled water were used as solvents. In order to prepare 1 g of spinel, 1.9389 g $Co(NO_3)$ $6H_2O$ and 1.1668 g $SnCl_4{\cdot}5H_2O$ were dissolved separately into a 15 ml mixture of ethanol and distilled water in an equal volume ratio (1:1). The solutions containing the nitrate and the chloride were stirred separately in a beaker at a temperature of 60 °C until a transparent solutions was observed. Then, the solutions were mixed at 90 °C with 470 ml of distilled water in a beaker with moderate stirring for 24 h, promoting the hydrolysis and polymerization. The beaker was covered with aluminum foil with the aim of avoiding water evaporation during the stirring period. After 24 h of stirring, 10 ml of ethylene glycol were added to promote gelation. An hour later, the aluminum foil was removed from the beaker and the temperature was decreased to 60 °C without stirring until gel formation. Samples of the gel obtained were calcined at three different temperatures of 900, 1300 and 1400 °C for 1, 5 and 8 h, using heating and cooling rates of 10 °C/min. After cooling to room temperature, the products were removed from the furnace and prepared for characterization by powder X-ray diffraction (XRD) and scanning electron microscopy (SEM).

The presence of ceramic phases was determined by X-ray diffraction technique (XRD; PANalytical model Empyrean) with Cu Kα radiation (λ = 1.5406 Å) operated at 45 kV, 40 mA and an X'Celerator detector in a Bragg–Brentano geometry. The scans were performed in the 2θ range from 10° to 120° with a step scan of 0.016° and 80 s per step in a continuous mode. Structure refinements and phase identification were performed using the X'Pert HighScore Plus software, version 3.0d and the ICDD PDF-4 plus database (ICDD International Centre for Diffraction Data, Newtown Square, PA). The products from the sol–gel processing were thermally analyzed in the range 30–1500 °C in a simultaneous TG–DSC–DTA equipment (TA-Instruments model SDT Q600). An amount of 20–30 mg of the samples were placed in a platinum crucible and heated at the rate of 10 °C/min in static air atmosphere, using alumina as reference material. Finally, the morphology of the as-prepared powders was observed by a scanning electron microscope (SEM, FEI – Nova Nano SEM 200).

The Rietveld's method was successfully applied for the determination of the quantitative phase of the all samples. This method is a least squares refinement procedure where the experimental step-scanned values are adapted to calculated ones. The profiles are considered to be known, and a model for a crystal structure available. The weight fraction (*Wi*) for each phase was obtained from the mathematical relationship for refinement:

$$W_i = \frac{S_i(ZMV)_i}{\sum_j S_j(ZMV)_j}, \qquad (1)$$

where *i* is the value of *j* for a particular phase among the *N* phases present, S_j is the refined scale factor, *Z* is the number of formula units per unit cell, *M* is the molecular weight of the formula unit and *V* is the unit cell volume.

Rietveld refinement has been done by adjusting major parameters: scale factor, flat background, zero-point shift, lattice parameters, orientation parameters, peak width parameters (*U*, *V*, *W*), asymmetry parameter and peak shape. Peak profiles were fitted with the pseudo-Voigt function.

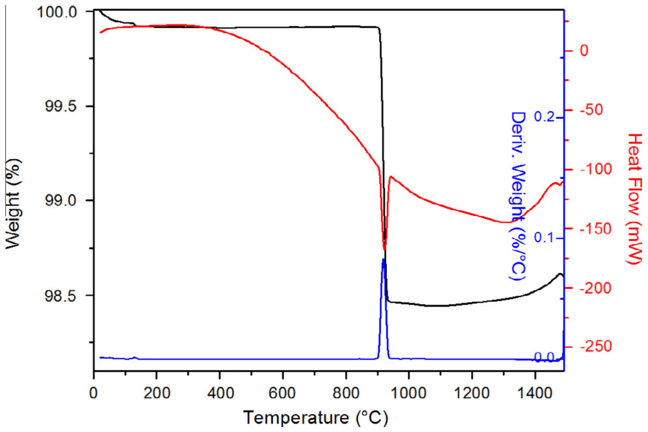

Fig. 1. TG–DTG–DSC curves for the decomposition of the precursor prepared by the sol–gel method at a heating rate of 10 °C/min.

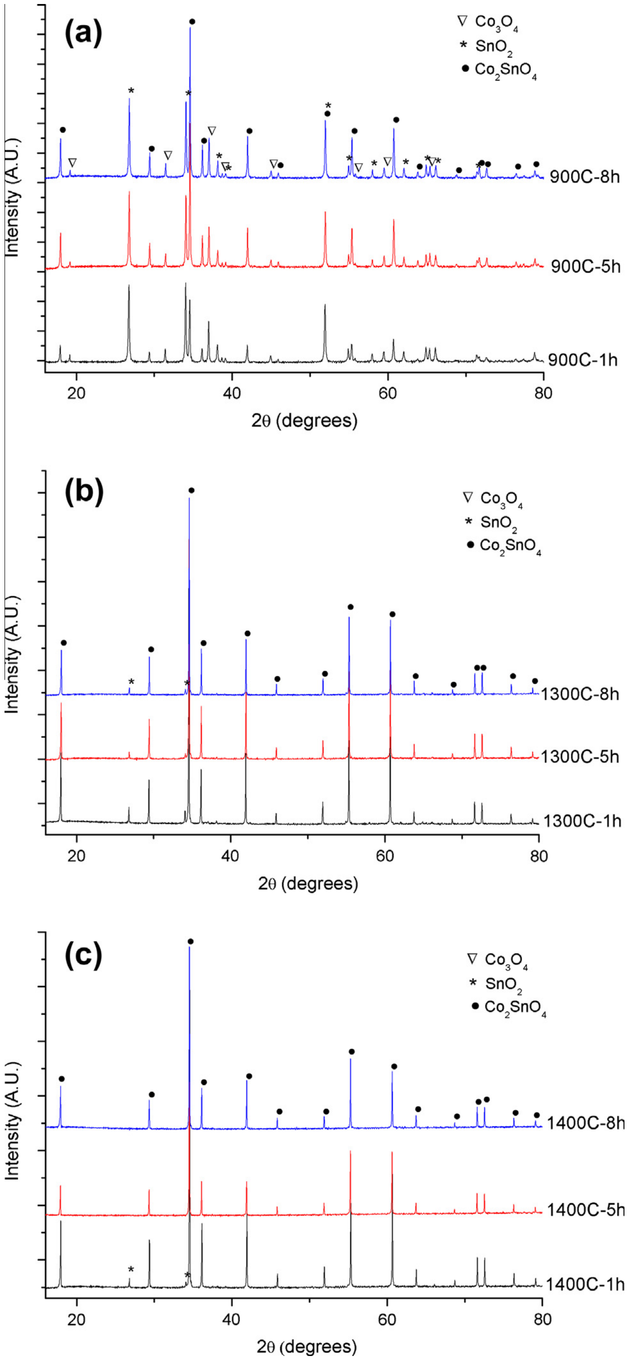

Fig. 2. XRD patterns of the powders synthesized by sol–gel method at (a) 900, (b) 1300 and (c) 1400 °C for 1, 5 and 8 h.

The quality of fitting is judged through the minimization of weighted residual error (R_w), through a Marquardt least-squares program and is defined as:

$$R_{wp} = \left[\frac{\sum_i w_i(I_o - I_c)^2}{\sum_l w_i I_o^2}\right]^{1/2}, \qquad (2)$$

The goodness of fit (*GoF*) is established by comparing R_{wp} with the expected error, $R_{\exp}$.

$$R_{\exp} = \left[\frac{N - P}{\sum_i w_i I_o^2}\right]^{1/2}, \qquad (3)$$