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INFLUENCE OF THE NETWORK FORMER ON THE PROPERTIES OF MAGNESIUM SPINELS

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Undoped and/or doped with 1 mol% of Co^{2+} Mg_2TiO_4 and Mg_2SnO_4 powders were synthesized by the polymeric precursor method. The influence of the network former (Sn^{4+} or Ti^{4+}) on the thermal, structural and optical properties was investigated. The recorded mass losses are due to the escape of water and adsorbed gases and to the elimination of the organic matter. Mg_2TiO_4 crystallizes at lower temperatures and also presents more ordered structure with a smaller unit call and having more intense green color than Mg_2SnO_4 has.

Keywords: *cobalt, Pechini, pigment, tin, titanium*

Introduction

Spinel is the structure type of a large variety of compounds displaying AB_2O_4 formula. This class of materials is important in the solid state chemistry due to several of their properties related to its structure [1].

Spinels are complex oxides with a regular structure, consisting of a FCC close-packed oxygen sublattice, in which 1/3 of the cations are located in tetrahedral sites and the remaining cations are in octahedral sites. They are often formed by two trivalent and one bivalent cation, being represented as $A^{2+}B_2^{3+}O_4$ [2, 3]. Differently from these spinels, in Mg_2TiO_4 and Mg_2SnO_4 there are two bivalent cations for each tetravalent one. The spinel formula can be written as $(A_{1-x}B_x)^{tet}(A_xB_{2-x})^{oct}O_4$, in which x is called the inversion parameter. A spinel is called to inverse when $x=1$ and normal when $x=0$. In this work, inverse spinels were studied, in which Mg^{2+} occupies both tetrahedral and octahedral sites and Sn^{4+} or Ti^{4+} occupy octahedral sites.

Mg_2TiO_4 is used as a heat resistor, dielectric for microwave technology, capacitor for temperature compensation and refractory material. On the other hand, Mg_2SnO_4 and other stannates, have been recently applied as electronic ceramic, such as thermally stable capacitors with low permittivity and small tangential losses [4, 5]. However, no reference was found in the literature describing the application of these spinels as pigments.

Color is an optical property having interests in several industrial areas, such as ceramics, textiles, cosmetics, plastics and paints. Color can be achieved by the addition of chromophore ions into crystalline structures of different compounds.

Chromophore addition to an inert host lattice, associated to a good chemical synthesis method can result in a high quality pigment. The quality of a ceramic pigment depends on its optical and physical properties. Such properties are directly related to the crystalline structure of the pigment, its chemical composition, purity, stability and some physical characteristics such as particle size distribution, particle shape, surface area, etc. [6].

In the present work Co^{2+} was added as a chromophore ion to Mg_2TiO_4 and Mg_2SnO_4 spinels. Polymeric precursor method was used to obtain powders with good stoichiometric control. This method is based on the chelation of metal cations in a polymeric network, obtained by the esterification of mixed metallic citrates with ethylene glycol. Then the polymeric network is heat-treated, in order to obtain a high quality ceramic material [7–10].

Experimental

Tin citrate was used as cationic precursor in the preparation of the precursor resins for the synthesis of the compounds displaying the molecular formula of Mg_2SnO_4. This citrate was obtained dissolving tin chloride

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(Baker – 100.0%) in a citric acid (Cargill – 99.5%) solution, under constant mixing, at 70°C. Ammonium hydroxide (Vetec – (28.0–30.0%)) was slowly added to this aqueous solution.

After some hours of continuous agitation, a white solid tin citrate was obtained. 3:1 citric acid:metal molar ratio was used.

For the synthesis of the Mg_2SnO_4 pigments, two solutions were prepared. The first one is composed of citric acid, magnesium nitrate (Vetec – 98.0%) and cobalt acetate (Alfa Aesar – 99.0%). The second one was prepared with tin citrate and citric acid. The solutions were mixed, with heating at 90°C. Finally, ethylene glycol (Vetec – 99.0%) was added to the new solution, with a 60:40 mass ratio of citric acid:ethylene glycol.

The synthesis of Mg_2TiO_4 was done similarly as above, according to [11].

Both resins were calcined at 300°C for 30 min, forming the powder precursor. The material was powdered passing through a 100 mesh sieve.

The powder precursor was characterized by thermal analysis, using Shimadzu TGA-50 thermobalance and a DTA-50 Shimadzu analyzer. The precursor was heated using 10°C min^{-1} heating rate up to 950°C, in air at a flow rate of 50 mL min^{-1}. About 10 mg of sample were weighed into alumina crucibles.

The powder precursor was heat-treated at 700°C for crystallization of the pigments. The structural transformation was evaluated by X-ray diffraction (D-5000 Siemens). Diffractograms were recorded with a 0.03° step and a step time of 1.0 s, using the CuK_α radiation.

The *L**, *a** and *b** color parameters of samples were measured using Gretag Macbeth Color-eye 2180 spectrophotometer in the 360–750 nm range, using D65 illumination. The CIE–*L***a***b** colorimetric method, recommended by CIE (Commission Internationale de l'Eclairage) was used in the evaluation. In this method, *L** is the lightness axis [black (0) white (100)], *b** is the blue (–) yellow (+) axis and *a** is the green (–) red (+) axis.

Results and discussion

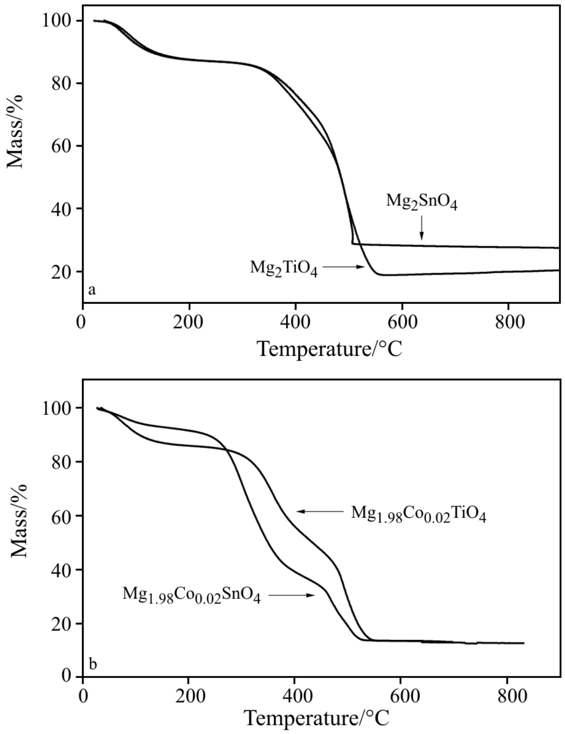

Fig. 1 TG curves of the a – undoped and b – Co^{2+}-doped powder precursor spinels

TG curves of the powder precursor of the pure and Co^{2+}-doped spinels (Fig. 1) present three mass loss steps. The first one is assigned to the elimination of water and of some gases adsorbed on the precursor surface; the second and third ones are related to the decomposition of the organic substance. The precursors of the undoped materials exhibit similar profiles (Fig. 1a). For Mg_2TiO_4 precursor, the mass loss is larger, as well as the temperature of thermal stability. In Co^{2+}-doped samples (Fig. 1b), the decomposition of the organic matter begins at higher temperatures for the Mg_2TiO_4 precursor. The profiles are also similar to each other.

The DTA curves exhibit one endothermic peak, due to the elimination of water, and two exothermic ones, where the first is a smaller one followed by a larger peak, both due to the combustion of the organic matter (Figs 2a and b). According to the data in Table 1 the temperature of the second DTA peak for Mg_2TiO_4 precursors are higher, as well as the process of mass loss finishes at a higher temperatures indicating the hindered elimination of the organic material.

Table 1 Temperatures taken from the TG and DTA curves

Sample	1st T_{peak} (DTA)/°C	2nd T_{peak} (DTA)/°C	Tempreature range/°C
Mg_2TiO_4	361	507	265–560
Mg_2SnO_4	399	499	284–512
$Mg_{1.98}Co_{0.02}TiO_4$	355	514	226–554
$Mg_{1.98}Co_{0.02}SnO_4$	373	498	200–536

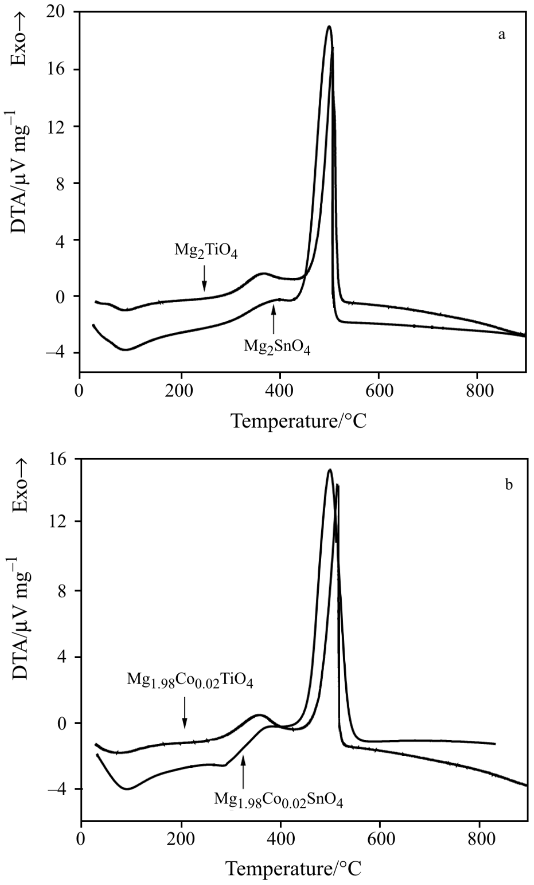

Fig. 2 DTA curves of the a – undoped and b – Co^{2+}-doped powder precursor spinels

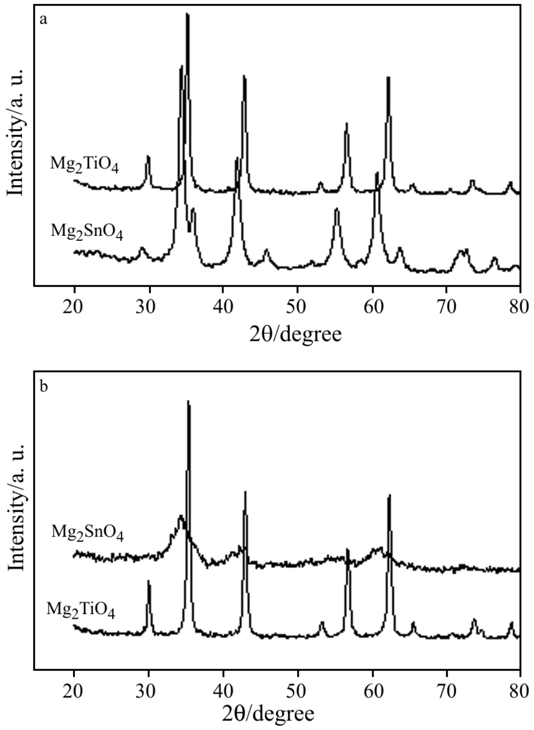

Fig. 3 XRD patterns of the spinels, after heat treatment at 700°C for 1 h; a – undoped samples; b – Co^{2+}-doped samples

XRD patterns are presented in Fig. 3. All samples are single phase, even after doping. Undoped samples are more crystalline than doped ones, while Mg_2TiO_4 spinels are more crystalline than the Mg_2SnO_4 ones. Comparing these observations to thermoanalytical results, it should be pointed out that carbon elimination is not especially related to the crystallization process. Mg_2TiO_4 precursors require a higher temperature for carbon combustion, but present a higher crystallinity than Mg_2SnO_4.

These results are in agreement with the analysis of XRD data (Table 2). The full width to half maximum data (FWHM), which are correctly related to the organization of the structure, indicate that Mg_2TiO_4 presents a higher long range periodicity than Mg_2SnO_4. This result may be related to the higher covalent character of the Sn–O bond, compared to Ti–O bond. The higher covalency leads to more directional bonds, increasing the distortion of the unit cell, making the crystallization process more difficult.

Table 2 Results of the XRD analysis

	FWHM/degree		Lattice parameter a/Å	
	Mg_2SnO_4	Mg_2TiO_4	Mg_2SnO_4	Mg_2TiO_4
Undoped	2.82	0.56	8.587	8.437
Co^{2+}-doped	3.03	0.52	8.597	8.428
Theoretical value	–	–	8.638	8.440

When cobalt is added to the material, FWHM values of Mg_2TiO_4 almost do not change, while an increase is observed for the Mg_2SnO_4. As tin-based spinel has already a low long range periodicity, the addition of a dopant makes crystallization process even more difficult, in spite of the lower covalent character of the Co^{2+}–O bond. According to the XRD pattern in Fig. 4b, crystallization of Co^{2+}-doped Mg_2SnO_4 starts at about 70°C with fairly defined peaks.

In relation to the lattice parameter, it should be observed that Mg_2SnO_4 unit cell is bigger than Mg_2TiO_4 one (Table 2). This is related to the higher ionic radii of Sn^{4+}, associated to a more covalent bond. The increase of the unit cell volume decreases the loss in the long range periodicity. It was also observed that the polymeric precursor method leads to a decrease in unit cell, comparing to the theoretical values. As the polymeric precursor is a soft chemical method, a unit cell with low density of defects is obtained, leading to its decrease. When Co^{2+} is added a small change in lattice parameter is observed for both samples.

The undoped pigments have pale yellow color, as presented in Fig. 4 and Table 3. This tonality is re-

Table 3 Chromatic coordinates of the pigments after calcination at 700°C

	Mg_2SnO_4	Mg_2TiO_4	$Mg_{1.98}Co_{0.02}SnO_4$	$Mg_{1.98}Co_{0.02}TiO_4$
*L**	83.73	81.97	76.79	67.28
*a**	0.22	0.49	–2.53	–18.28
*b**	4.25	1.99	–0.10	–8.81

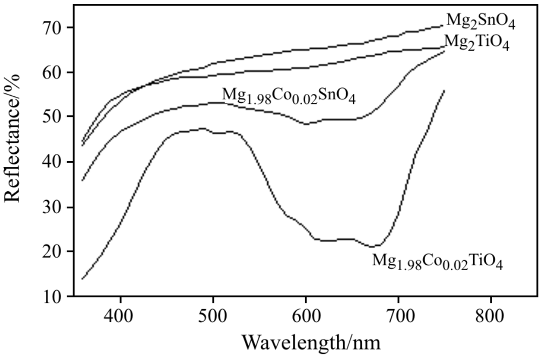

Fig. 4 Reflectance spectra of the undoped and Co^{2+}-doped spinels, after calcination at 700°C for 1 h

lated to Ti^{4+} (or Sn^{4+})$\leftrightarrow O^{2-}$ charge transfer [12]. As Sn^{4+} presents a higher reduction potential, a higher $+b^*$ value is observed.

In spite of the low concentration (1 mol%), cobalt addition leads to a meaningful change in colorimetric coordinates. $Mg_{1.98}Co_{0.02}SnO_4$ pigment presents a pale green color, with $-b^*$ value close to zero. $Mg_{1.98}Co_{0.02}TiO_4$ presents more intense colors, with higher $-a^*$ and $-b^*$ values, indicating a combination of blue and green colors (Table 3).

The green/blue colors observed in the two systems is due to the sites occupied by the chromophore ion, Co^{2+}. In a recent study on Zn_2TiO_4 spinel doped with the same amount of cobalt, a yellow color was observed. In this work, Co^{2+} occupies octahedral sites [13]. In the present work, both spinels present green color, indicating that Co^{2+} occupies tetrahedral and octahedral sites, leading to a mixture of yellow and blue colors.

The difference in the intensity of the colors may be related to the ligand field in each system. Mg_2TiO_4 spinels present a much smaller unit cell than Mg_2SnO_4. This effect leads to a stronger ligand field, with a higher repulsion of d orbitals and O^{2-} ions. As a consequence, a higher splitting of d orbitals is observed in titanate spinels leading to more intense colors.

Figure 5 displays the energy values of the optical band gap of the pigments. The gap is defined as the energy interval between bands in the solids: the valence band predominantly formed by the 2p orbitals of the oxygen, and the conduction band, formed by d orbitals of the metal [14–16].

All samples presented similar gap energy values calculated according to the Tauc method [17]. These results indicate that the addition of cobalt as well as the former network did not change the gap of the material. Another possibility is the low sensitivity of the method used in the determination of the gap energy.

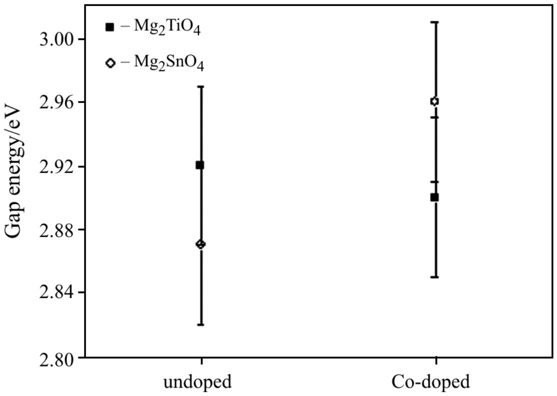

Fig. 5 Gap energy of Mg_2SnO_4 and Mg_2TiO_4 spinels after calcination at 700°C for 1 h

Conclusions

The main mass loss step observed in the TG curve of the precursor is due to the combustion of the organic substance. It was observed that carbon elimination is not strictly related to the crystallization process as Mg_2TiO_4 precursors need a higher temperature for carbon combustion, but having a higher crystallinity than Mg_2SnO_4. Both systems are single phases. Mg_2SnO_4 is a more disordered system than Mg_2TiO_4 with a bigger unit cell. As a consequence, colors with lower intensity were observed. Both Co-doped spinels presented green color, indicating that Co^{2+} occupies octahedral and tetrahedral sites.

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