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SYNTHESIS AND THERMAL CHARACTERIZATION OF ZIRCONIUM TITANATE PIGMENTS

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Abstract

The objective of this work was to obtain modern pigments based on zirconium titanate doped with nickel and cobalt using polymeric precursor method. Thermal evolution of $ZrTiO_4$ phase was determined. After primary calcination, the material still exhibits two thermal composition events. Calcination was done between 500 and 1000°C, to morphological and structural characterization. Surface area decreased exponentially with temperature increase, while crystallite size increased. ZTCo and ZTNi pigments were applied on ceramic tiles and the good quality of the pigment was observed.

Keywords: pigment, polymeric precursors, thermal decomposition, zirconium titanate

Introduction

Ceramic pigments are inorganic compounds, the quality of which depends on its optical and physical properties. The quality of a ceramic pigment is directly related to its crystalline structure, its chemical composition, purity and some physical characteristics as particle size distribution, particle morphology others.

Some properties may be observed in relation to a ceramic pigment application, as capability of developing color (pigmenting capability). Among optical properties, opacity, which indicates the capability of avoiding light transmission through matrix, is an important one. White pigments diffract all visible light spectrum more efficiently than absorb it. Black pigments behave exactly in the opposite way. The color of the pigment is due to the absorption of some wavelength of the visible spectra by the particles, dispersing the rest [1–3].

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At present, the research about modern pigments is directed to the development of pigments easier to reproduce. To attain this objective, chemical synthesis is being used. The chemical methods (sol-gel, Pechini, others) lead to materials with a good stoichiometric control, high reproducibility, with pigmenting characteristics [4, 5].

Zirconium titanate is a material with high chemical inertia and thermal stability. Moreover, it exhibits white color, which permits observing any color change, when zirconium or titanium are replaced by chromophore ions, favoring its use as ceramic pigment.

The zirconium titanate phase studied in this work is the high temperature one, that exhibits an orthorhombic unit cell, with a structure similar to α-PbO_2 [6].

The synthesis method used in this work was Pechini [7, 8] or polymeric precursors one that leads to particles with an excellent stoichiometric control. The general idea in Pechini's method is to reduce the individuality of the different metallic ions forming a stable neighborhood of the metallic complexes. With the growth of the polymeric system, this complex is fixed in the rigid net of the organic polymer, decreasing metals segregation. When this polymer is calcined at temperatures above 500°C, metallic oxides are formed.

In this work, zirconium titanate doped with cobalt or nickel was synthesized using Pechini method. Thermal, structural and morphological characterization was done and activation energy for particle and crystallite growth was calculated.

Experimental

In a beaker under mixing and heating at 80°C, citric acid was dissolved in distilled water. Later, titanium isopropoxide was slowly added to this solution leading to the formation of titanium citrate. Zirconium citrate was synthesized in a similar manner, using zirconium *n*-propoxide as precursor. Resin was prepared using zirconium citrate and titanium citrate in equimolar amounts. Dopant (nickel nitrate or cobalt nitrate) was added to the solution in order to obtain dopant amounts of 0.1, 0.2, 0.5 and 1 mol%. Later, ethylene glycol was added to the solution. This resin was calcined at 300ºC/1 h, leading to an expanded resin. This material was powdered and calcined at temperatures varying from 500 to 1000ºC/1 h.

Pigments synthesized in this work were characterized in relation to its thermal aspects using thermogravimetry and differential thermal analysis. To obtain thermogravimetric curves (TG), a thermobalance (TGA-50, Shimadzu) was used with a heating rate of 10°C min^{-1}, air atmosphere with a flux of 20 mL min^{-1} and sample mass of about 7 mg. For DTA analysis (DTA-50, Shimadzu), a heating rate of 10°C min^{-1} was used with static air atmosphere and sample mass of about 8 mg.

To evaluate structural and morphologic aspects, X-ray diffraction (D-5000, Siemens), BET surface area analyser (Asap 2000, Micromeritics) and scanning electronic microscope (SEM) were used.

Results and discussion

In all thermogravimetric curves analyzed, two thermal decomposition events are observed: the first one is due to water loss and some gases adsorbed in particle surface; the second one is due to organic material decomposition and cation oxidation, as it may be observed in Fig. 1.

The second decomposition event starts at about 280°C and finishes at about 500°C, Fig. 1. This temperature range is observed for all doping amounts, independently of the cation used as dopant. The total mass loss of the material varies from 50 to 60%. A small decrease at decomposition temperature is observed as dopant amount increases.

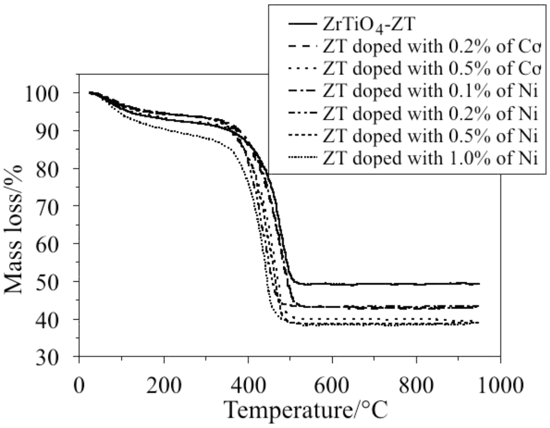

Fig. 1 TG curves of $ZrTiO_4$ with different quantities and types of dopants

In all samples, DTA curves exhibits two exothermic peaks (Fig. 2). The first one starts at about 230°C and finishes at about 500°C. The intensity of the first exothermic peak indicates a great amount of energy released. This is due to a peculiar and fundamental characteristic of Pechini method: the use of a large amount of organic compounds. During calcining, organic compounds exhibit an exothermic reaction as-

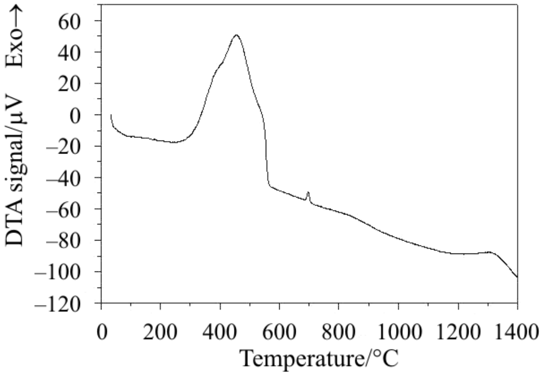

Fig. 2 DTA curve of $ZrTiO_4$ doped with 0.5 mol% of cobalt

sociated to carbonic chain combustion with a high number of thermal decomposition reactions due to the different organic matrix. Comparing Figs 1 and 2, it may be observed that the first exothermic peak is associated to a high mass loss.

The second exothermic peak, at about 700°C, is observed in all DTA curves, not associated to any mass loss. According to Bianco [9], this peak may be attributed to $ZrTiO_4$ crystallization. This indicates that between 500°C (end of decomposition) and 700°C (crystallization), the material is amorphous.

All samples (with different quantities and types of dopants) exhibit only one crystalline phase, the high temperature phase of zirconium titanate, without an order–disorder transition, as observed by Bianco [10]. The beginning of crystallization is observed at 600°C and crystallinity increases gradually up to 1000°C, the temperature of maximum crystallinity obtained in this work. This is observed for nickel and cobalt, in all dopant amounts (Figs 3 and 4). An important point is that no intermediate phase is observed.

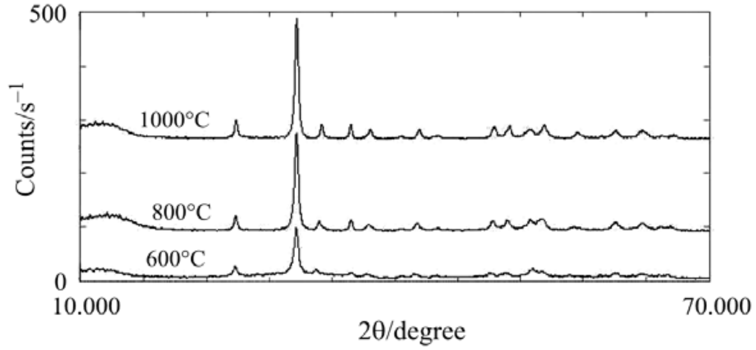

Fig. 3 X-ray difractograms of $ZrTiO_4$ doped with 1.0 mol% of cobalt, calcined at 600, 800 and 1000°C

The temperature of crystallization beginning to be observed by X-ray diffraction (Fig. 3) is different from the temperature observed in DTA curves (Fig. 2). This is due to the different analysis conditions, as DTA is realized in a dynamic condition (with a heating rate of 15°C min^{-1}), while samples for XRD are calcined at 600°C for 2 h.

Crystallite size was calculated using the full width to half maximum of the main peak of the X-ray diffractogram and the Scherrer equation. It is observed that the higher the calcining temperature, the higher the crystallite size (Table 1). This effect is due to the fact that crystallite growing is thermally activated. First, crystallite nucleation occurs followed by its growth, which depends on calcining temperature. This behavior is observed for $ZrTiO_4$ doped with nickel or cobalt, in all doping percentages.

For nickel, crystallite size at 600°C is almost the same for all dopings, but exhibits a random variation at other temperatures. For cobalt, a difference of crystallite size of about 23% is observed at the same temperature. Samples with 0.1 mol% of cobalt have a smaller crystallite size than samples with 0.2 and 1.0 mol%. Samples with 0.2 and 1.0 mol% do not exhibit meaningful differences between crystallite size with almost superimposed results.

Table 1 Crystallite size of $ZrTiO_4$ doped with 1.0 mol% of the transition metals

Dopant amount/mol%	Co/nm	Ni/nm
0.1	206.50	145.08
0.2	225.70	198.57
1.0	234.37	205.18

Surface area results (S_{BET}) show that an exponential decrease of S_{BET} with temperature increase is observed for all dopings, independently of the chromophore ion. This decrease indicates that a sintering among agglomerates or a crystallite growth may be occurring. For samples doped with nickel, no meaningful change in surface area in relation to dopant quantity was observed and curves are almost superimposed, specially over 800°C. At 500°C, surface area variation in relation to doping is random. For samples doped with Co, a small decrease in surface area (and increase in particle size) with dopant increase is observed. S_{BET} curves in relation to temperature have the same profile, independently of the amount of dopant.

In Table 2, particle size results are presented for samples with 1 mol% of nickel and cobalt. It may be observed that samples doped with Co exhibit the highest particle size. This also indicates that S_{BET} does not depend on the presence and type of dopant at higher temperatures.

Table 2 Morphological properties of the pigments with 1.0 mol% of Ni and Co

Temp./°C	Ni			Co		
	$^{*}D_p$/nm	$^{**}D_c$/nm	D_p/D_c	D_p/nm	D_c/nm	D_p/D_c
600	17.49	14.72	1.19	18.68	17.46	1.07
700	36.74	17.69	2.08	41.53	19.04	2.18
800	66.90	18.88	3.54	94.46	20.15	4.69
900	133.49	19.20	6.95	134.25	20.55	6.53
1000	280.21	20.52	13.65	270.38	23.44	11.53

$^{*}D_p$ – particle size, $^{**}D_c$ – crystallite size

According to Table 2, it may also be observed that particles studied exhibit a particle increase higher than a crystallite increase. This indicates that a sintering among particles is probably occurring, as confirmed by microscopy analysis (Fig. 4).

Using Arrhenius equation ($\ln D = \ln D_0 - E_a/RT$), activation energy for particle and crystallite growth was calculated. A graph of $\ln D$ as a function of $1/T$ was done, where D is the particle or crystallite size (Fig. 5).

As it may be observed in Tables 3 and 4, activation energy for particle growth is higher than for crystallite growth, as diffusion among crystallites is favoured by smallest distance among them. In spite of this, particle size increases about 15 times, while crystallite size increases less than 1.5 times. This may be due to sintering among particles, leading to a highest increase in their size. Comparing activation energies of zirconium titanate doped with Ni and Co, it may be observed that oxides doped with Ni exhibit higher activation energy values than oxides doped with Co. In this sense, $ZrTiO_4$ doped with Ni needs a higher temperature for particle and crystallite growth.

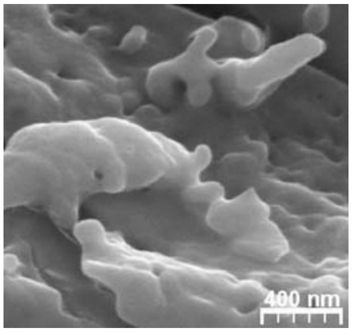

Fig. 4 SEM image of $ZrTiO_4$ doped with 1.0 mol% of nickel calcined at 900°C

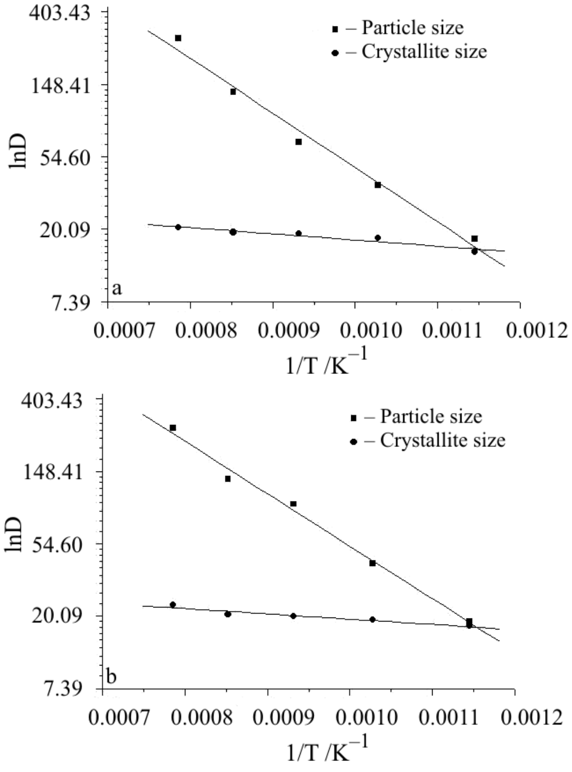

Fig. 5 Arrhenius plot for activation energy calculation: a – material doped with Ni, b – material doped with Co

Table 3 Activation energy for particle growth

Material	Activation energy for particle growth/J	R	ΔE_a/%
$ZrTiO_4$ doped with 1% of Ni	62.684	0.992	7.2
$ZrTiO_4$ doped with 1% of Co	7.266	0.996	5.2

Table 4 Activation energy for crystallite growth

Material	Activation energy for crystallite growth/J	R	ΔE_a/%
$ZrTiO_4$ doped with 1% of Ni	7.108	0.960	16.7
$ZrTiO_4$ doped with 1% of Co	6.069	0.961	16.6

Conclusions

Zirconium titanate can be synthesized using the polymeric precursor method with dopant percentages up to 1 mol% of transition metals (Co and Ni), to obtain only one phase. Materials with a relatively high surface area were obtained. Above 700°C, an increase in surface area was observed due to the sintering among particles. Activation energies for particle growth was higher than for crystallite growth, probably due to proximity among crystallites, making diffusion easier.

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