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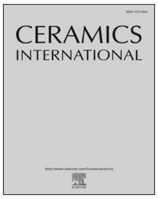

Review article

Synthesis and characterization of Y (In, Mn) O_3 blue pigment using the complex polymerization method (CPM)

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ABSTRACT

In this paper, a new synthetic pathway is proposed for the system $YIn_{1\text{-}x}Mn_xO_3$, a bright blue inorganic pigment, discovered in 2009. Blue pigment samples with increasing concentration of Mn^{3+} (x = 0.08, 0.12 and 0.16) were prepared using the complex polymerization method (CPM) and compared with those synthesized via solid state reaction. All powders, the amorphous precursor from CPM and the starting materials for solid state method, were calcined at 1000, 1100, 1200 and 1300 °C for 12 h, and the resulting blue pigments were characterized by X-ray diffraction (XRD), colorimetric system CIE L*a*b* and Near infrared (NIR) reflectance measurements. XRD patterns and Rietveld Refinement show that the lowest temperature at which single hexagonal phase (isostructural to $YInO_3$) is formed is 1000 °C for CPM method and 1300 °C for conventional solid state method, respectively. The L*a*b* values demonstrate that the coloration of powders prepared by CPM exhibit temperature dependence below 1300 °C, a color shade shift from grayish blue to intense deep blue is observed when heating the samples from 1000 to 1300 °C. Blue pigments obtained by CPM have smaller particle size due to low temperatures and excellent near-infrared reflectance comparable to those by solid state method. Thus, providing advantages for application process and energy efficiency.

1. Introduction

The use of the cobalt aluminate spinel phase ($CoAl_2O_4$) as a ceramic pigment has been studied for years. Thus, different ways of obtaining this material have been developed in order to discover better features and performances, so the study of pigments with a better performance and lower toxicity has been developed. The use of the blue pigment has always been investigated and nowadays it is applied in modern technologies for the production of ceramics, tiles for decoration, and jet printers ink, which enables high performance ceramic coatings [1–7], as well as in developing cool pigments, which are currently called eco-friendly [8–10].

However, recent studies have been made on the preparation of the materials to be applied in blue ceramic pigments without cobalt ion in their structure [11–16]. The limited availability of cobalt raw materials has made it important to minimize or even avoid the use of cobalt in the composition of ceramic pigments [17–19].

The physical and chemical properties of the pigments can be influenced by shape, size and size distribution of the particles, which depend on the synthesis method.

The variety of methods have been developed to obtain not only different pigments, but also blue pigments, such as aerosol pyrolysis [18,20–23], synthesis by hydrothermal [24], combustion [25], sol-gel method [26], synthesized by a conventional solid state method [21,26] and Complex Polymerization Method (CPM) [1,2,27,28].

The single-phase $YIn_{1\text{-}x}Mn_xO_3$ blue pigments solid solution was prepared by heating mixtures of the Y_2O_3, In_2O_3 and Mn_2O_3. The powders were heat treated at 1200 °C for 12 h followed by another heating treatment at 1300 °C with intermediate grinding [29].

Recently, the $YIn_{1\text{-}x}Mn_XO_3$ was synthesized by pyrolysis of aerosols at 600 °C, followed by an annealing treatment at 1100 °C [18]. The authors suggest that $YIn_{1-x}Mn_xO_3$ blue pigments have good properties to be used by the ceramic industry and they can replace pigments with cobalt [30,31]. The details on the structure changes for the $YMn_{1\text{-}x}In_xO_3$ system relative to the conventional solid state synthesis, obtained satisfactory results because it analyzed their substitution in the coordination sites, the order and disorder in the structure and the exchanges of yttrium and manganese in the structure [30].

In this paper, $YIn_{1\text{-}x}Mn_XO_3$ (x = 0.08, 0.12 and 0.16 mol) blue pigments were synthesized by the Complex Polymerization Method (CPM)

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at high temperatures (1000, 1100, 1200 and 1300 °C) for 12 h. In previous studies, the performance of the complex polymerization method (MPC) using $CoAl_2O_4$ [1,28] was studied, so that the Co^{2+} ion exchange by Mn^{+3} has been increasingly studied and in this work the use of MPC at low temperatures [21].

The Complex Polymerization Method (CPM) based on the Pechini method offers a possibility of preparing complexes of good homogeneity at molecular scale, small patterns and a good stoichiometric control. As in reactions between materials in the solid state or decompositions, many variables can influence the synthesis of oxides by CPM [1,2,27,28]. This method has a low cost, low temperature, small patterns and it has a shorter reaction time. The comparison between the two methods of synthesis by MPC and by the synthesis of the solid state were analyzed and compared according to previous studies [21,52] and the advantages used by the MPC obtaining a blue pigment at low temperatures, became of great interest for this work [36]. The main novelty of research is compared the methods solid state has been studied a long time with complex polymerization method (CPM), the novelty this work is used CPM method to low temperatures and substitution in manganese who result a color shade shift from grayish blue to intense deep blue.

2. Experimental section

2.1. Synthesis processes

The samples were prepared in two steps. First, $YIn_{1-x}Mn_xO_3$ powders were obtained when the starting chemicals were added in the following order: indium (III) nitrate hydrate $[In(NO_3)_3.X\ H_2O]$ (29.9% min, Alfa Aesar), yttrium (III) nitrate hexahydrate $[Y(NO_3)_3.6H_2O]$ (99.9% purity Alfa Aesar), manganese (II) nitrate $[Mn(NO_3)_2.4\ H_2O]$ (99.98% purity, Alfa Aesar), citric acid $[C_6H_8O]$ (99% purity, Synth), ethylene glycol $[\ HOCH_2CH_2O_4]$ (99% purity, Synth) and Ammonium hydroxide (NH_4OH).

At first the Mn^{3+} ions were added following percentages in x = 0.08, approximately 70 ml of distilled water was added when the citric acid dissolution was complete (and when utilized), and the metal nitrates were added to stoichiometric amounts of yttrium, indium and manganese, respectively. The nitrate solutions were heated while stirring, and the citric acid was added in a molar ratio of 2: 1 to metal nitrates. Herein, the citric acid plays the role of a cross linking agent. Then, the pH of the resulting solutions was adjusted to 7 using aqueous NH_4OH, and the neutralized solutions were heated until the formation of a dry gel. A dark brown amorphous powder was obtained after heating the translucent dry gel, and the dark-brown powders were further calcinated at temperature of synthesis of 1000 °C, 1100 °C, 1200 °C and 1300 °C for 12 h at a heating rate of 5 °C/min.

At the second step the Mn^{3+} ions were added following the percentages in x = 0.08, 0.12 and 0.16 mol%. In this synthesis, it was added approximately 70 ml of distilled when the citric acid was added in a molar ratio of 2:1 to metal nitrates. When the citric acid dissolution was complete, stoichiometric amounts of yttrium, indium and manganese, were added to the precursor metal, respectively. Finally, the polymerization of the material resulted in a translucent dry gel, a viscous and consistent solution. The resin became a dark-brown powder after being heated at 350 °C for 2 h, which allows the pyrolysis of the organic compounds. These dark-brown powders were crystallized and after that calcinated at a temperature of synthesis of 1000 °C, 1100 °C, 1200 °C and 1300 °C for 12 h at a heating rate of 5 °C/min.

After all the conditions of the two steps were established, the results were compared using color meters and thus, the following syntheses were performed according to the best condition established with an increase in their concentration of Mn^{3+} (x = 0.08, 0.12 and 0.16) by CPM and its calcination at a temperature of synthesis of 1000 °C, 1100 °C, 1200 °C and 1300 °C for 12 h at a heating rate of 5 °C/min.

The conventional solid state was realized using a concentration of Mn^{3+} (x = 0.08) were stoichiometric amounts of Y_2O_3 (Nucor Research Chemicals 99.9%), In_2O_3 (Aldrich, 99.99%), Mn_2O_3 (Sigma-Aldrich, 99%), were weighed and thoroughly ground using an agate mortar and pestle, calcined at 1000 °C and 1300 °C for 12 h at a heating rate of 5 °C/min.

2.2. Characterization

The structure of the crystalline phases in the calcined powders was investigated by X-ray diffraction (XRD) using a Rigaku MiniFlex II diffractometer with CuKα radiation (λ = 1.5418 Å). For the phase identification, the measurements were carried out in the range of 2θ within 10–60° and the step speed of 0.02°/min with fixed time of 1 s.

The lattice parameters and position were determined by means of the Rietveld refinement method and were analyzed by the Structure Analysis System (GSAS) program with the EXPGUI graphical interface program and the lattice parameters and atomic positions obtained were used to model these unit cells using the Visualization for Electronic and Structural Analysis (VESTA) program, version 3.1.2.

The values of the crystallite size and average strain value were obtained, using the Scherrer equation, which are related to the volume-weighted crystallite size, (D) to the integral width (taken on a 2θ scale) of the size broadened profile. By applying some weighted average strain value, the approximate value is obtained from the integral width of the extended strain profile, and it was obtained by the GSAS program, as represented in Eqs. (1) and (2) [53].

$$<D>_v = \lambda/(\beta^S \cos\theta) \tag{1}$$

$$\tilde{e} = \frac{1}{4}\beta^D \cot\theta \tag{2}$$

The dispersion of the atoms of the samples were investigated by EDS spectroscopy using a field-emission gun scanning electron microscopy (FEG-SEM; Carl Zeiss, Supra 35-VP Model, Germany) operated at 14 kV.

The colorimetric parameters for the $YIn_{1-x}Mn_xO_3$ structure were made on the CieL*a*b* system, the color measurements were realized using the Konica Minolta CM-700d Spectrophotometer (Standard illuminant D65) to measure L*, a*, b* color coordinates, using the software spectra magic NX.

Near infrared (NIR) spectroscopy data reflectance (up to 2500 nm) was collected using a Jasco V-670 Spectrophotometer.

3. Results and discussion

The patterns of the X-ray diffraction of the samples synthesized by the CPM are shown in Fig. 1. All diffractions of the samples $YIn_{1-x}Mn_XO_3$ were obtained according to the doping of Mn (0.08, 0.12 and 0.16). All the diffraction peaks can be indexed to the hexagonal structure of $YMnO_3$ (JCPDS No 251070) or $YInO_3$ (JCPDS NO 70-133) having the P63cm space group [38], in this case all of the diffraction was indexed with $YInO_3$ (JCPDS 70-0133). Its crystallization has the presence of peaks that vary from a lower intensity to a higher intensity with the single phase of YIn_2O_3, as can be observed in JCPDS 70-0133 and this is due to the increase in temperature in which at 1000 °C, there are small peaks up to 1300 °C with higher peak intensities, these peaks acquire a higher intensity of crystallization as shown in Fig. 1. The peaks revealed that the prepared particles have an increase in intensity of 2θ when the manganese is replaced. The results of the Network Parameters and Unit Cell Volumes have their values confirmed by the values previously reported by Smith et al. and thus, they have similar values when a = 6.25 (Å) and c = 12.16 (Å). Thus, observing Table 1, it is confirmed the structure values through the use of the Rietveld refinement method [18,19]. According to the results at 1300 °C, it was observed an increase of the crystallinity of the $YIn_{1-x}Mn_XO_3$ phase by CPM.

The results showed that the structure shows similar parameters at