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Journal of Solid State Chemistry 181 (2008) 487–492

JOURNAL OF SOLID STATE CHEMISTRY

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Synthesis and characterization of environmentally benign calcium-doped $Pr_2Mo_2O_9$ pigments: Applications in coloring of plastics

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Received 28 September 2007; received in revised form 9 December 2007; accepted 22 December 2007
Available online 31 December 2007

Abstract

A new class of environmentally benign rare earth pigments of general formula $Pr_{2-x}Ca_xMo_2O_{9-\delta}$ (x ranges from 0 to 1.0) displaying colors ranging from green to yellow were synthesized by traditional solid-state route, as alternatives to lead, cadmium and chromium colorants. The products were characterized by X-ray powder diffraction, UV–vis spectroscopy and CIE-$L^*a^*b^*$ 1976 color scales. The coloring mechanism is based on the strong absorptions of the pigments in the blue and red regions due to electronic transitions between $4f^2 \rightarrow 4f^1 5d^1$ states of Pr^{3+}. The designed pigments consist of non-toxic elements and further found to be thermally and chemically stable. The yellow–green pigments were found to be interesting alternatives to existing toxic pigments for coloration of plastics.

Keywords: Novel rare earth yellow pigments; Environmentally benign; Band gap engineering; Coloring of plastics

1. Introduction

There is a strong incentive to design new colorants based on inorganic materials to substitute for industrial pigments that are based on heavy elements hazardous to health and the environment [1]. Inorganic pigments are widely used in various applications such as paints, inks, plastics, rubbers, ceramics, enamels and glasses [2]. Yellow is particularly important color in the pigment industry and the consumption of the yellow exceeds that of any other colored pigments [3]. There are various important yellow pigment families: tin vanadia yellows, praseodymium zircon, zircon vanadia yellow, cadmium yellow and lead antimonite. Among them, praseodymium yellow ($ZrSiO_4$:Pr) has been known as one of the environmentally benign inorganic colorants, which can be applied to paints, inks, plastics, rubbers, ceramics, enamels and glasses because of its thermal stability [4,5]. However, this pigment requires high temperature calcinations (>1273 K) for the preparation, which tends to induce particle growth of the pigment. Hence, it is difficult to apply the praseodymium yellow to paints and inks in which fine dispersion of the pigment is essential. Other yellow pigments commonly used such as $Pb_2Sb_2O_7$, $PbCrO_4$, CdS are now being expelled from the market because of their toxicity.

The characteristics required for commercial use of pigments are: color-tone and saturation, color covering, tinting strength, brightening and brilliance ability, non-reactivity, insolubility and dispersibility [6,7]. In addition to absorbing light, their ability to scatter or reflect light also contributes to their functionality. Recently, many rare earth-based inorganic pigments have been proposed by several researchers including our group [8–12]. Among several pigments for the alternative non-toxic yellow pigments, CeO_2 and related materials have been attracted because of the opacity, low toxicity, and high temperature stability [13–15]. The coloring mechanism is based on the charge-transfer band from O_{2p} to Ce_{4f} in the semiconducting CeO_2. The band gap between the anionic O_{2p} valence band and the cationic Ce_{4f} conduction band can be modified by the formation of solid solutions, which introduces an additional electronic level between the valence and conduction bands. As a result, shift of the charge-transfer band is observed. Earlier investigations reveal that the classical toxic inorganic pigments can be

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0022-4596/$ - see front matter © 2007 Elsevier Inc. All rights reserved.
doi:10.1016/j.jssc.2007.12.024

replaced by solid solutions of perovskites $CaTaO_2N$ and $LaTaON_2$, which gives colors ranging from yellow to deep red [9]. Although these pigments are non-toxic and show excellent color hue, it is necessary to heat the starting materials in a flow of toxic and inflammable ammonia gas for a long time (20–60 h) to synthesize them. Therefore, research needs to be performed in developing novel yellow inorganic pigments with various advantages over traditional pigment formulations.

Thus, the present paper is focused on the development of novel yellow pigments based on calcium-doped $Pr_2Mo_2O_9$ system from an environmental point of view. The new pigments of the formula $Pr_{2-x}Ca_xMo_2O_{9-\delta}$ (x ranges from 0 to 1.0) have been synthesized by solid-state reaction of the respective oxides and characterized for their structure and optical properties.

2. Experimental

2.1. Sample preparation

Several compositions based on $Pr_{2-x}Ca_xMo_2O_{9-\delta}$ (x ranges from 0 to 1.0) stoichiometry were prepared by corresponding oxides: Pr_6O_{11} (99.9%), $CaCO_3$ (99%) and $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$ (99.9%). In this method, the reactants were mixed and homogenized by wet milling with acetone in an agate mortar for 30 min. The homogeneous mixture was calcined in platinum crucibles in an electric furnace at a temperature of 1050 °C for 3 h. The heating of the furnace was programmed to increase the temperature initially at 10 °C/min up to 900 °C and afterwards the heating rate was decreased to 5 °C/min up to 1050 °C. In order to ensure the completion of the reaction, the calcinations process was repeated thrice for the same sample. To refine and homogenize the particle size after calcinations, the resulting products were ground in an agate mortar.

2.2. Coloration of plastics

Poly(methyl methacrylate) (PMMA; S.D. Fine Chemicals, India) was utilized as a binder phase for fabricating the pigmented compact. The typical pigment samples, $Pr_{1.9}Ca_{0.1}Mo_2O_{9-\delta}$ (10%) and $Pr_{1.4}Ca_{0.6}Mo_2O_{9-\delta}$ (10%) was ultrasonicated (Vibronics, 250 W, India) in an alcohol/water (1:4) mixture for 10 min to ensure the complete dispersion of the pigment particles. A viscous solution consists of PMMA (90 wt%) was made using a conventional electrical coil heater. The pigment dispersion was slowly added while stirring and converted into a thick paste. The paste after 2 h of curing, compressed uniaxially into a form of cylindrical discs using a hydraulic press (Lawrence & Maya, India) at a pressure of 25 MPa. Both sides of the pigmented polymer were lapped using a fine grade emery sheet for obtaining a polished surface. The intensity of the color of plastics will depend on the concentration of the pigment.

2.3. Characterization techniques

Phase analysis of the colored samples was performed by X-ray powder diffraction using Ni-filtered Cu$K\alpha$ radiation with a Philips X'pert Pro difractometer. Data were collected by step-scanning from 10° to 70° 2θ. UV–vis spectroscopy and colorimetric study of the samples were carried out in a Shimadzu, UV-2450 spectrophotometer in the 380–780 nm range using barium sulfate as a reference. The color properties are described in terms of CIE-$L^*a^*b^*$ 1976 color scales. The values a^* (the axis red–green) and b^* (the axis yellow–blue) indicate the color hue. The value L^* represents the lightness or darkness of the color as related to a neutral gray scale.

Scanning electron micrographs of the samples were taken on a scanning electron microscope (JEOL JSM-5600LV). The thermal stability of the colorant was also checked by Pyris Diamond TG/DTA Perkin-Elmer make. The particle diameter of the sample was measured by the laser scattering particle size distribution analyzer (CILAS 1180 Liquid).

3. Results and discussion

Fig. 1 shows the powder X-ray diffraction patterns for $Pr_{2-x}Ca_xMo_2O_{9-\delta}$ with different doping content of Ca, where $x = 0$, 0.10 and 0.20, respectively. The XRD pattern of the pure $Pr_2Mo_2O_9$ sample can be indexed very well as a cubic structure of $P213$ with a lattice constant of 0.7068 nm [16,17]. Since Ca^{2+} (ionic radius: 0.099 nm) is slightly smaller in size than Pr^{3+} (ionic radius 0.112 nm) and in addition, the substitution of a lower valence ion in the Pr^{3+} sites leads to creation of O^{2-} vacancies, the cell volume lowers with increasing Ca content up to 10% as can be seen from Fig. 2 [18]. With increase of calcium doping content,

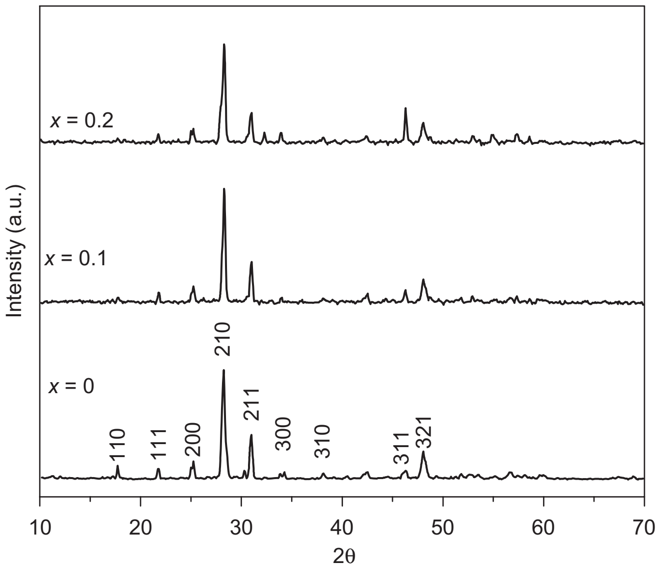

Fig. 1. XRD patterns of the $Pr_{2-x}Ca_xMo_2O_{9-\delta}$ ($x = 0$, 0.1 and 0.2) pigments.