

THERMAL STUDY OF THE CERAMIC PIGMENTS $\text{Co}_x\text{Zn}_{(7-x)}\text{Sb}_2\text{O}_{12}$

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Abstract

Using the Pechini method, pigments with spinel structure ($\text{Zn}_7\text{Sb}_2\text{O}_{12}$) were synthesized by substitution of the cation Zn^{2+} by Co^{2+} , in compounds with different concentrations of Sb_2O_3 . The doping resulted in $\text{Co}_x\text{Zn}_{(7-x)}\text{Sb}_2\text{O}_{12}$ phases ($x=1-7$) that were isomorphs to spinel, denominated as samples A and B. After thermal treatment at 400°C for 1 h, the powders were characterized by thermogravimetry (TG) and differential thermal analysis (DTA). The results indicate a different behavior when a higher amount of Sb_2O_3 is used, due to the presence of a secondary phase (ilmenite).

Keywords: ceramic, pigment, thermal analysis

Introduction

In the field of ceramic tiles, the use of pigments is not a novelty but a necessity, as the tonality variations of pieces are causes of tile rejection or different tile classifications at the end of the production process. Thus, the impact of an improvement in the quality of the pigments and, consequently, of the ceramic products can cause a high benefit in the cost [1]. The aesthetic aspect, specially the color, frequently represents the conditional parameter for obtaining a ceramic product, the selection of which is rarely determined by functional properties [2]. Thus, the development of pigments presents an area of great scientific and technological interest.

A group of oxides with important applications in pigments are the spinels, which present high thermal stability. Spinel has the general formula $\text{AO}\cdot\text{B}_2\text{O}_3$ (where *A* and *B* are metals), and are formed by the association of a trivalent oxide (of acid character) with a bivalent oxide (of basic character) [3, 4].

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The conventional methods to obtain ceramic powders are not appropriate for many advanced applications due to the low reactivity, low reproducibility and inhomogeneity, as well as an imprecise control of the stoichiometry. Better results can be obtained by the chemical synthesis route, because it's possible to have good control over stoichiometry, powder morphology and phase purity [5].

Chemical synthesis based on metal chelation was developed by Pechini [6, 7]. This method consists in the formation of a polymeric chain from a polyalcohol and a polycarboxylic acid, with metallic cations distributed homogeneously along the chain. When the polymeric chain is calcined, a high quality ceramic powder is obtained compared to powders synthesized by solid-state reaction.

The synthesis of zinc-antimony spinel $\text{Zn}_7\text{Sb}_2\text{O}_{12}$ was done by the Pechini method in this work. The purpose was the study of the influence of the amount of Sb_2O_3 on the crystallization of the zinc-antimony spinel phase, doped with different concentrations of cobalt, and the study of the thermal behavior of the phases formed.

Experimental

Two concentrations of antimony oxide were used in the synthesis of the spinel phase ($\text{Zn}_7\text{Sb}_2\text{O}_{12}$), doped with transition metal cations, Co^{2+} , according to the stoichiometry $\text{Co}_x\text{Zn}_{(7-x)}\text{Sb}_2\text{O}_{12}$ ($x=1-7$) using the Pechini method. Different materials were synthesized and were denominated as samples A:7 ($\text{ZnO}+\text{CoO}$): Sb_2O_3 and B:7 ($\text{ZnO}+\text{CoO}$): $2\text{Sb}_2\text{O}_3$.

Ethylene glycol (Reagen) and citric acid (Vetec) were mixed in a beaker with heating and stirring. The solution was kept at a controlled temperature of 60–70°C. After complete dissolution, the antimony oxide (Vetec) was slowly added. Finally, zinc acetate (Vetec) and cobalt acetate (Vetec) were added.

The temperature at which the polymer formation reaction started changed according to the percentage of the metal to be chelated, which gave to each composition distinct characteristics of viscosity and color. A typical reaction started at around 110°C. Because of the exothermic character of the reaction, the polymerization occurred at 130–140°C by the esterification reaction of the citrate salt with the ethylene glycol. At the end of the reaction, the viscosity increased and the gas elimination stopped, leading to the formation of a polymeric gel (resin). After this step, the resin was heat treated at 400°C for 1 h (primary calcination).

During the primary calcination, two phenomena are observed at the same time: the increase of the resin viscosity and the elimination of H_2O , CO and CO_2 due to the partial decomposition of the resin. These phenomena lead to the imprisonment of gases which act as expanding agents, leading to the formation of a semi-carbonized foam. The product of the primary calcination was removed from the beaker, powdered in a porcelain mortar and passed through a 100 mesh sieve.

The thermal effect of oxidation of the samples as well as the formation of the crystalline phases were studied by DTA (Shimadzu, DTA-50) and thermogravimetry (Shimadzu TGA-50), under a synthetic air atmosphere with flow rate of 20 mL min^{-1} and heating rate of $10^\circ\text{C min}^{-1}$. The reference material for DTA was Al_2O_3 .

Results and discussion

The thermogravimetric curves of the phases $\text{CoZn}_6\text{Sb}_2\text{O}_{12}$ and $\text{Co}_3\text{Zn}_4\text{Sb}_2\text{O}_{12}$ from the samples containing different amounts of Sb_2O_3 show two stages: the first, related to the elimination of adsorbed water and the second, to the evolution of the CO , CO_2 and H_2O gases, leading to a mass loss with many thermodecomposition reactions.

According to the data of Table 1, it is possible to observe that water adsorption increases with an increase in the amount of Sb_2O_3 . The samples B1 and B2 (with a higher concentration of Sb_2O_3), show higher mass loss in the first stage, compared to the samples A1 and A2.

Table 1 Results of TG curves for the phases $\text{CoZn}_6\text{Sb}_2\text{O}_{12}$ and $\text{Co}_3\text{Zn}_4\text{Sb}_2\text{O}_{12}$ synthesized by different amounts of Sb_2O_3

Phase	Samples	Stage	Range/ $^{\circ}\text{C}$	Main peak temp./ $^{\circ}\text{C}$	Mass loss/%
$\text{CoZn}_6\text{Sb}_2\text{O}_{12}$	A1	I	25–198	75	2.7
		II	313–548	457	42.4
	B1	I	26–225	74	6.4
		II	332–651	497	24.5
$\text{Co}_3\text{Zn}_4\text{Sb}_2\text{O}_{12}$	A2	I	25–94	50	1.9
		II	250–530	402	17.5
	B2	I	25–122	63	3.5
		II	311–702	477	30.0

In the second stage, the mass losses for the samples B1 and B2 occur at higher temperatures, as it may be observed in Table 1. This is due to the higher stability of the sample with higher concentration of Sb_2O_3 favoring a faster decomposition at higher temperatures. The samples A1 and A2 not only decompose at lower temperatures, but also attain their stability at lower temperatures.

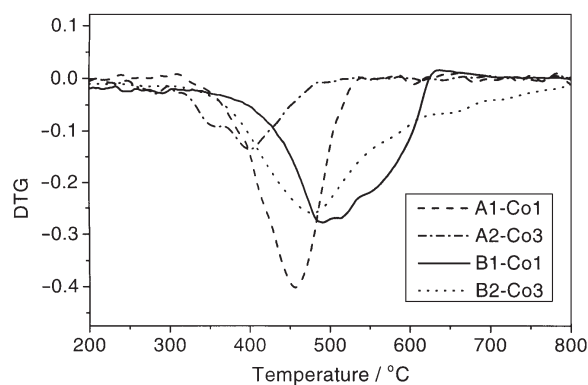


Fig. 1 DTG curves of the samples A and B. Analysis conditions: synthetic air atmosphere with flow rate of 20 mL min^{-1} and heating rate of $10^{\circ}\text{C min}^{-1}$

In relation to the mass loss, the different phases show different behaviours. for the phase $\text{CoZn}_6\text{Sb}_2\text{O}_{12}$, the sample A1 (with smaller amount of Sb_2O_3) presents higher mass loss. For the phase $\text{Co}_3\text{Zn}_4\text{Sb}_2\text{O}_{12}$, the sample B1 shows the highest mass loss. These differences in the mass loss values may be due to a non-uniform temperature throughout the material during the primary calcination.

All samples show superposed peaks for the decomposition of the organic material, considering that chains of lower molecular mass tend to decomposes at lower temperatures [8], and also for the oxidation of the metallic cations in different steps, with different mass losses for each one of them (Fig. 1).

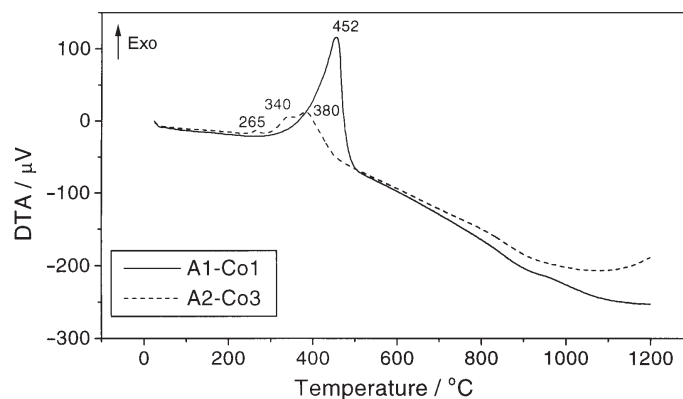


Fig. 2 DTA curves for the samples A1 and A2, with different concentrations of cobalt. Analysis conditions: synthetic air atmosphere with flow rate of 20 mL min^{-1} and heating rate of $10^\circ\text{C min}^{-1}$

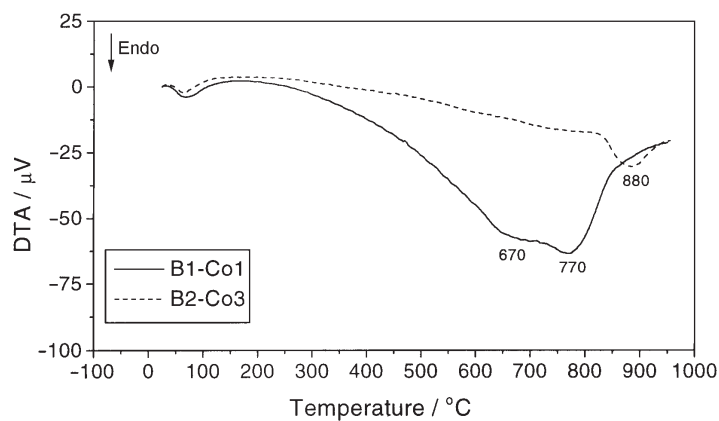


Fig. 3 DTA curves for the samples B1 and B2, with different concentrations of cobalt. Analysis conditions: synthetic air atmosphere with flow rate of 20 mL min^{-1} and heating rate of $10^\circ\text{C min}^{-1}$

As the samples are composed of organic material, they decompose by combustion, with an exothermic reaction. In this way, the DTA curves of the samples A1 and A2 show exothermic peaks (Fig. 2).

The $\text{Co}_3\text{Zn}_4\text{Sb}_2\text{O}_{12}$ phase (sample A1) shows a single peak at 452°C in DTA curve as well as in the DTG curve, that also shows only one decomposition peak. The $\text{Co}_3\text{Zn}_4\text{Sb}_2\text{O}_{12}$ phase (sample A2) shows three peaks at 265, 340 and 380°C, close to the decomposition temperatures indicated by the DTG curve. The poor definition of the peaks is associated with the processes of decomposition of the organic material, which occurs over a temperature range.

For the samples B1 and B2, with the higher amount of Sb_2O_3 , endothermic peaks are observed (Fig. 3). The $\text{CoZn}_6\text{Sb}_2\text{O}_{12}$ phase (sample B1) shows two peaks around 670 and 770°C, while the $\text{Co}_3\text{Zn}_4\text{Sb}_2\text{O}_{12}$ phase, shows a single peak around 880°C. This peak could be associated with the Co_2O_3 decomposition that occurs at 895°C [9], with crystallization or with a structural organization. Because no mass loss is observed at this temperature and materials synthesized using the Pechini method tend to crystallize at lower temperatures [10], the peak at 880°C and the peaks of the phase $\text{CoZn}_6\text{Sb}_2\text{O}_{12}$ may be related to structural organization, as an order-disorder transition. Because endothermic peaks are not observed for the samples A1 and A2, it may also be concluded that the highest concentration of Sb_2O_3 leads to the crystallization of an unstable structure, that reorganizes itself at higher temperatures.

Conclusions

The results indicate that an increase of the Sb_2O_3 concentration (samples B1 and B2), leads to more stable structures, with higher decomposition temperatures of the organic material. The materials studied show different yields and different temperature decomposition: samples B1 and B2 decompose at higher temperatures.

The decomposition peaks are also observed in DTA curves, for samples A1 and A2. For samples B1 and B2, endothermic peaks related to structural organization are observed.

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