PECHINI SYNTHESIS AND CHARACTERIZATION OF Eu^{3+} DOPED ZnCo_2O_4 SPINELS

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Abstract

Spinel oxides with the composition ZnCo_2O_4 and $\text{ZnCo}_2\text{O}_4:\text{Eu}^{3+}$ have been synthesized by the Pechini method and characterized by X-ray diffraction, infrared spectroscopy, thermal analysis and scanning electron microscopy. IR spectroscopy revealed the presence of ν_1 and ν_2 bands, typical of spinel structures. The formation of monophase cubic spinel structure was confirmed by X-ray diffraction patterns. Extra lines corresponding to other phase has been observed in the powders calcined at 900 °C. The results showed the extremely lower synthesis temperature than those presents in conventional methods.

Keywords: Pechini method, Spinel oxides, $\text{ZnCo}_2\text{O}_4:\text{Eu}^{3+}$.

Introduction

A large group of compounds with general formula AB_2X_4 , where A and B are different cations and X is an anion (usually oxygen), crystallize in the (Sp) spinel structure. In this structure, the cation distribution may be quantified using the degree of inversion, δ , which is the fraction of A ions on octahedral sites. Therefore, two extreme types of behavior may be distinguished resulting in normal ($\delta = 0$) and inverse ($\delta = 1$) spinel. ZnCo_2O_4 is a normal spinel containing Zn^{2+} and Co^{3+} ions on its tetrahedral and octahedral sites, respectively. These compounds are important in many branches of solid state science [West, A. R, 1991; Smart et al., 1996; Jendrzejewska, I., 2000]. Mixed oxides with spinel structure have been studied for decades, due to its wide applications such as ceramic pigments with high thermal and chemical stability [Strek et al., 2000], in addition to the production of refractory [Candeia, 2004], magnetic [Yan et al., 2000; Jani et al, 2001], and catalytic materials [Omata et al., 1996; Jacobs et al., 1994; Jalowiecki et al., 1987; Ghorpade et al., 1998] and others [Chokkaram et al., 1997].

The most used method employed in the preparation of spinels involves solid-state reaction of mechanically mixed metal oxides at high temperatures [Lavela et al, 2000; Norman et al, 1999; Kim et al., 2000]. Alternatively, the Pechini method [Pechini M. P., 1967], based on polymeric precursors, does not require high-temperature calcination to obtain spinels in addition to allowing good stoichiometric control and reproducibility. This method consists on the formation of a polymeric resin between a metallic acid chelate and polyhydroxide alcohol by polyesterification.

The main purpose of this study is, therefore, to synthesize ZnCo_2O_4 and Eu^{3+} doped ZnCo_2O_4 ($\text{ZnCo}_2\text{O}_4:\text{Eu}^{3+}$) by the Pechini method [Pechini M. P., 1967], in order to verify the effect of the synthesis parameters on structural, morphological and surface properties. These factors are considered important due to their effects on the crystalline structure, which affect the properties of

the oxides. The thermal behavior was also investigated by monitoring thermogravimetric (TG) and differential thermal analyses (DTA).

Experimental

The powders were prepared by using metal nitrates (VETEC) as starting materials. Aqueous solution of cobalt nitrate and citric acid were mixed at a molar ratio 1:3, under stirring for 30 min at 70 °C. A stoichiometric amount of $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ was mixed with the cobalt citrate solution for 30 min at 70 °C followed by addition of 1 wt. % $\text{Eu}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$. The temperature was slowly increased up to 90 °C and ethylene glycol was added at a 60:40 ratio (citric acid:ethylene glycol). The solution was stirred on a hot plate, which allowed the temperature to be controlled until it became a dark gel (polymeric resin). This gel was calcined at 300 °C for 2 hours resulting in the precursor powder. This material was calcined in the temperature range 500-900 °C for 4 hours. The resulting powders were characterized by thermogravimetric analysis (TG), differential thermal analysis (DTA), X-ray diffraction (XRD), Fourier-transform infrared spectroscopy (FTIR), particle size analysis and scanning electron microscopy (SEM).

Thermogravimetric curves were obtained on a Perkin-Elmer TGA-7 instrument and DTA curves on a Perkin-Elmer DTA-1700 instrument at a heating rate of 5 °C min⁻¹ in air flowing at a rate of 50 cm³ min⁻¹. X-ray diffraction patterns were obtained from a Shimadzu XRD-6000 diffractometer using CuK_α radiation ($\lambda = 1.5418 \text{ \AA}$). The FTIR spectra were performed on a ABB BOMER instrument model MB104 using KBr pellets in the interval of 4000 to 500 cm⁻¹. Particle size was obtained in a SILAS model 1064 analyzer. The microstructure of the powders was revealed observing Au-coated samples under a Philips ESEM-XL30 scanning electron microscope set at the high-vacuum mode. The presence of europium in the zinc cobaltate matrix was confirmed by EDS analysis.

Results and discussion

The thermogravimetric curves of the ZnCo_2O_4 and $\text{ZnCo}_2\text{O}_4 \cdot \text{Eu}^{3+}$ precursor powders are showed in the Figures 1a and 1b, respectively. It is observed that the citrates were totally decomposed at approximately 500 °C, followed by oxide formation. This analysis indicated which temperature should be used for the calcination of the precursor powder in order to obtain the desired phases. Samples heated from 500 to 900 °C revealed no additional mass loss.

Differential thermal analysis curves (Figures 2a and 2b) of the precursor powders showed exothermic and endothermic events. The precursor powder decomposition is characterized by more than one exothermic process with peaks between 150 °C and 313 °C, due to the decomposition of residual organic substances. The endothermic peak showed at about 900 °C is attributed to a structural modification of spinel phase.

Figure 1. Thermogravimetric curves of precursor powders for (a) ZnCo_2O_4 and (b) $\text{ZnCo}_2\text{O}_4: \text{Eu}^{3+}$

Figure 2. Differential thermal analysis curves of precursor powders for (a) ZnCo_2O_4 and (b) $\text{ZnCo}_2\text{O}_4: \text{Eu}^{3+}$

X-ray diffraction patterns of the powders calcinated at different temperatures are shown in Figure 3a and 3b for ZnCo_2O_4 and $\text{ZnCo}_2\text{O}_4: \text{Eu}^{3+}$, respectively. The presence of the spinel phase could be observed at relatively low calcination temperatures. It is possible to visualize the increase in the crystallinity with increasing the heat treatment temperature.

It is also noticeable that the peaks of ZnCo_2O_4 were detected in the powders calcinated at 500 °C. All powders consist of single-phase materials with spinel type structure except for a small

amount of ZnO for the powders calcined at 900 °C. All peaks were indexed as a cubic cell, $Fd3m$ space group (JCPDS 23-1390). The presence of Eu^{3+} ions in the doped spinel oxides seems to play two basic roles: they may substitute the trivalent or divalent ions in the spinel structure; or they can be occluded on surface spinel [Strek et al, 2000]. According to Strek et al. [Strek et al, 2000] the latter possibility is the most likely one.

Figure 3. X-ray diffraction pattern for (a) ZnCo_2O_4 and (b) $\text{ZnCo}_2\text{O}_4:\text{Eu}^{3+}$ powders calcined at different temperatures.

FTIR spectra for ZnCo_2O_4 and $\text{ZnCo}_2\text{O}_4:\text{Eu}^{3+}$ calcined at different temperatures are shown in Figure 4. The spectra shows two bands characteristic of spinel structures: one in the 590-560 cm^{-1} region (ν_1) and another one in the 685-665 cm^{-1} interval (ν_2). According to group theory, spinel type oxides should exhibit four IR bands ν_1 - ν_4 [Lefez et al, 1996]. In the present study, however, measurements were carried out up to 500 cm^{-1} thus limiting the discussion to the high frequency bands (ν_1 and ν_2) of the IR spectrum. The frequencies ν_1 and ν_2 are assigned to F_{1u} vibrations of the octahedral groups of the ZnCo_2O_4 spinel [Lefez et al, 1996; Basak and Ghose, 1994; Kustova et al, 2000; Preudhomme et al, 1971]. The FTIR spectrum should not show any changes in the frequencies ν_1 and ν_2 resulting from the presence of Eu^{3+} ions in the doped spinel oxides.

Figure 4. FTIR spectra for (a) ZnCo_2O_4 and (b) $\text{ZnCo}_2\text{O}_4:\text{Eu}^{3+}$ powders calcined at different temperatures.

The powders morphologies were observed by SEM micrographs and the presence of europium in the zinc cobaltate matrix was confirmed by EDS analyses. Figure 5 shows the micrographs of $\text{ZnCo}_2\text{O}_4 \cdot \text{Eu}^{3+}$ powder calcined at 900°C . It is observed the presence of regular-shaped spinel nanocrystals. The average particle size of the powders decrease from 11 to $9\ \mu\text{m}$ and from 7 to $4\ \mu\text{m}$ as the calcination temperature increased from 500 to 900°C for ZnCo_2O_4 and for $\text{ZnCo}_2\text{O}_4 \cdot \text{Eu}^{3+}$, respectively. The disparities in the particle size and particle size distributions may be attributed to the preparation method and calcination temperatures used.

Figure 5. EDS (left) and SEM (right) micrographs for $\text{ZnCo}_2\text{O}_4 \cdot \text{Eu}^{3+}$ powder calcined at 900°C .

Conclusions

The characterization of the samples has shown that the desired spinel prepared by the Pechini method is single phase. Relevant features of the results obtained are the relatively low temperature required for spinel formation, which cannot be achieved by conventional synthesis methods. Crystallization of spinel phase was observed at 500°C and the formation of monophase cubic spinel structure was detected at 700°C . Extra diffraction peaks corresponding to ZnO phase has been observed in the powders calcinated at 900°C . The DTA analysis confirms a structural modification occurred at 900°C . Particle size and crystallinity increased as the calcination temperature increasing. Therefore we can conclude that the synthesis method used was appropriate for the synthesis of the spinel-type powders at low temperature and ambient atmosphere.

Acknowledgments

The authors acknowledge CNPq for the financial supports.

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O Grupo Tchê Química agradece ao reconhecimento recebido pelo colegas da Universidade Federal do Rio Grande do Norte, que pela segunda vez nos escolheu como meio de divulgação da sua produção científica e tecnológica. Esperamos continuar correspondendo às expectativas.