Journal of Thermal Analysis and Calorimetry, Vol. 79 (2005) 455–459

THE EFFECTS OF Co, Ni AND Mn ON THE THERMAL PROCESSING OF Zn_2TiO_4 PIGMENTS

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The objective of this work was to obtain ceramic pigments starting from Zn_2TiO_4 and containing chromophore ions (Co, Ni and Mn in 1–20 mol%), using the polymeric precursor method. Zn_2TiO_4 displays an inverse spinel structure and can accommodate different chromophores in its lattice. The characterization was carried out by means of TG, DTA and XRD. From the TG curves, it can be stated that the pigments are stable above 600°C. X-ray diffraction patterns of the materials containing Co are single phase, whereas the addition of Ni and Mn leads to second phases from 1 and 20% of substitution, respectively.

Keywords: *pigments, polymeric precursor method, spinel,* Zn_2TiO_4

Introduction

Most of the ceramic pigments consists of inorganic compounds, being formed by a host lattice, in which is integrated the pigmenting or chromophore component (usually a transition metal cation or an internal transition cation) and the possible modifier components that stabilize, confer or reaffirm the pigmenting properties (pigmenting power and color hue) [1–3].

Titanium dioxide presents appropriate properties to be used as ceramic pigment and besides this is the main industrially used white pigment. Several works have been undertaken demonstrating that the combination of titanium oxide with spinel-forming-transition metals can lead to obtain chemically and thermally stable pigments, whose colors vary depending on the transition metal used [4]. According to Eppler [2, 3] and Burgyan [4], titanium oxide can be combined with zinc oxide, forming a white color spinel.

Spinels are complex oxides, displaying a regular structure, in which the oxygen ion array consists of a face centered cubic structure. One third of the metal ions are located in the tetrahedral sites and the remaining ions are in the octahedral sites. The spinels can be formed by the association of two trivalent cations with a bivalent ion or two bivalent cations with a tetravalent cation or one hexavalent cation with two monovalent cations (for example $MoAg_2O_4$) [5].

A synthesis method that allows to obtain a good distribution of the chromophore ions within the host lattice is the polymeric precursor method or the Pechini method [6]. The polymeric precursor method consists of the chelation of the metallic cations within the lattice of the polymer, obtained from the esterification of the metallic citrate with ethylene glycol. The polymer lattice is heated in an oxygen-containing atmosphere, resulting in a ceramic powder with high quality, when compared to the powders synthesized by the solid state reaction, normally known as mixture of oxides. Such ceramic powder presents an accurate stoichiometric control and good sinterability, and also allows a good control of the particle size and morphology of the powder [7, 8].

The general objective of this work is to obtain ceramic pigments with spinel structure and appropriate characteristics to the use in floor industries and ceramic coatings, synthesized starting from the polymeric precursor method.

Experimental

The reagents used in the synthesis of the spinel phase by the polymeric precursor method are listed in Table 1.

Initially, titanium citrate was prepared, using a 3.0 to 1.0 mole citric acid to metal ratio. In a beaker under agitation and then heated to 80°C, the citric acid was dissolved in distilled water. After this procedure, titanium isopropoxide was added slowly, up to its complete dissolution.

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1388–6150/$20.00

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Table 1 Properties of the used reagents

Reagent	Chemical formula	Purity/%	Supplier
Citric acid – CA	$C_6H_8O_7{\cdot}H_2O$	99.5	Vetec
Ethylene glycol – EG	$HO{\cdot}CH_2{\cdot}CH_2{\cdot}OH$	99.0	Avocado
Cobalt acetate	$C_4H_6CoO_4{\cdot}4H_2O$	99.0	Vetec
Nickel acetate	$C_4H_6NiO_4{\cdot}4H_2O$	99.0	Vetec
Manganese acetate	$C_4H_6MnO_4{\cdot}4H_2O$	99.0	Vetec
Zinc nitrate	$Zn(NO_3)_2{\cdot}6H_2O$	99.0	Synth

In a beaker kept under stirring were added titanium citrate, citric acid, zinc nitrate, the source of the chromophore ion and at last ethylene glycol (at a mass proportion of 60% CA to 40% EG). After solubilization of all the reagents, the solution was heated up to about 100 ºC in order to form a gel, the so-called polymeric resin. The precursor was heat treated in an oven at 350°C, under an oxygen atmosphere to remove a part of the organic material, leading to the powder precursor formation (still rich in organic material).

After de-agglomeration in a 120 mesh, the powder precursor was heat treated in an oven at 500, 600, 700, 800, 900 and 1000°C for 60 min.

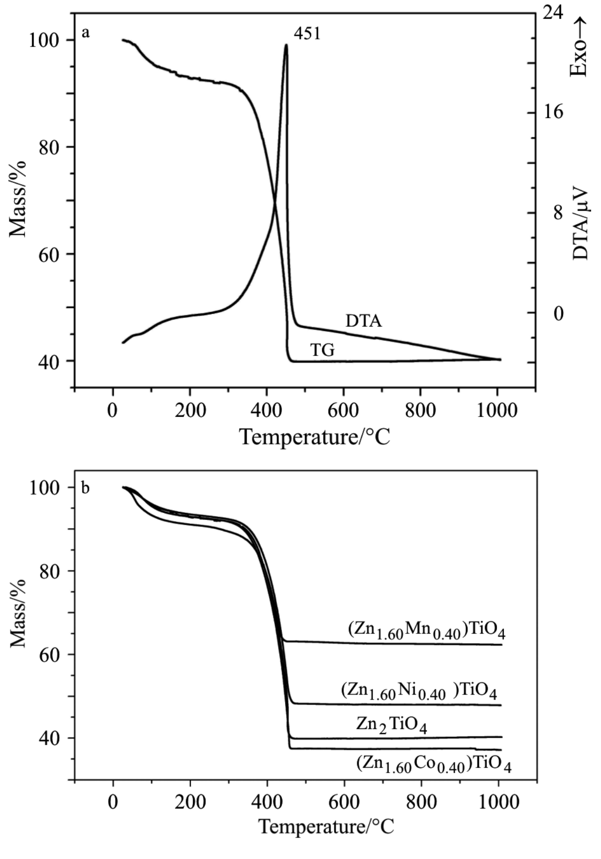

Fig. 1 Thermoanalytical profiles of the powder precursor for the spinel: a – Zn_2TiO_4, b – Zn_2TiO_4 undoped and doped with 20% in mole of *M*=Co, Mn and Ni

TG and DTG curves were recorded using a Shimadzu, TGA-50 thermobalance. The DTA curves were obtained using a Shimadzu, DTA-50 analyzer. Air atmosphere, with a flow rate of 100 mL min^{-1} and a dynamic heating rate (β=10°C min^{-1}) were applied. About 10 mg of initial amount of samples were placed to alumina pans.

The X-ray diffraction patterns (XRD) were determined using a Siemens D-5000 diffractometer, and CuK_α radiation.

Results and discussion

The results of thermal analysis concerning to the powder precursor for the Zn_2TiO_4 matrix are presented in Figs 1 and 2. The other curves displayed a similar profile.

In all the thermogravimetric curves analyzed, two thermal decomposition steps were observed. The first one was attributed to the loss of H_2O and some gases adsorbed on the surface of the powder [9]. The second step was ascribed to the decomposition and burnout of the organic matter. The polymer is transformed to CO_2 and H_2O (pyrolysis process, exothermic reaction) and the carboxyls linked to the metals are the last ones to be eliminated. These results are presented in Tables 2 and 3.

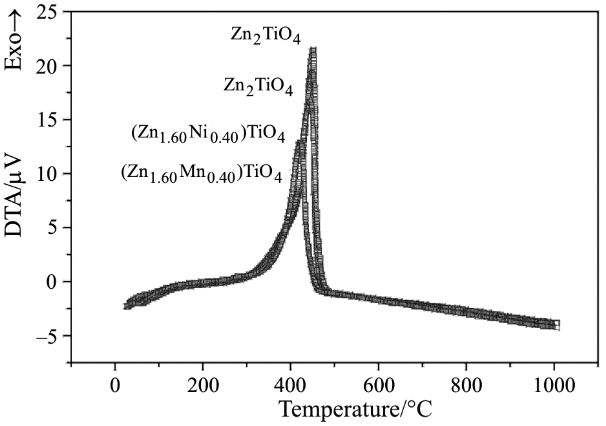

Fig. 2 DTA curves of the powder precursors of undoped Zn_2TiO_4 and doped with 20% in mol of CoO, NiO and MnO

Table 2 Temperatures and mass losses determined on the base of TG curves

Spinel	Event	Temperature range/°C	Mass loss/%
Zn_2TiO_4	1	25–252	8
	2	252–504	52
$(Zn_{1.98}Co_{0.02})TiO_4$	1	25–264	8
	2	264–508	38
$(Zn_{1.90}Co_{0.10})TiO_4$	1	26–225	8
	2	225–502	40
$(Zn_{1.80}Co_{0.20})TiO_4$	1	26–241	8
	2	241–494	45
$(Zn_{1.60}Co_{0.40})TiO_4$	1	32–223	7
	2	223–510	55
$(Zn_{1.98}Ni_{0.02})TiO_4$	1	36–222	7
	2	222–512	54
$(Zn_{1.90}Ni_{0.10})TiO_4$	1	26–248	7
	2	248–498	51
$(Zn_{1.80}Ni_{0.20})TiO_4$	1	26–235	6
	2	235–524	53
$(Zn_{1.60}Ni_{0.40})TiO_4$	1	31–206	7
	2	206–520	45
$(Zn_{1.98}Mn_{0.02})TiO_4$	1	30–239	7
	2	239–520	57
$(Zn_{1.90}Mn_{0.10})TiO_4$	1	31–283	9
	2	283–463	33
$(Zn_{1.80}Mn_{0.20})TiO_4$	1	30–248	8
	2	248–514	48
$(Zn_{1.60}Mn_{0.40})TiO_4$	1	23–213	9
	2	213–487	28

Table 3 Peak temperatures taken from the DTG and DTA curves

Spinel	DTG T_{peak}/ºC	DTA T_{peak}/ºC
Zn_2TiO_4	451	451
$(Zn_{1.98}Co_{0.02})TiO_4$	445	441
$(Zn_{1.90}Co_{0.10})TiO_4$	443	440
$(Zn_{1.80}Co_{0.20})TiO_4$	439	438
$(Zn_{1.60}Co_{0.40})TiO_4$	453	450
$(Zn_{1.98}Ni_{0.02})TiO_4$	459	455
$(Zn_{1.90}Ni_{0.10})TiO_4$	456	453
$(Zn_{1.80}Ni_{0.20})TiO_4$	460	456
$(Zn_{1.60}Ni_{0.40})TiO_4$	449	444
$(Zn_{1.98}Mn_{0.02})TiO_4$	466	460
$(Zn_{1.90}Mn_{0.10})TiO_4$	453	450
$(Zn_{1.80}Mn_{0.20})TiO_4$	448	443
$(Zn_{1.60}Mn_{0.40})TiO_4$	426	422

It is noticed that, in all the analyzed samples, the cobalt substitution with 1, 5, 10 and 20% yielded an average mass loss of 44%. This was close to the Mn-substituted spinel precursors which achieved 41% of mass loss. Thus, it indicates that both metals (Co and Mn) show similar behaviors. The Ni-substituted spinels precursors showed an average mass loss of 51%.

It was proved that the increasing concentration of the chromophore ion in the structure reduces the DTG and DTA peak temperatures. For the $(Zn_{1.98}Mn_{0.02})TiO_4$ spinel, the temperature is 460°C, whereas for the $(Zn_{1.60}Mn_{0.40})TiO_4$ spinel, the corresponding peak temperature is 422°C, as they are presented in Table 3.

The DTG peak temperatures (Table 3) of the $(Zn_{1.60}M_{0.40})TiO_4$ spinels in which M=Co, Ni and Mn were 451, 449 and 426ºC, respectively.

Comparing the TG curves, the exothermic DTA peaks can be attributed to the combustion of the organic material. It was observed that the peak temperature decreases from the $(Zn_{1.60}Co_{0.40})TiO_4$ precursor to the $(Zn_{1.60}Mn_{0.40})TiO_4$ (Table 3).

In general, a lower decomposition temperature can be representative to the smaller size of carbonic chain. The presence of wide peaks indicates the existence of a chain size distribution, as the polyester breakage takes place in several different ways.

The evolution of the crystalline phases as a function of temperature is evidenced in Fig. 3a, which shows the X-ray diffraction pattern of pure Zn_2TiO_4 heat treated in the 500–1000°C temperature range. Figure 3b depicts the X-ray diffraction patterns of the pure and the Co, Ni and Mn substituted Zn_2TiO_4 spinel samples, either pure or presenting the substitution level of 20% of Co, Ni and Mn.

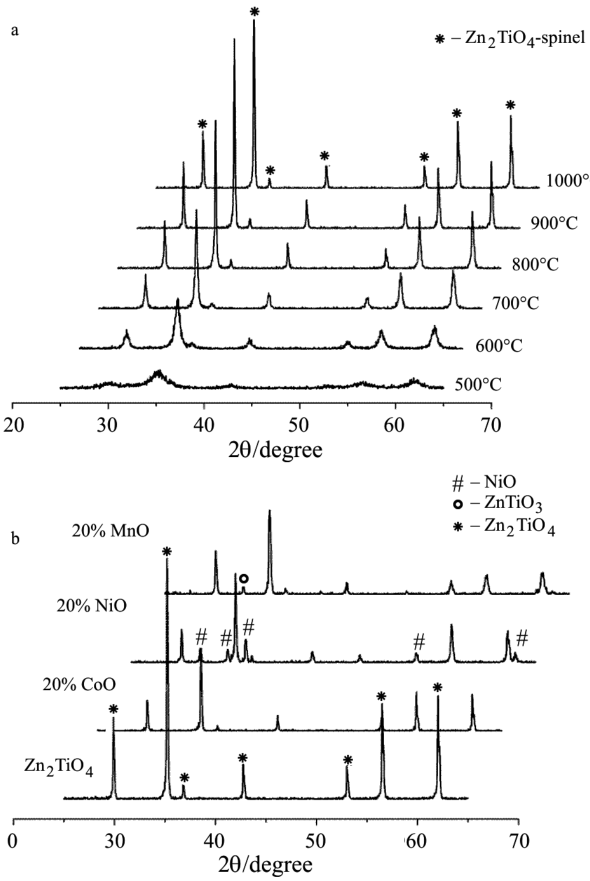

Fig. 3 a – X-ray diffraction patterns for the pure Zn_2TiO_4 spinel, heat treated at different temperatures; b – X ray diffraction patterns of the pure Zn_2TiO_4 spinel and the $(Zn_{1.60}M_{0.40})TiO_4$ spinel system containing 20% of Co, Ni and Mn, treated at 1000°C (*M*=Co, Ni and Mn)

It was proven that the pure Zn_2TiO_4 spinel and the $(Zn_{2-x}Co_x)TiO_4$ spinel systems exhibited a single phase (on the detection level of the method). On the contrary, above 1% of doping level, for the case of nickel and above 20%, for the case of manganese, secondary phases (NiO and $ZnTiO_3$) were also shown. An increase of the crystallinity with the increase of the temperature in all the diffraction patterns was also noticed. When the heat treatment temperature raises, the previously amorphous material becomes crystalline.

In general, a displacement of the main peak is observed when the chromophore concentration increases. The main peak of the nickel-modified substance presents a slight displacement, as Ni is not introduced into the lattice for substitutions above 1%, as indicated by the presence of secondary phases. Since the ionic radius of cobalt is close to the radius of zinc, this latter one can be replaced without the formation of secondary phases. In comparison with the Ni-containing compounds, a more pronounced peak displacement is observed. The Mn-substituted spinel was the one which exhibited the highest displacement, once it substitutes zinc in the lattice and possesses a larger difference of ionic radius, compared to Zn.

The crystallite sizes were calculated from the Scherrer equation [10] (Eq. (1)), and are presented in Fig. 4.

$$t = \frac{0.9\lambda}{\beta cos\theta} \qquad (1)$$

where λ is the CuK_{α_1} wavelength, θ is the diffraction angle, β the full width at half maximum (FWHM) of the diffraction peak.

β obeys the relationship $\beta = (B_{obs}^2 - b^2)^{1/2}$ where B_{obs} is the FWHM value of the sample and *b* the FWHM value of a standard, in present case, quartz.

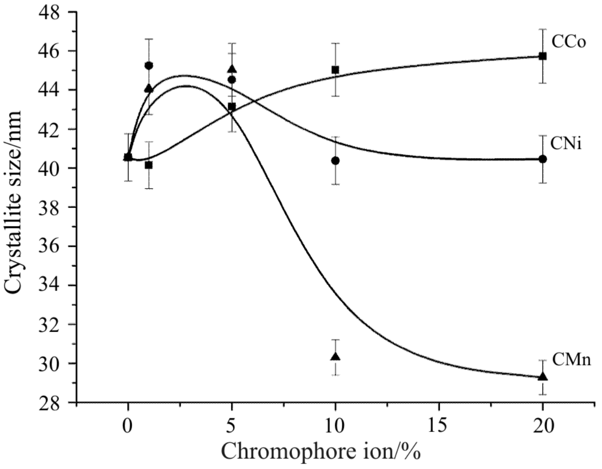

Fig. 4 Evolution of the crystallite size as a function of the chromophore concentration

For the cobalt-containing compounds, an increase in the crystallite sizes, as a function of the Co^{2+} concentration was observed, indicating an increase of mass diffusion. For the nickel and the manganese substitution, an initial increase was observed, followed by a reduction in the crystallite size. The reduction has different reasons for each cases. For the case of nickel, the reduction is a consequence of the NiO precipitation, removing the chromophore of the lattice, and as a consequence the crystallite size becomes similar to the value corresponding to the matrix. For the case of manganese, the strong reduction can be a consequence of the lattice distortion, since the ionic radius of Mn^{2+} is about 10% higher than the Zn^{2+}.

The relative crystallinity (*RC*) was calculated from the ratio between the intensities of the diffraction peaks, taking into account all the diffraction peaks observed for all the studied samples, according to Eq. (2). The relative crystallinity of the substituted spinels was calculated comparing the XRD patterns of all the samples heated to 1000°C.The results are presented in Fig. 5.

$$RC(\%) = \frac{I - I_0}{I_{100} - I_0} \cdot 100 \qquad (2)$$

where I=intensity of the highest peak (100%) the sample; I_0=intensity of the diffraction peak having the lowest intensity, among all samples; I_{100}=intensity of the diffraction peak with the highest intensity, among all samples.

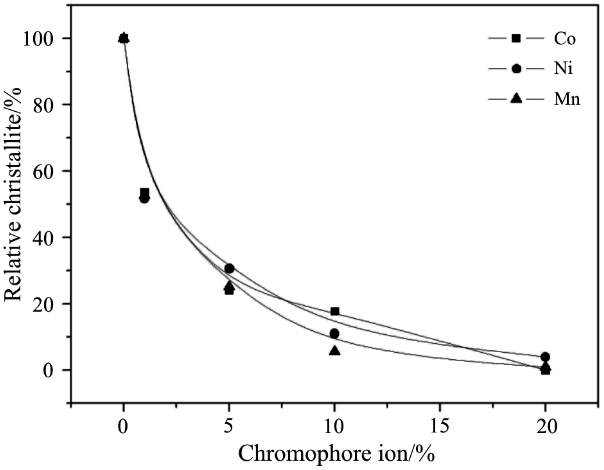

Fig. 5 Evolution of the relative crystallinity as a function of the chromophore concentration for samples treated at 1000°C for 1 h

All the chromophore ions led to a reduction in the crystallinity of the system, indicating a more complicated nucleation and/or crystal growth process. This might be a consequence of a distortion in the crystalline lattice.

Conclusions

Zinc titanate can be synthesized using the polymeric precursor method, and its zinc atoms can be replaced by transition metals (Co, Ni and Mn). The precursor resin presented two decomposition stages, the first was attributed to the elimination of water and of some gases adsorbed on the surface of the powder. The second stage was ascribed to the thermal decomposition and burnout of the organic components. By means of X-ray diffraction, it was verified that the pure Zn_2TiO_4 spinel and the $Zn_{2-x}Co_xTiO_4$ spinel system (in which x=0.02, 0.10, 0.20 and 0.40) show a single crystalline phase, on detection level of the XRD. On the contrary, for the nickel-substituted pigment a secondary phase, NiO, was observed at and above 5% of substitution. For the manganese-substituted pigment, the secondary phase $ZnTiO_3$ is noticed over 20% of substitution level while the other samples show a single spinel phase. In all the synthesized pigments it was noticed that the increase of the heat treatment temperature increases the crystallinity.

Acknowledgements

The authors acknowledge CNPq (Brazilian govern entity which promotes scientific and technological development) and Northeast Bank (BN) for financial support of this work.

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