



Sol–gel synthesis and properties of europium–strontium copper silicates blue pigments with high near-infrared reflectance



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ARTICLE INFO

Article history:

Received 30 November 2015

Received in revised form

25 March 2016

Accepted 5 April 2016

Available online 6 April 2016

Keywords:

Eco-friendly colorants

Europium-doped SrCuSi₄O₁₀

Near-infrared reflectance

Sol–gel

Blue pigments

ABSTRACT

Environmentally benign near-infrared reflective blue pigments Sr_{1-x}Eu_xCuSi₄O_{10+δ} (x ranges from 0 to 0.4) were synthesized via sol–gel method. The pigment samples were characterized by thermogravimetry and differential scanning calorimetry, Fourier transform infrared spectroscopy, X-ray diffraction technique, X-ray energy dispersive spectroscopy, scanning electron microscopy, UV–vis–NIR diffuse reflectance spectroscopy and the Commission Internationale de l'Eclairage 1976 L*a*b* colorimetric method. The prepared powders exhibited single-phase tetragonal crystalline structure. The color of the pigments changed from sky-blue to dark blue due to the substitution of Eu for Sr in SrCuSi₄O₁₀. With increasing Eu content, the near-infrared solar reflectance increased first and then declined. Adding specific amount of Eu can enhance the near-infrared reflectance and solar reflectance. The prepared pigments presented an optimum near-infrared solar reflectance of 72.31% when the doping content of Eu is 20 mol%.

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1. Introduction

Of late, cool pigments with high near-infrared (NIR) reflectance have drawn extensive attention because of their excellent performance in preserving lower exterior surface temperatures of buildings and decreasing power waste [1–3]. As is reported, around 5% of the solar radiation power in the Air Mass 1.5 Global (AM1.5G) solar irradiance spectrum is constituted by ultraviolet radiation (200–400 nm), 43% by visible radiation (400–700 nm), and 52% by the NIR radiation (700–2500 nm) [4,5]. Thus it is significantly necessary to develop NIR reflective pigments to reduce the heat build-up on the earth and diminish energy loss. NIR reflective pigments have a wide range of applications in both civil and military fields such as architectural roof, pavements, glazing and aircraft surface pigmentation, etc [6,7].

Currently the most widely used blue pigments are Cobalt blue (CoAl₂O₄), Ultramarine (Na₇Al₆Si₆O₂₄S₃), and Prussian blue (Fe₄[Fe(CN)₆]₃). However, these colorants are restricted by

government legislation and regulations in many countries due to their environmental and durability issues [8,9]. Thus it has become a concern to investigate novel eco-friendly and durable NIR reflective blue inorganic pigments. Recently, rare earth compounds based NIR reflective pigments have been proposed as viable alternatives to conventional pigments due to their low toxicity and high stability. Sheethu Jose et al. [10] synthesized a series of toxic metal free intense blue color inorganic pigments with the general formula Sr_{1-x}La_xCu_{1-y}Li_ySi₄O₁₀ by traditional solid state routes, exhibiting a high NIR reflectance of 67%. Sheethu Jose et al. [11] synthesized intense blue nano-pigments YIn_{0.9}Mn_{0.1}O₃–ZnO with high solar reflectance of 70% by a sol–gel combustion method. Aijun Han et al. [12] prepared nanocrystalline YFe_xMn_{1-x}O₃ pigments by modified citrate method at a certain calcination temperature, which displayed a wide range of colors from blue–green to pale blue and then dark blue as well as pronounced reflective performance.

The present work is focused on the synthesis of a series of NIR reflective blue inorganic pigments with the formula Sr_{1-x}Eu_xCuSi₄O_{10+δ} (x ranges from 0 to 0.4) by sol–gel method. Crystallization temperature, crystal structure, morphological feature, chromatic and near-infrared reflective properties of these pigments were also investigated in detail.

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2. Experimental section

2.1. Materials and methods

A series of pigments with the general formula $\text{Sr}_{1-x}\text{Eu}_x\text{CuSi}_4\text{O}_{10+\delta}$ ($x = 0, 0.1, 0.2, 0.3, 0.4$) were synthesized by sol–gel method. Cupric oxide (CuO, 99.0%), europium oxide (Eu_2O_3 , 99.9%), nitric acid (HNO_3 , 65%), strontium nitrate ($\text{Sr}(\text{NO}_3)_2$, 99.5%), citrate acid ($\text{C}_6\text{H}_8\text{O}_7 \cdot \text{H}_2\text{O}$, 99.5%), ethylene glycol ($\text{C}_2\text{H}_6\text{O}_2$, 99.0%), and ludox ($\text{SiO}_2 \cdot n\text{H}_2\text{O}$, 25%) were used as starting materials.

Initially, stoichiometric amount of CuO and Eu_2O_3 were dissolved in dilute nitric acid to form transparent solution, and then $\text{Sr}(\text{NO}_3)_2$ was added in stoichiometric proportion with the total metal cation molar concentration of 2–3 M. Citrate acid, which was used as the chelating agent, was weighted in the molar ratio 1.0:1.0 with respect to the cations (Sr, Eu and Cu), and then was dissolved in ethylene glycol solvent. Subsequently an appropriate amount of ludox was added in the citric acid solution under constant stirring. After pouring the mixed fluid into the nitrate solution, the clear precursor solution was finally obtained.

The resultant solution was heated at 80 °C to induce the complexing reaction under constant stirring for about 5 h. An organic gel was formed with evaporation of water. Further drying was carried out in a vacuum oven at 70 °C for 24 h. Then the dry gel was ground in an agate mortar and transferred in a muffle furnace to calcinate at different temperatures (300–1000 °C) for 2 h. The obtained pigments were triturated and sieved to get fine and homogeneous powders.

The pigments were pressed on boric acid substrate in a stainless die under a pressure of 40 MPa for 3 min. The final samples with a dimension of 27 mm in diameter and 5 mm in thickness were applied to the following optical test.

2.2. Characterization techniques

The thermal performance of precursor powders was recorded by thermogravimetry and differential scanning calorimetry (TG-DSC, Mettler TG-DSC1/1600HT), in air atmosphere in the temperature range of 50–800 °C with a heating rate of 15 °C/min. Infrared spectra of samples were measured via a Fourier transform infrared spectrometer (FTIR, Vertex70, Bruker, Germany) in a wavenumber range from 400 to 4000 cm^{-1} at room temperature. The phase composition of the powders was detected by X-ray diffraction (XRD, Rigaku, RINT-2000) with Cu-K α radiation (1.5405 Å), operated with voltage and current settings of 40 kV and 40 mA, respectively. Data were collected by step scanning over a 2θ range from 10° to 70° with a step size of 0.0167° at scan rate of 5°/min. The elemental composition of the sample was analyzed by X-ray energy dispersive spectroscopy (EDS, EX350, Horiba). The morphology of the powders was characterized by a field emission high-resolution scanning electron microscopy (SEM, SU-70, Hitachi), operated with an acceleration voltage of 30 kV. Before measurement, the powders were coated with a thin gold layer via ion sputtering.

The reflectance spectra measurements of the pigment samples was carried out by a UV–vis–NIR spectrophotometer (Shimadzu, UV-3600 with an integrating sphere attachment) using polytetrafluoroethylene (PTFE) in NIR range (700–2500 nm) and Barium sulphate (BaSO_4) in visible range (380–750 nm) as a reference respectively. The NIR solar reflectance at wavelengths between 700 and 2500 nm is the irradiance-weighted average of its experimentally achieved spectral reflectance and calculated in accordance with the ASTM standard number G173-03(2012). NIR solar reflectance can be regarded as a significant indicator of heat build-up affected by the sun on the surface of a substance.

The colorimetric values of the pigments were measured on a Color-Eye automatic differential colorimeter (X-Rite, 7000 A) using the Commission Internationale de l'Eclairage (CIE) 1976 $L^*a^*b^*$ colorimetric method. L^* is the lightness axis (0 for black and 100 for white). The parameter a^* (negative values for green and positive values for red) and b^* (negative values for blue and positive values for yellow) denote the hue or color dimensions. The parameter C^* (chroma) represents the chromatic saturation and is defined as $C^* = [(a^*)^2 + (b^*)^2]^{1/2}$. The hue angle, h° is stated in degrees in the range of 0–360° and calculated by the formula $h^\circ = \tan^{-1}(b^*/a^*)$.

3. Results and discussion

3.1. TG and DSC analysis

Fig. 1 presents the TG-DSC results of the pigment precursor sample $\text{Sr}_{0.9}\text{Eu}_{0.1}\text{CuSi}_4\text{O}_{10+\delta}$. The mass loss of about 6% from 50 °C to 300 °C is owing to the removal of water and the decomposition of some nitrate and organics. The mass loss of approximately 59% from 300 °C to around 500 °C accompanied by an intense exothermic peak at 475.18 °C is ascribed to the pyrolysis of polymeric precursor, which indicates the formation of the product $\text{Sr}_{0.9}\text{Eu}_{0.1}\text{CuSi}_4\text{O}_{10+\delta}$. When the temperature is above 500 °C, the weight of the sample remained stable because of the accomplishment of the combustion.

3.2. FTIR spectra

The optimum calcination temperature required for the crystallization of the pigment sample $\text{SrCuSi}_4\text{O}_{10}$ was investigated. The FTIR spectra of the precursor and $\text{SrCuSi}_4\text{O}_{10}$ samples calcined at different temperatures for 2 h are given in Fig. 2. As is shown, the FTIR spectra of the precursor heated at 300 °C apparently display a broad absorption band at around 3400 cm^{-1} , which is due to the characteristic stretching vibrations of –OH. The absorption peaks at 1558 cm^{-1} , 1461 cm^{-1} and 1109 cm^{-1} are assigned to unsymmetrical stretching vibration of O=C=O, bending vibration of C–H and stretching vibration of C–O–C respectively, caused by the decomposition of carboxylate and other organics. With temperature rising up to 900 °C, the peaks of the hydroxyl groups and other organic groups are attenuated and finally disappear. Meanwhile, new absorption peaks appear below 1300 cm^{-1} , including the peaks at 1161 cm^{-1} , 1054 cm^{-1} , 1009 cm^{-1} and 479 cm^{-1} attributed to the

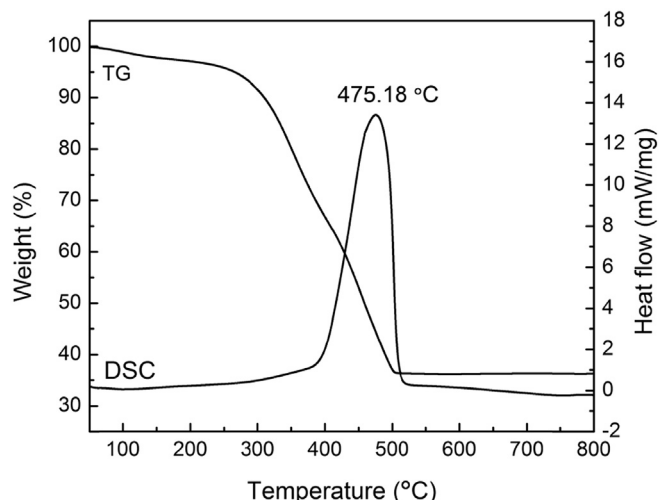


Fig. 1. TG-DSC curves of $\text{Sr}_{0.9}\text{Eu}_{0.1}\text{CuSi}_4\text{O}_{10+\delta}$ precursor.

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