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The Y_2BaCuO_5 oxide as green pigment in ceramics

F. Fernández[a,*], C. Colón[a], A. Durán[a], R. Barajas[a], A. d'Ors[b], M. Becerril[b], J. Llopis[c], S.E. Paje[c], R. Sáez-Puche[d], I. Julián[d]

[a]*Dpto. Q. Industrial y Polímeros, EUITI UPM, E-28012 Madrid, Spain*
[b]*Escuela Madrileña de Cerámica de la Moncloa, Ayuntamiento de Madrid, E-28008 Madrid, Spain*
[c]*Dpto. Física de Materiales, Fac. CC. Físicas, UCM, E-28040 Madrid, Spain*
[d]*Dpto. Q. Inorgánica, Fac. CC. Químicas, UCM E-28040 Madrid, Spain*

Abstract

Fine particles of green yttrium–barium–copper–oxide pigments Y_2BaCuO_5 have been prepared using two different synthesis methods. The process of combustion of mixed nitrates and urea needs a maximal temperature of 900°C and provides samples formed by aggregates of homogeneous small particles with a size of about 0.3 μm. However, the ceramic method requires 1050°C as synthesis temperature, and yields rather higher particle sizes. Even after grinding, these samples are formed by heterogeneous particles with mean sizes of about 3 μm. Diffuse reflectance spectra reveal that the samples obtained using the former method present a higher brilliancy, so they have been selected to be tested as green pigment in ceramics with good results. © 1998 Elsevier Science S.A.

Keywords: Pigments; Y_2BaCuO_5; Green phases; Ceramics

1. Introduction

Inorganic pigments used in plastics, polymers, paints, glasses or ceramics, have traditionally been based on transition metal compounds or heavy metals [1].

During the last years, the increase in the use of these materials has created some environmental problems and most of the developed countries have started to elaborate laws that will limit or even forbid the use of some of them in the near future. At this point lanthanide compounds, due to their low toxicity, could be good candidates to be used in the pigments field. In this sense, recently γ-Ce_2S_3 has been successfully used as a red pigment in plastics, replacing the classical cadmium sulfoselenide [2].

The green-coloured R_2BaCuO_5 oxides (R=Sm–Lu) form a family of isostructural compounds which adopts the so-called Sm_2BaCuO_5 type, showing orthorhombic structure with the Pnma as space group [3]. This structure is rather complex but it can be described as formed by isolated square CuO_5 pyramids connected by monocapped trigonal prisms RO_7. Recently many studies have been reported concerning the structure and magnetic properties of these stoichiometric compounds [4–6]. The application of this kind of compounds as pigments has also been proposed [7].

The purpose of this work is to test the Y_2BaCuO_5 oxide as a potential green pigment in ceramics. In order to obtain samples with appropriate particle sizes and good optical properties, two different synthesis methods have been used and compared.

2. Experimental

Y_2BaCuO_5 has been prepared by solid state reaction, from stoichiometric amounts of CuO (99.99%), $BaCO_3$ (AR) and Y_2O_3 (99.99%). The ground mixture was heated in air at 1050°C for 12 h to obtain the sample as a polycrystalline material, which was subsequently ground for 3 h in a ball-mill.

The second synthesis procedure is based on the combustion of the mixed copper, barium and yttrium nitrates dispersed in urea [8,9]. This mixture has been prepared by solving the stoichiometric amounts of Y_2O_3, $BaCO_3$ and $Cu(NO_3)_2{\cdot}6H_2O$ in the minimum amount of HNO_3 (60%); then $CO(NH_2)_2$ was added. The solution was heated on a hot plate in order to evaporate water and to obtain a voluminous and foamy sample composed of the melted nitrates and urea. This gel was heated and decomposed at 271°C producing the precursor which, ground and calcined at 900°C, yields the Y_2BaCuO_5 oxide. A

*Corresponding author.

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further grind is necessary to disperse the final product particles.

Thermal analysis experiments were recorded using a Stanton STA-781 operating with an open crucible in static air from room temperature to 1000°C with a heating rate of 5°C min^{-1}.

Powder X-ray diffraction was carried out on a Siemens Kristalloflex K810 diffractometer with a D-500 goniometer provided with a graphite monochromator and using Cu Kα radiation. The data were collected from 5 to 120° in the 2θ range by step scanning in increments of 0.04° and a counting time of 12 s per step. All the data were analysed by the Rietveld method using the FULLPROF program [10].

Particle size distribution and the morphology of the samples were studied with a JEOL-JSM 6400 scanning electron microscope.

Diffuse reflectance spectra of the powders obtained from the ceramic and combustion methods were registered in the 220–1800 nm range using a spectrophotometer Shimadzu 3100. The spectrophotometer was attached with an integrating sphere and reflectance accessories.

3. Results and discussion

The thermal decomposition of the solution of nitrates and urea has been followed by DTA and TGA analysis (Fig. 1). The TGA shows the first two stages in the 57–145°C temperature range, and the total weight loss of 9% can be attributed to the loss of crystallisation water of the copper and yttrium nitrates, and the decomposition of the excess HNO_3 (60%) that we need in the preparation. Two endothermic effects have been observed in the temperature range mentioned in the DTA diagram. By increasing the temperature, the net weight loss of 42% between 220 and 271°C is due to the exothermic decomposition of the urea and nitrates according to the following reaction:

$$6NO_3^- + 6H^+ + 5(NH_2)_2CO \rightarrow 8N_2 + 13H_2O + 5CO_2$$

It is worth noting that this decomposition is accompanied by the loss of CO_2 and N_2 gases, which facilitates the formation of fine particles of yttrium–copper oxides and barium carbonate (barium oxide is not formed due to the presence of CO_2). Actually, the X-ray diffraction pattern obtained after heating the sample at 500°C for 1 h (Fig. 2), indicates the presence of Y_2O_3, CuO and both barium nitrate and carbonate. The weight loss of 20% observed at 600°C together with the endothermic effect in the DTA diagram has been attributed to the decomposition of the $Ba(NO_3)_2$, which is fully confirmed by the X-ray diffraction data obtained after heating at 600°C for 1 h (Fig. 2). It is worth noting that simultaneously the $BaCO_3$ phase increases, and the further thermal treatment at higher temperatures produces the decomposition of this carbonate giving rise to the formation of the Y_2BaCuO_5 oxide, as can be observed in Fig. 2. The maxima broadening exhibited by these X-ray diffraction patterns are due to the fine particle nature of the sample. To avoid the sinterization of the particles no further treatment was done.

Scanning electron microscopy micrographs reveal that the sample obtained by the so-called combustion method is formed by aggregates of small rounded particles with a mean size of about 0.3 μm (see Fig. 3a). However, the samples obtained from the ceramic method are constituted by bigger sharp-shaped particles with a rather heterogeneous particle size distribution, as can be observed in Fig. 3b. After grinding for 3 h, a more homogeneous particle size distribution is reached, with a mean size of 3 μm, as shown in Fig. 3c.

The green colour of these pigments has been characterised from the diffuse reflectance spectra at room temperature, which show a well-defined reflectance band centered at 531 nm as result of two absorption bands, one at 700 nm assigned to the d–d electronic transitions characteristics of

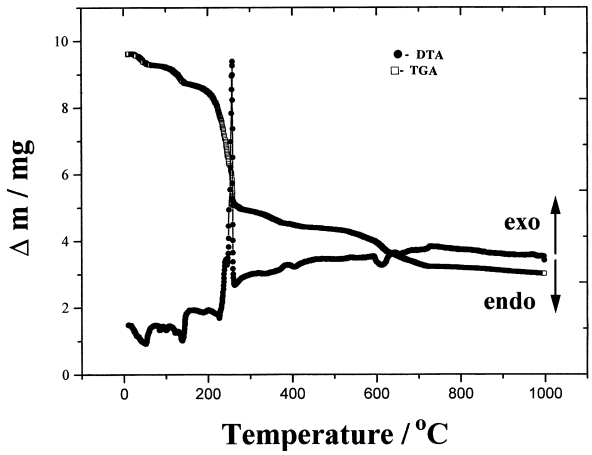

Fig. 1. TGA and DTA diagrams showing the evolution of the combustion method.

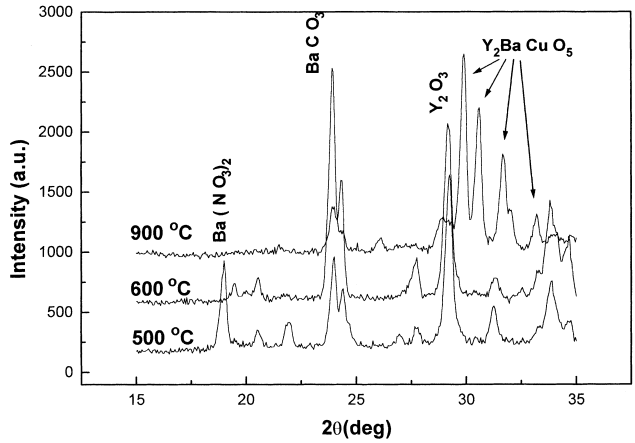

Fig. 2. X-ray diffraction patterns obtained at different temperatures in the decomposition process of lanthanide and copper nitrates, barium carbonate and urea.

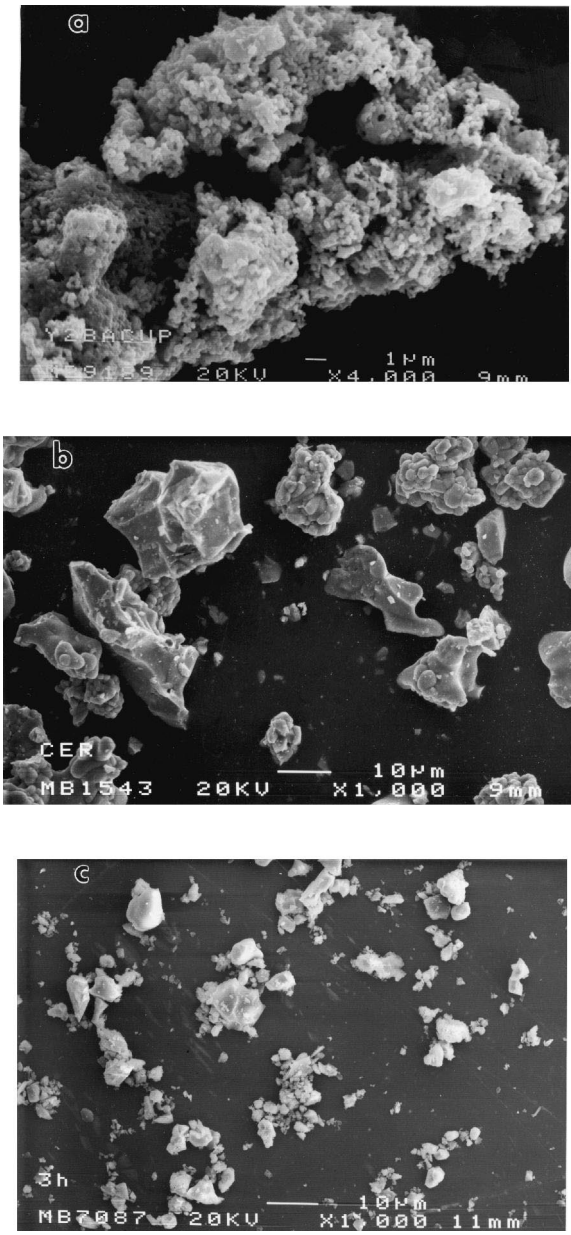

Fig. 3. Scanning electron micrographs for different samples of Y_2BaCuO_5: (a) combustion method, (b) ceramic method, (c) ceramic method grinding for 3 h.

Cu^{2+} and another one at 350 nm, probably a charge transfer band. At $\lambda<350$ nm the reflectance is almost the same for both combustion and ceramic samples, but a sudden increase is observed in the reflectance at $\lambda>400$ nm for the former Y_2BaCuO_5. Height of the peak for this sample is six times higher than that of the sample obtained from the ceramic procedure, as can be observed in Fig. 4. Although their X-ray diffraction patterns are almost identical, the optical data indicate that the combustion samples formed by aggregates of small particles (Fig. 3c) show a brighter green colour due to their greater surface for the light reflection.

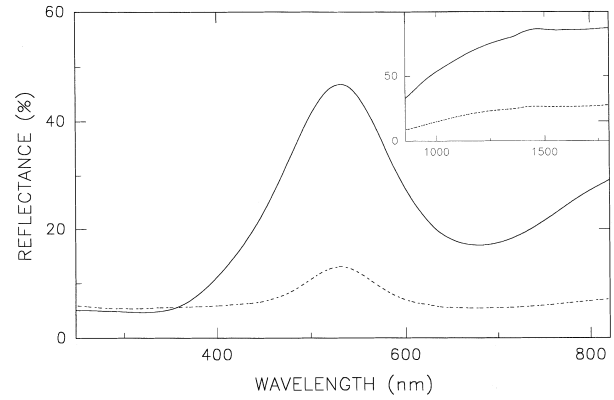

Fig. 4. Diffuse reflectance spectra of Y_2BaCuO_5: (a) combustion method, continuous line; (b) ceramic method, dotted line.

In a preliminary study, the samples obtained from both methods have been tested in ceramics. The pigment prepared by the combustion method yields better results as was expected, taking into account its better optical properties. These later materials have been selected for the study of their behaviour as pigments in ceramics under different conditions. The Y_2BaCuO_5 pigment was dispersed in weight proportions of 1, 4, 8 and 12% in the paste obtained with water and the three different types of varnish, whose compositions are given in Table 1. The green homogeneous paste is applied on the ceramics samples and slowly dried at 80°C. Then all the ceramic samples were heated at 1040°C obtaining different shades depending on the pH of the varnish [1]: light-green-coloured glazes have been obtained using varnishes 1 and 3, and a turquoise colour in the case of varnish 2. The intensity of the colour gradually increases with the pigment concentration, but in all cases the highest colour intensity is reached with a pigment proportion of 8%. By increasing this pigment proportion we do not observe any change in colour intensity, which remains as in the 8% samples.

A comparative study has also been done using the traditional green pigment CuO as a reference [1]. The CuO oxide was dispersed in a weight proportion of 5% in the three different types of varnish, and in all cases similar shades to that of the the Y_2BaCuO_5 4% samples were obtained. In all cases the coloration of the CuO glazes was less homogeneous than in the Y_2BaCuO_5 ones, due to the lower thermal stability of the former compound.

In conclusion, the green Y_2BaCuO_5 oxide obtained using the combustion method presents appropriate particle sizes and optical properties to be suitable for being used as pigment in ceramics. Inorganic green pigments are based in chromium compounds suspected of having carcinogenic effects [1], or in copper oxide which decomposes above 900°C. Containing a rather lower copper concentration, Y_2BaCuO_5 produces the same shades and a more homogeneous coloration than the green pigment CuO. Adding its lower toxicity and higher thermal stability, Y_2BaCuO_5 constitutes an interesting alternative in the pigments field.

Table 1
Chemical composition (molar ratio) of the varnishes used in the ceramic tests

	Na_2O	K_2O	CaO	ZnO	PbO	BaO	Al_2O_3	B_2O_3	SiO_2	ZrO_2
Varnish 1	0.10	0.10	0.20	0.18	0.42		0.50	0.30	2.20	0.15
Varnish 2	0.10	0.10	0.20		0.40	0.20	0.30	0.15	2.00	
Varnish 3	0.10	0.10	0.10	0.30	0.40		0.30	0.15	1.60	

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