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THERMAL STUDY OF $Co_xZn_{7-x}Sb_2O_{12}$ SPINEL OBTAINED BY PECHINI METHOD USING DIFFERENT ALCOHOLS

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Abstract

With the aim of obtaining materials with applications in pigments, $Co_xZn_{7-x}Sb_2O_{12}$ spinels were synthesized using the Pechini method. This method consists in the formation of a polymeric net, where the metallic cations are homogeneously distributed. In this work, two types of alcohol (ethyl glycol and ethylene glycol) were used for the synthesis of a zinc antimoniate spinel, $Co_xZn_{7-x}Sb_2O_{12}$ (x=0–7). The materials were characterized by termogravimetry (TG) and differential thermal analysis (DTA). TG results indicated a decrease in total mass loss when cobalt was added to the solution substituting zinc, for samples prepared using the two different alcohols. Decomposition temperatures, obtained by TG and DTA, presented a decreasing behavior as cobalt was added to the material. In relation to the alcohols, all results indicated a better polymerization of the resin when ethylene glycol was used, being the most indicated one for cation immobilization. X-ray diffraction did not show differences between the two alcohols – both presented the spinel phase $(Co, Zn)_{2.33}Sb_{0.67}O_4$. Samples with higher quantity of cobalt also presented ilmenite phase $(Co, Zn)Sb_2O_6$.

Keywords: DTA, Pechini, spinel, thermogravimetry

Introduction

The Brazilian Ceramic Tile Industry has made huge investments to modernize all plant facilities. With entrepreneurial capacity and boldness, the current production outlook is one of the best in the world, regarding technology applied and overall commitment with international regulations. In this sense, the development of new pigments has become really important, as soon as it implies esthetic aspects. Different pigments may be obtained using mixed oxide ceramics. In the last years, this class of

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materials has received a growing interest, not only by pigment industries, but also by electronic [1] and magnetic ones.

Color is an important characteristic of many ceramic products [2]. The ceramic pigment quality depends on its optical and physical properties. These properties are directly related to the crystalline structure of the pigment, its chemical composition, purity, stability and some physical properties, as granulometric distribution, particle shape, surface area, etc. [3]. Ions of interest for pigmenting are those with their own color. Ionic color is due to d or f shells partially occupied, permitting transitions among their energy levels. This way, the most common coloring ions are those of the first transition series [4]: V, Cr, Mn, Fe, Co, Ni and Cu. In addition, rare earth's cations, as Ce, Pr and Nd, are occasionally used.

Most of time, pigments used for ceramic coloring are inorganic products composed of mixed cation oxides [5]. Mixed cation oxides with spinel structure have many applications. Spinels are a big group of compounds with general formula AB_2O_4, where A and B are bivalent and trivalent cations, respectively [6]. They are known as pigments with high thermal stability, appropriate to give color to glasses and ceramics. Some spinels are also excellent refractory, magnetic and catalytic materials.

Due to the need of synthesizing ceramic materials at low temperatures, many chemical methodologies have been investigated, as sol-gel, coprecipitation and polymeric precursors [7, 8].

Polymeric precursors method was developed by Pechini in 1967 [9, 10] and popularized by Anderson [11]. The objective of this method is the immobilization of the metallic ions in a rigid polymeric net [7]. This polymeric net is obtained from a solution containing ethylene glycol, citric acid and the respective cation. The Pechini

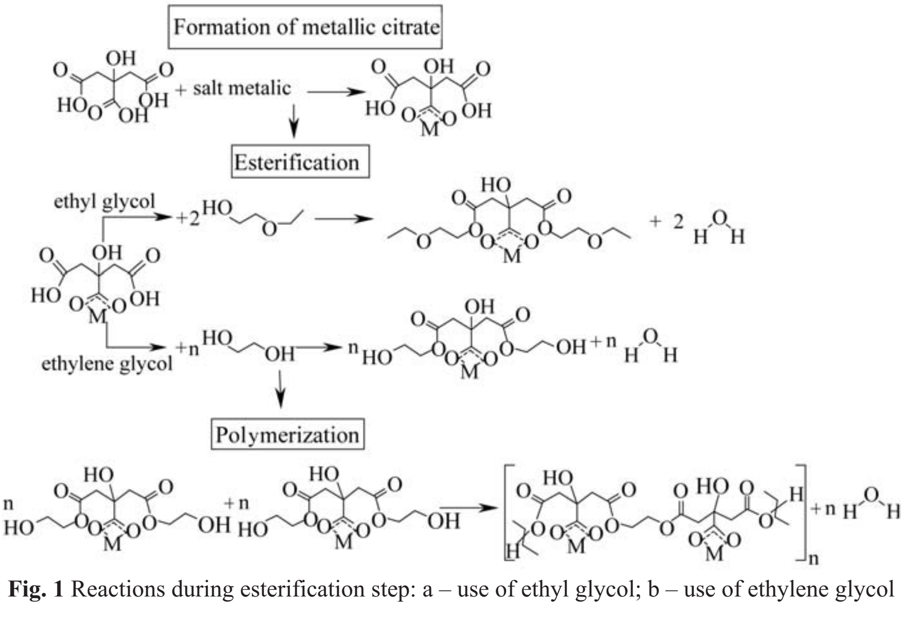

Fig. 1 Reactions during esterification step: a – use of ethyl glycol; b – use of ethylene glycol

method has received a lot of attention due to its simplicity. Many ceramic compounds have been successfully synthesized using this process.

According to literature results, three reactions occur during Pechini method, leading to the formation of the polymeric precursor: metallic chelate formation, ester formation and polyesterification [12].

In this work, the spinel $Co_xZn_{7-x}Sb_2O_{12}$ (x=0–7) was synthesized by Pechini method, using two alcohols during esterification reaction: ethyl glycol and ethylene glycol, according to Fig. 1.

Experimental

Precursors used in the synthesis of $Co_xZn_{7-x}Sb_2O_{12}$ (x=0–7) are described in Table 1. An aqueous solution of citric acid was diluted in ethyl glycol or ethylene glycol in the proportions of 60/40 mass/mass [1, 13] under agitation and heating at 60–70ºC. After complete solubilization, antimonium oxide was added, with some drops of nitric acid to make dissolution easier. After that, zinc acetate and/or cobalt nitrate were added to the solution, in stoichiometric amounts. After solubilization, temperature was increased to 90–110ºC, leading to esterification. This temperature of polymer formation varied according to metal amount to be chelated, leading to each composition distinct characteristics as viscosity and color.

Table 1 Precursors used in the spinel synthesis

Precursor	Chemical formula	MW	Purity/%
Citric acid	$C_6H_8O_7{\cdot}H_2O$	210.14	99.5
Ethylene glycol	$HOCH_2CH_2OH$	62.07	99.5
Ethyl glycol	$HOCH_2CH_2OCH_2CH_3$	90.12	99.0
Antimony oxide	Sb_2O_3	291.50	99.8
Zinc acetate	$C_4H_6O_4Zn{\cdot}2H_2O$	219.20	99.0
Cobalt acetate	$C_4H_6O_4Co{\cdot}4H_2O$	249.08	99.0

Primary calcination of the resin was done at 350ºC for one hour, leading to the partial decomposition of the polymer. In this step, a volumetric expansion of the system was observed, leading to a porous material, denominated expanded resin, constituted of a semi-carbonized material, with a fragile macroscopic net, similar to a sponge. The material was removed from beaker, deagglomerated in porcelain mortar and passed through 200 mesh sieve. This material was analyzed by simultaneous thermogravimetric and differential thermal analysis (TA-Instruments – SDT 2960), with a heating rate of 10ºC min^{-1}, in air flux, to observe mass loss and possible energy transitions.

After that, the material was calcined at temperatures varying from 700 to 1000ºC, with an interval of 100ºC among them, for one hour, with a heating rate of 10ºC min^{-1}.

Crystalline phase formation at different temperatures was analyzed by X-ray diffraction (Siemens – D5000).

Results and discussion

The results of TG/DTA analysis of all samples indicated two decomposition events: the first one related to water and adsorbed gases loss and the second one due to organic material decomposition and metallic cations oxidation (Fig. 2).

The second thermodecomposition stage for materials synthesized using ethyl glycol is in the range of 290–500ºC and for ethylene glycol is in the range of 300–530ºC. These temperature ranges vary according to the cobalt quantity in the system.

Results indicated that a decrease in total mass loss was observed as cobalt was added to the solution substituting zinc, for materials prepared using the two different alcohols, as it may be observed in Fig. 3. As the same amount of organic material was used in all samples, this fact indicates that samples with higher amount of cobalt present a higher decomposition during primary calcination. This may be due to the formation of a polymer with smaller chain size, or to a less stable structure.

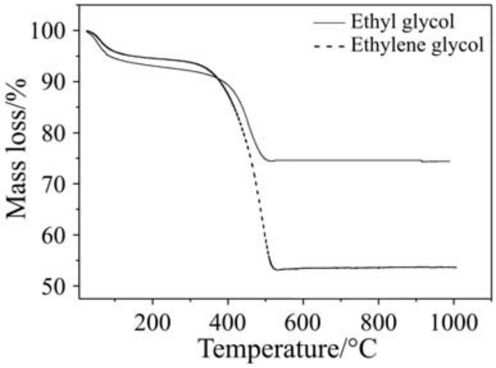

Fig. 2 Thermogravimetric curves of $Zn_7Sb_2O_{12}$ synthesized using ethyl glycol and ethylene glycol

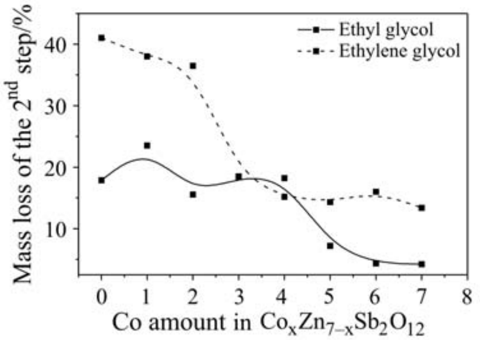

Fig. 3 Comparison of the mass losses of the second step as a function of cobalt quantity in the material

Comparing the 2nd event (Table 2) of thermodecomposition between the two alcohols, a smaller mass loss of the materials prepared using ethyl glycol in relation to ethylene glycol is observed. This is due to the smaller chain size, as ethyl glycol leads to a smaller degree of polymerization during resin formation, when compared to ethylene glycol. As shown in Fig. 1, this fact is due to the presence of only one hydroxyl group in ethyl glycol, while ethylene glycol presents two hydroxyl groups. As stated above, a smaller polymer chain size is easier to decompose, leading to a higher mass loss during primary calcination.

Table 2 Results of TG/DTA analysis for ethyl glycol and ethylene glycol

	Ethyl glycol			Ethylene glycol		
	TG		DTA	TG		DTA
Phases	1st event/ %	2nd event/ %	Peak temp./ °C	1st event/ %	2nd event/ %	Peak temp./ °C
$Zn_7Sb_2O_{12}$	6.5	17.8	450	5.0	41.0	484
$Co_1Zn_6Sb_2O_{12}$	2.8	23.5	423	4.3	38.0	465
$Co_2Zn_5Sb_2O_{12}$	7.4	15.5	395	3.7	36.5	401
$Co_3Zn_4Sb_2O_{12}$	5.4	18.4	387	5.1	18.5	374
$Co_4Zn_3Sb_2O_{12}$	4.7	18.2	352	3.3	15.2	364
$Co_5Zn_2Sb_2O_{12}$	6.8	7.2	323	5.9	14.3	351
$Co_6Zn_1Sb_2O_{12}$	6.0	4.4	258	7.4	16.0	348
$Co_7Sb_2O_{12}$	4.5	4.2	261	4.9	13.4	339

DTA analysis presented exothermic transitions in all samples, for both alcohols (Fig. 4). Transition temperatures presented a decreasing behavior as cobalt was added to the material (Fig. 5). It may also be observed that peak temperatures of ethyl glycol were smaller than those presented in ethylene glycol (Table 2) due to the smaller chain size of the polymer formed when ethyl glicol is used. These results are in agreement to TG ones.

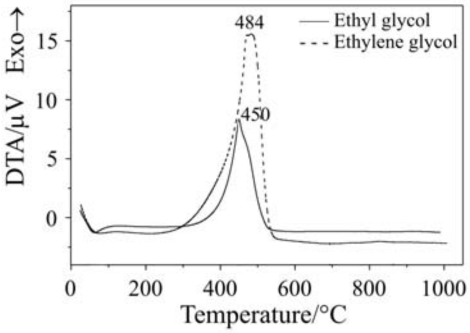

Fig. 4 DTA curves of $Zn_7Sb_2O_{12}$ synthesized using ethyl glycol and ethylene glycol

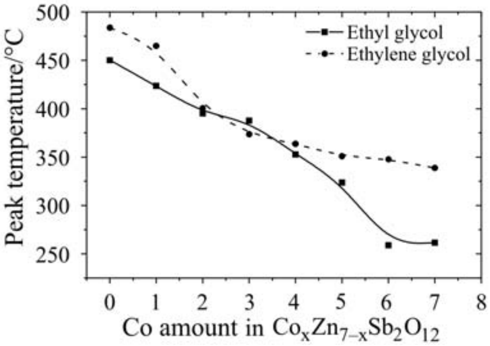

Fig. 5 Comparison between DTA peak temperatures as a function of cobalt quantity

Using X-ray diffraction, it was possible to observe phase formation of the sample material $Co_3Zn_4Sb_2O_{12}$, at different temperatures (700 to 1000ºC with a calcination time of 1 h). Both routes lead to the formation of only one phase in all calcination temperatures, as it may observed in Figs 6a and b. This indicates that no intermediate phase

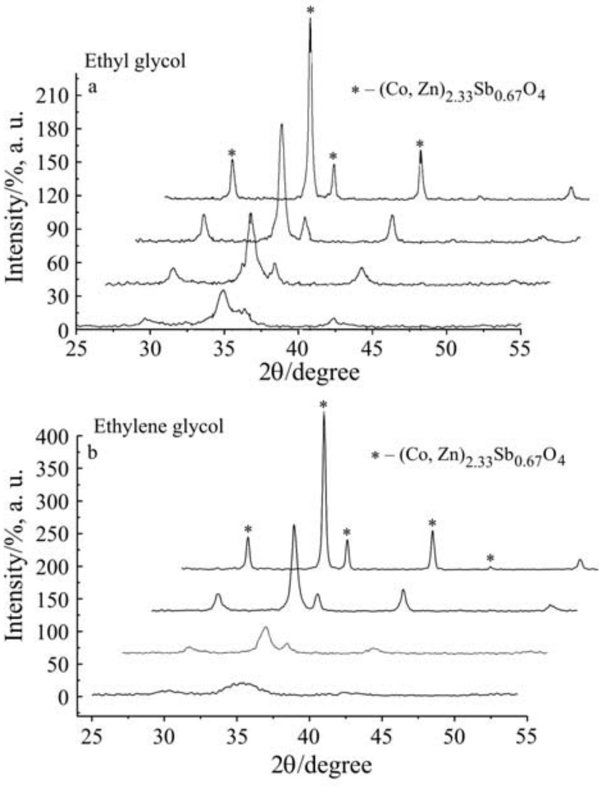

Fig. 6 X-ray diffractogram of the precursor $Co_3Zn_4Sb_2O_{12}$ at different temperatures: a – ethyl glycol, b – ethylene glycol

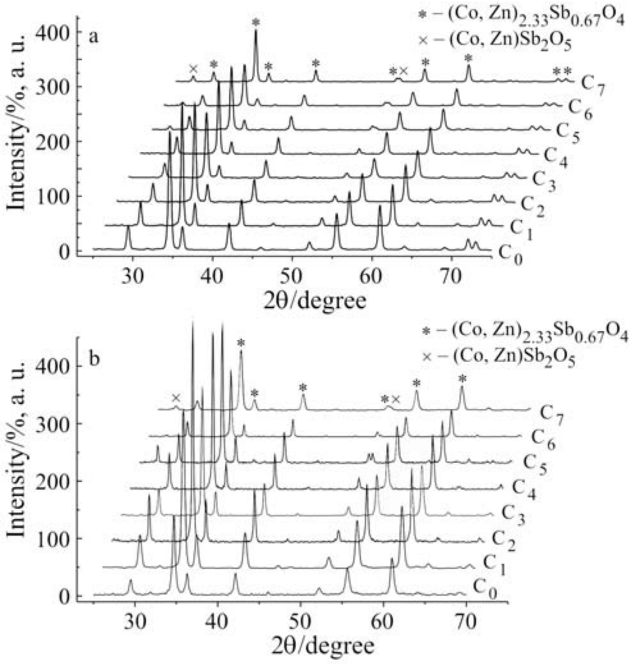

Fig. 7 X-ray diffractogram of the precursor $Co_xZn_{7-x}Sb_2O_{12}$, with different quantities of cobalt, calcined at 1000°C; a – ethyl glycol, b – ethylene glycol

is formed, before spinel crystallization. It may also be observed that crystallinity increases with increasing temperature.

X-ray diffractograms of samples calcined at 1000ºC, with different amounts of cobalt, are presented in Fig. 7.

Samples with higher quantities of cobalt (x=5, 6 and 7) presented the phases $(Co, Zn)_{2.33}Sb_{0.67}O_4$ and $(Co, Zn)Sb_2O_6$. The other samples presented only one phase. An important point is that both routes presented the same behavior, in spite of the different degree of polymerization.

Conclusions

All results indicated a better polymerization of ethylene glycol. This is due to the presence of two functional groups in ethylene glycol leading to polyesterification. This is not observed in ethyl glycol that has only one functional group. It is important to emphasize that a better polymerization leads to the immobilization of cations in the polymeric net, and consequently to a higher homogeneity of the final production, as this immobilization avoids cation segregation. In spite of this, X-ray diffraction did not show differences between the two alcohols – both presented the spinel phase $(Co, Zn)_{2.33}Sb_{0.67}O_4$. Samples with higher quantity of cobalt also presented ilmenite phase $(Co, Zn)Sb_2O_6$.

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