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Synthesis by the polymeric precursor method and characterization of undoped and Sn, Cr and V-doped $ZrTiO_4$

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Abstract

In this work, zirconium titanate doped with 0.1, 0.2, and 0.4 mole% of tin, chromium and vanadium was synthesized by the polymeric precursors method and characterized by thermal analysis (TG/DTA), X-ray diffraction (XRD), nitrogen adsorption and scanning electronic microscopy (SEM). The powder presented two mass losses attributed to the exit of water and to the pyrolysis of the organic material. The surface area reduction observed from 500 °C indicates the beginning of the sintering process. All the dopants led to changes in the lattice parameters and to the decrease of both crystallite size and particle size.

Keywords: $ZrTiO_4$; Crystallization; Doping; Polymeric precursor method; Nuclei grow

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1. Introduction

$ZrTiO_4$ (ZT) is used in the electronic industry, where exists a demand for dielectric materials of high performance [1]. It also finds a vast application as catalyst in some oxidation reactions [2]. Above 1400 °C, $ZrTiO_4$ displays an α-PbO_2 orthorhombic structure with a random distribution of the Zr^{4+} and Ti^{4+} cations at the equivalent octahedric sites.

The oxygen atoms form a compact hexagonal arrangement, with Ti^{4+} and Zr^{4+} cations occupying, at equiatomic amounts, the octahedric sites of the lattice (Fig. 1), where each metal is coordinated by six oxygens [3].

Zirconium titanate chemical preparation methods, especially the co-precipitation and sol–gel synthesis routes, offer advantages over traditional processing techniques because of the higher purity, better homogeneity, lower processing temperature and the development of interesting material properties, such as room temperature photoluminescence [4].

The polymeric precursor method (PPM) [5,6] is associated with the formation of a metallic complex using a hydroxycarboxylic acid, such as citric acid. Polymerization is promoted by heating the complex in the presence of a polyhydroxy alcohol, such as ethylene glycol [7]. A homogeneous resin, the polymeric precursor, is produced, in which the metal ions are uniformly distributed within the organic matrix [8].

2. Experimental

Fig. 2 schematically presents the preparation of $ZrTi_{1-x}M_xO_4$ (M = V, Sn and Cr and $x = 0$, 0.1%, 0.2% and 0.4%) from the polymeric precursor method. The titanium and zirconium citrates were prepared from titanium isopropoxide [Riedel-de-Haën] and zirconium n-propoxide [Quimex], respectively. The tin citrate was prepared from $SnCl_2 \cdot 2H_2O$ [9] and the other dopant sources used were V_2O_5 and $Cr(NO_3)_3 \cdot 9H_2O$.

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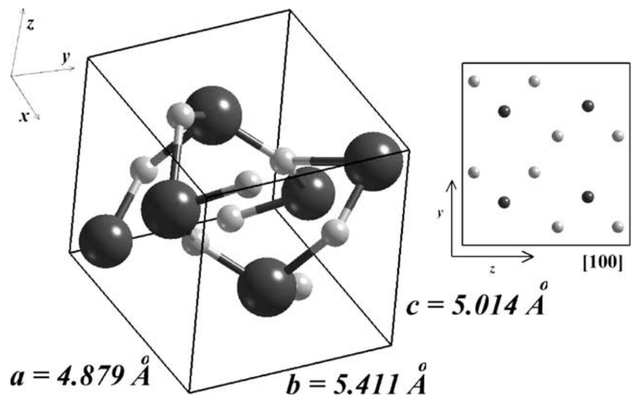

Fig. 1. $ZrTiO_4$ orthorhombic unit cell and crystal structure viewed along [1 0 0]. The metal and the oxygens are represented by grey and black spheres, respectively.

After the water evaporation, the resin was heat treated at 300 °C for 1 h, in a static atmosphere, leading to the partial decomposition of the polymeric gel, forming an expanded resin, constituted of partially pyrolyzed material. The product of the primary heat treatment was removed from the beaker, de-agglomerated and ground in a porcelain mortar until passing through a 100-mesh sieve.

Thereafter, we studied the morphological and structural behavior of $ZrTi_{1-x}M_xO_4$ for M = V, Sn and Cr and $x = 0$, 0.1%, 0.2% and 0.4%.

The thermal decomposition of the organic precursor was evaluated in a simultaneous TG/DTA thermobalance (TA Instruments), in alumina crucibles, at a temperature ranging from room temperature up to 900 °C and using a heating rate of 10 °C min^{-1}. The atmosphere used was synthetic air, keeping a constant flow rate of 100 mL min^{-1}.

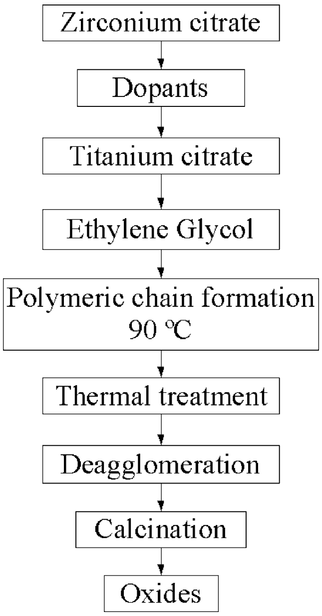

Fig. 2. Schematic flow chart for polymeric precursor processing of doped $ZrTiO_4$ powder.

The powders were heat treated in a static air atmosphere and with a heating rate of 10 °C min^{-1} in 2 h steps. The first heating step was at 350 °C for 2 h, for the organic matter pyrolysis and the second heating step, at 400, 500, 600 or 700 °C.

In order to evaluate the crystalline evolution and to determine the unit cell volume, it was used a Rigaku DMax 2500 PC X-ray diffractometer, with Cu Kα radiation ($\lambda = 1.5406$ Å), operating at room temperature. The crystallite diameter (D_{crys}) was determined from the (1 1 1) diffraction peak of the $ZrTiO_4$ phase (2θ in the range from 30.4 to 30.6), according to the Scherrer equation (Eq. (1)) and using a fine SiO_2 external standard [10],

$$B = \frac{k\lambda}{D_{\mathrm{crys}} \cos\theta}, \tag{1}$$

where B is the full width at half maximum (FWHM), θ the Bragg angle, k is a constant and λ is the wavelength of the Cu Kα radiation.

The surface area measurements of the oxides were carried out in a Micromeritcs, ASAP 2000 78 equipment, using N_2 as the adsorption/desorption gas. The particle diameter (D_{BET}) was evaluated according to Eq. (2), in which $\gamma = 5.084\,\mathrm{g\,cm^{-3}}$, the $ZrTiO_4$ theoretical density:

$$D_{\mathrm{BET}} = \frac{6}{\gamma \cdot S_{\mathrm{BET}}}. \tag{2}$$

The scanning electron microcopy (SEM) images of samples heat treated at the temperatures of 400, 500, 600 and 700 °C were acquired with a Zeiss-DSM 940A apparatus.

3. Results and discussion

Thermal analysis (Fig. 3) demonstrated that the weight loss occurred in two well-defined stages. The first one (30–200 °C), was associated to the water and solvent evaporation and to the desorption of the gas adsorbed on the powder surface. The second and a more significant weight loss stage took place from 200 to 500 °C, and was related to the removal of the organic matter remaining from the synthesis process.

The exothermic DTA peak at 720 °C is characteristic of the crystalline phase formation. Fig. 4 presents the crystallization peak displacement of the oxides, as a function of the doping.

After being submitted to the heat treatments at 400, 500 and 600 °C for 2 h, the oxides do not present a well-defined structure, presenting no characteristic peak of a crystalline phase, thus displaying an amorphous character. This result corroborates the crystallization temperature of the oxides determined by DTA, which indicates a crystallization temperature of about 700 °C. It can be noticed that crystallization temperature, as determined by DTA, presents the tendency to decrease as a function of the doping. The doped and undoped powders treated at 700 °C presented the same crystalline phase, $ZrTiO_4$ (JCPDS file number 34–415),