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ScienceDirect
Dyes and Pigments 75 (2007) 687−692
DYES and PIGMENTS
www.elsevier.com/locate/dyepig

Cerium molybdenum oxides for environmentally benign pigments

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Received 20 June 2006; received in revised form 3 July 2006; accepted 6 July 2006
Available online 8 September 2006

Abstract

A new class of environmentally benign yellow rare earth pigments as alternatives to lead, cadmium and chromium pigments is presented. These pigments are based on cerium molybdenum oxides corresponding to the structural formulae $NaCe_{0.5}(MoO_4)$ and $Ce(MoO_4)_2$. The coloring properties of the compositions prepared by varying the Ce:Mo ratio in the presence and absence of phosphates have been evaluated. The reflectance spectra and photoacoustic spectra indicate the absorption in visible and ultraviolet regions under 500 nm, which could originate from the O_{2p}−Ce_{4f} and the O_{2p}−Mo_{3d} double charge transfer transitions, and as a result the pigments show yellow color. In the presence of a phosphate, the products are homogeneous and crystalline at temperatures of 700 °C itself and exist as multiphasic with white colored $CePO_4$ being present in association with cerium molybdenum oxide. Further, the particle size of the cerium molybdenum oxide sample was lower in the presence of phosphate (116 nm).

Keywords: Inorganic pigments; Ceramic pigments; High temperature pigments; Pigments of cerium; Molybdenum; Phosphate

1. Introduction

Inorganic pigments are widely used in various applications such as paints, inks, plastics, rubbers, ceramics, enamels and glasses [1,2]. The pigments for coloring ceramics, usually inorganic products composed of metal oxides or compounds formed from the host of metal oxides, must possess thermal and chemical stabilities at high temperature and must be inert to the chemical action of the molten glaze [3]. The majority of inorganic pigments for the above applications currently employed are derived from toxic metals such as cadmium, lead, chromium or cobalt [1]. Thus, serious need arises to search for materials of environmentally friendly and economically viable materials for the replacement of toxic components of pigments. Development of safe inorganic alternatives is essential, as the use of high-performance organic pigments have some limitations because of their thermal and ultraviolet (UV) ray radiation instabilities. Pigments based on CeO_2 are inorganic pigments with high temperature stability and in the orange-pink hue when doped with praseodymium [4]. Lanthanum oxide (La_2O_3) and praseodymium dioxide (PrO_2) dissolve in cerium oxide at 1300 °C forming a solid solution of the three oxides. CeO_2−PrO_2−La_2O_3 pigments give very interesting red hues in the ceramic glaze. These heat and chemical-resistant pigments have a fluorite structure and represent potential environmentally friendly inorganic pigments [4].

Recently pigments based on rare earth phosphates [5], $Ce_{1-x}M_xW_2O_8$ (M = Zr or Ti) were reported in the yellow segment [6], along side the pigments based on Pr-$ZrSiO_4$ [7] and $RE_2Mo_2O_9$, where RE = La or Pr [8]. The intense color arises from mostly charge transfer interactions between a donor and acceptor with the metal ions playing the role of an acceptor. Several of these pigments employ high temperature calcinations in the synthesis process to form the $ZrSiO_4$ (zircon) phase, which tends to induce particle growth of the pigments. Consequently, it is difficult to apply the praseodymium yellow

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0143-7208/$ - see front matter © 2006 Elsevier Ltd. All rights reserved.
doi:10.1016/j.dyepig.2006.07.021

to paints and inks in which fine dispersion of the pigment is essential [6]. Pigments are generally not produced by directly mixing the dopant oxides and the base metal oxide, viz., zircons. It is assumed that the doping is facilitated if the uncalcined product is as homogeneous as possible [9]. The sensitivity of the preparative method complicates both the reproducibility and scale up of the process. By appropriate choice of starting materials, it is often possible to bring about homogeneity in the calcined product. Further, the use of mineralizers to achieve a complete or near complete reaction of all components has been reported [10].

In the present study, new pigments based on crystalline cerium molybdenum oxide, $NaCe_{0.5}(MoO_2)$ have been synthesized by a simple solid-state reaction at high temperature and their color properties were characterized from the view point of possible ecological inorganic pigments. The role of mineralizers like sodium phosphate in enhancing the color value of the colorant is discussed.

2. Experimental

$Ce_2(CO_3)_3 \cdot xH_2O$, and $Na_2MoO_4 \cdot 2H_2O$ were mixed in varying stoichiometric ratio (1.0:0.0 to 1:0.08) in the presence or absence of Na_2HPO_4 (0.0–1.0), in an agate mortar with a pestle. The mixture was calcined at varying temperatures (600–1100 °C) for 2 h in air. The obtained powders were characterized by means of X-ray powder diffraction (XRD) using Ni filtered Cu Kα radiation with a Philips X'pert Pro diffractometer. Morphological analysis was performed with a JEOL JSM 5600LV scanning electron microscope (SEM).

The diffuse reflectance UV–vis spectra were recorded using a Perkin–Elmer lambda 35 UV–vis spectrophotometer equipped with a Labsphere RSA-PE-20 diffuse reflectance accessory. Barium sulfate was used as a white standard. The principle of operation involved projection of light of a known spectral energy on the pellet of pigment kept at 90° to the light source and measurement of the intensity of the reflected light using photo detectors. CIE illuminant D65 was used in all the color measurements. The CIELab (1976) color space was used for color measurement [11–13]; the colorimetric values were computed using an Advanced Spectroscopy Software (Perkin–Elmer).

Light scattering measurements were carried out at 90° on a photon correlation spectrometer (PCS) from Malvern Instruments – Zetasizer 3000 HSA equipped with a digital autocorrelator. The NNLS method of correlation and analysis was employed. The concentration of oxide pigments was set to 0.2 mg/ml for all measurements. Electrophoretic mobility measurements were performed using the same setting equipped with a platinum electrode. The electrode was cleaned for 10 min in an ultrasonic bath prior to each measurement and pre-equilibrated for 2 min in an aliquot of the sample. For zeta potential measurements, the samples were diluted in isopropyl alcohol. The dispersion was prepared by sonicating in an ultrasound cleaner of 30 kHz for 10 min prior to measurements.

The photoacoustic spectrophotometer employed in this work consisted of a 450 W Xenon lamp (Jobin Yvon), an electromechanical chopper (PAR 650), a lock-in amplifier (Perkin–Elmer 7225 DSP) and the PA cell made of stainless steel. The experimental setup is explained elsewhere [14]. For the photoacoustic measurement, the pigment powders were pelletized to about 4 mm diameters and placed inside the photoacoustic cell. An electromechanical chopper chops white light from the Xenon lamp and the chopped beam falls on the sample inside the cell. The diameter of the light spot incident over the sample is around 0.3 cm. Light is absorbed on the surface of the sample. The microphone in the PA cell detects the photoacoustic signal generated. The microphone is placed behind the sample, so that only transmitted waves are detected. This is then fed to a lock-in amplifier where the readings are recorded.

3. Results and discussion

Formulations developed in the study of varying Ce and Mo ratios with or without phosphate were homogenized in a ball mill and subsequently treated in a muffle furnace. Unless otherwise mentioned, a temperature of 900 °C at a rate of 5 °C/min and a residence time of 120 min were employed.

The XRD patterns of the colorant oxide in the presence (prepared with a stoichiometric ratio of Ce:Mo:P – 1.0:0.08:0.6)/absence of phosphate (Ce:Mo – 1.0:0.8) are given in Fig. 1. The intense and sharp peaks found in the diffraction patterns reveal the crystalline nature of the pigments. In the absence of phosphate, crystalline $NaCe_{0.5}(MoO_4)$ appears with a small amount of $Ce(MoO_4)_2$ and in the presence of phosphate, small amounts of $CePO_4$ existed as well. The crystallite size was calculated from Debye–Scherrer formula, $D = 0.9\lambda/\beta \cos\theta$, where D is the crystallite size, λ is the wavelength of the X-ray used, β and θ are the half width of X-ray diffraction lines and half diffraction angle of 2θ, respectively. The crystallite

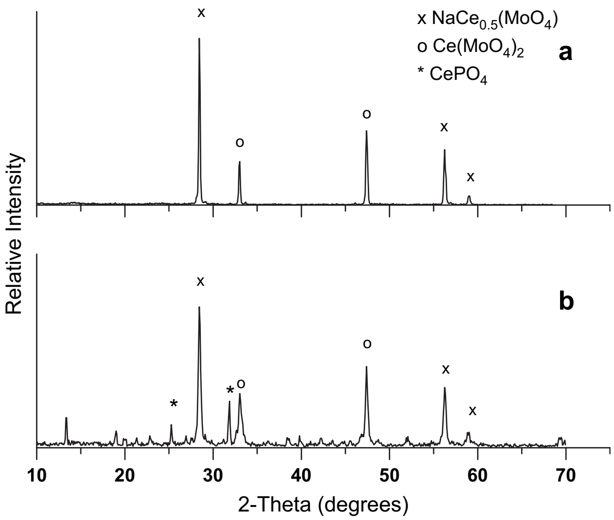

Fig. 1. X-ray diffraction patterns of cerium molybdenum oxide in the (a) absence and (b) presence of phosphate.

size was found to be 36–39 nm for the colorant irrespective of the presence/absence of phosphate. The bandgap values are calculated using Kubelka–Munk function which is given by $K\text{–}M = (1 - R)^2/2R$, where R is the reflectance value. A plot of $K\text{–}M$ and wavelength is drawn and the absorption edge is determined from the plot. The value of the wavelength is substituted in the formula E (eV) = 1236/wavelength (nm). The reflectance spectra of the pigments in the presence and absence of phosphate are presented in Fig. 2. The color parameters L^*, a^* and b^* and the corresponding values along with the bandgap energies (E_g) are presented in Table 1. In the reflectance spectra, absorbance in the range of 420–500 nm (blue) corresponds to the appearance of yellow color, which is more intense in the presence of phosphate. It can be seen that the a^* and b^* values increased in the presence of phosphate, showing that the hue of the pigments shifted from white to yellow in the presence of phosphate. The results are further confirmed with a low bandgap energy (E_g) value for the sample in the presence of phosphate (2.45 eV). This change in color from white to yellow could be attributed to the fact that the phosphate, which functioned as a mineralizer, promoted the reaction between cerium and molybdenum, resulting in yellow colored oxides.

The color coordinates and bandgap energy values of the pigments when the molybdenum content of the mixture was varied (Ce:Mo:P – 1.0:0.0:0.6 to 1.0:0.08:0.6) are tabulated in Table 1. As the molybdenum content increases, the a^* and b^* values increased indicating a substantial increase in yellow color. This is further confirmed by the bandgap energy value which is the lowest when Mo content was the highest (2.45 eV). The incorporation of more and more molybdenum will cause changes of the width or the position of conduction bands, which is possibly the reason for narrowing of the optical gap, that is, the change of the yellow hue. The changes in the reflectance spectra with phosphate content being varied (Ce:Mo:P – 1.0:0.08:0.0 to 1.0:0.08:1.0) are presented in Fig. 3 and the corresponding $L^*a^*b^*$ and E_g values in Table 1. The pigments show increasing yellowness up to a Ce:Mo:P ratio of 1.0:0.08:0.6 as indicated by an increase in a^* and b^* values and subsequently a decrease in yellowness (lower b^* values). The hue angle h is defined as starting at $+a^*$ axis and is expressed in degrees. An h value of 90° would indicate yellow color [11–13]. That the h value in all cases is close to 90° indicates that the hue was yellow. No major changes in the hue were observed in the presence/absence of phosphate or molybdate as the values varied only by ±2°. Larger C^* values indicate a higher chroma or saturation. Chroma can also be referred to as cleanliness of the color [11–13]. In the presence of phosphate the chroma value or cleanliness of the yellow color improves drastically. The bandgap energies also change correspondingly, with the lowest E_g value (2.32 eV) observed when the Ce:Mo:P ratio was 1.0:0.08:0.6. This is expected as at increasing concentrations of phosphate, $CePO_4$ would dominate and pure $CePO_4$ has been reported to be white in color [5].

In order to understand the significance of temperature the pigments prepared with a Ce:Mo:P mole ratio of 1.0:0.08:0.6 were pulverized and then treated at varying temperatures from 600 to 1100 °C. The XRD of the samples at varying temperatures are presented in Fig. 4. No significant change was noticed in the crystallinity or crystallite size (26.5–49.5 nm) with varying temperature of preparation. The homogeneous and crystalline nature of the sample has also been noticed from the SEM micrographs of the colorant in the absence of phosphate (Fig. 5). From the figure, it is quite clear that the surface of the sample is spherical and has an even grain distribution; the average grain size is about 300 nm.

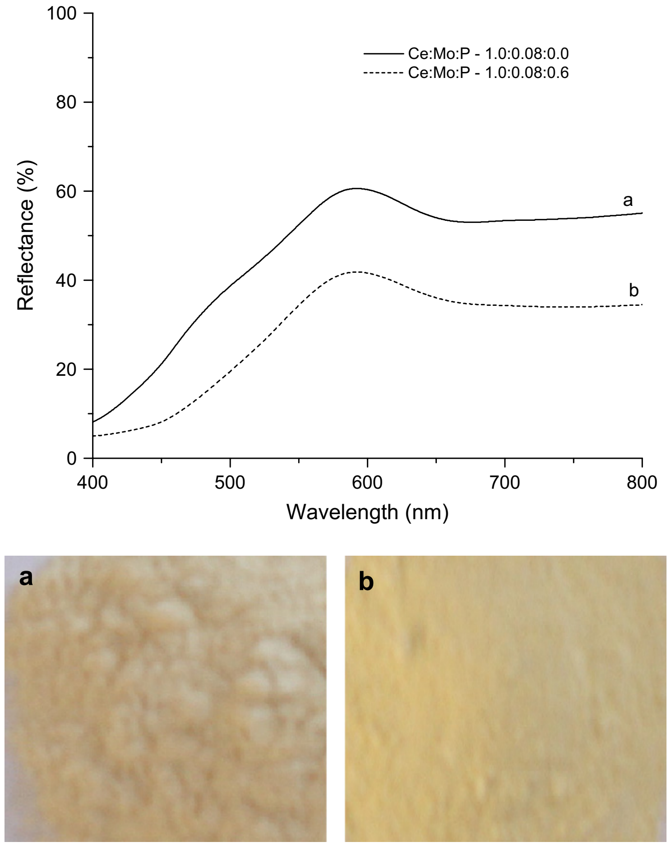

Fig. 2. Reflectance spectra and representative photographs of the pigments in the (a) absence and (b) presence of phosphate.

Table 1
Color coordinates and bandgap energies for colorant in the presence/absence of phosphate

Ce:Mo:P	Color coordinates					Band gap energy (eV)
	L^*	a^*	b^*	h (°)	C^*	
Presence/absence of phosphate						
1.0:0.08:0.0	76.1	−0.1	36.9	88.2	21.9	2.68
1.0:0.08:0.6	63.2	3.5	45.2	88.7	48.2	2.45
Variation of molybdate						
1.0:0.00:0.6	89.5	−8.6	33.4	89.7	39.9	2.60
1.0:0.04:0.6	69.2	−2.1	41.3	90.3	36.8	2.60
1.0:0.08:0.6	63.2	3.5	45.2	88.7	48.2	2.45
Variation of phosphate						
1.0:0.08:0.3	83.8	1.0	40.0	92.2	42.2	2.68
1.0:0.08:0.6	63.2	3.5	45.2	88.7	48.2	2.45
1.0:0.08:1.0	89.9	−4.7	37.2	89.2	45.6	2.68

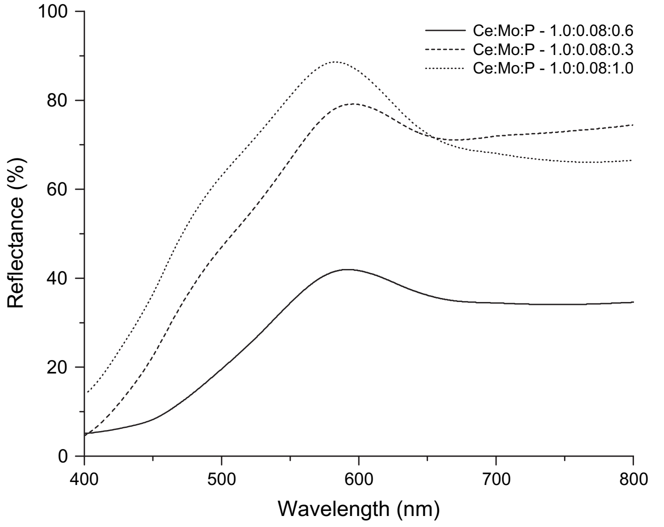

Fig. 3. Reflectance spectra for cerium molybdenum oxide doped with varying quantities of phosphate.

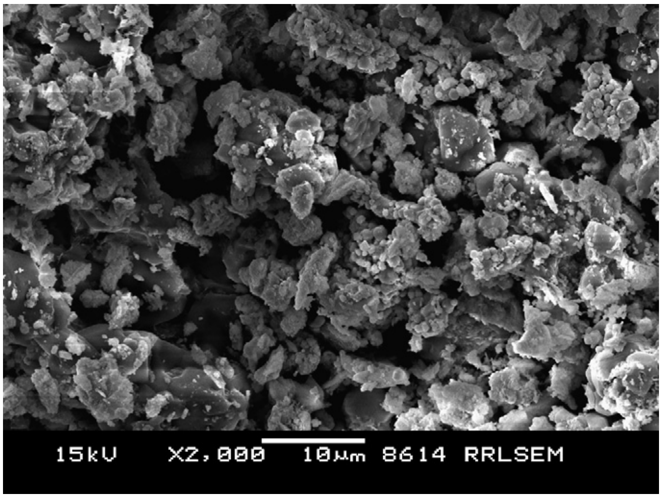

Fig. 5. SEM micrograph of cerium molybdenum oxide in the absence of phosphate.

Particle size distribution is an important parameter in the understanding of the color of the oxides. Photon correlation spectroscopic measurements of the cerium molybdenum oxides in the presence/absence of phosphate indicated that the particles dispersed in a solvent (isopropyl alcohol) were found to be more stabilized (as indicated by a higher zeta potential value of 9.3 ± 0.2 as against 0.5 ± 0.4 mV in the absence of the phosphate). As expected, the non-agglomerated colorant in the presence of phosphate ion was of lower particle size (116 nm) compared to that in its absence (400 nm). The existence of the particles as non-agglomerated in isopropyl alcohol is very advantageous with regard to the formation of homogeneous particle coatings on substrates.

The photoacoustic spectra for the colorant with Ce:Mo:P mole ratio being 1.0:0.08:0.6 are presented in Fig. 6 and the FT-IR spectra of the colorant in the presence/absence of phosphate in Fig. 7.

The existence of a $4f^1$ electron in Ce^{3+} configuration [Xe] $4f^1 5d6s$ markedly affects the electronic spectra of the ion. The ground state is the $^2F_{7/2,5/2}$ state, and the first excited state configuration is [Xe] $4f5d^1 6s$, leading to the $^2D_{5/2,3/2}$ state. The strong absorption observed at around 460 nm is based on 4f–5d transition. In addition to the principal change of the 4f–5d transition, the partial production of Ce^{4+} is also suggested as cerium has been reported in the tetravalent form in double cerium phosphates of $B_{0.5}Ce_2(PO_4)_3$ (where B = Mg, Ca, Sr and Cd) [15]. By the formation of tetravalent cerium ion, the O_{2p}–Ce_{4f} charge transfer transition also appears in the UV region and the Ce^{4+} produced affects the optical absorption of the 4f–5d transition. The 4f–5d transition correlates to the optical basicity which is modified by the partial oxidation of Ce^{3+} in the $CePO_4$ lattice, and the basicity increases after the oxidation of Ce^{3+} to Ce^{4+} (at the temperature

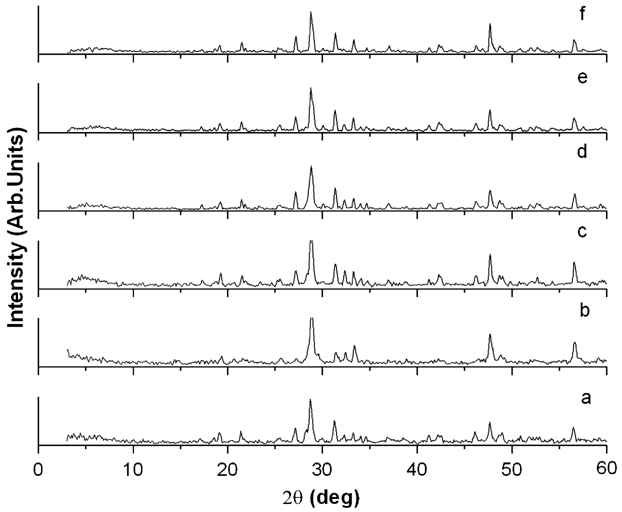

Fig. 4. X-ray diffraction pattern for the mixed oxide in the presence of phosphate (a – 600 °C, b – 700 °C, c – 800 °C, d – 900 °C, e – 1000 °C and f – 1100 °C).

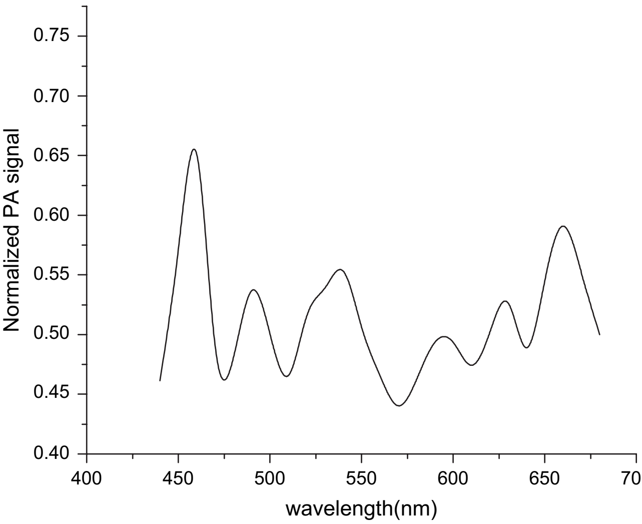

Fig. 6. Photoacoustic spectra of cerium molybdenum oxide in the presence of phosphate (Ce:Mo:P – 1.0:0.08:0.6).

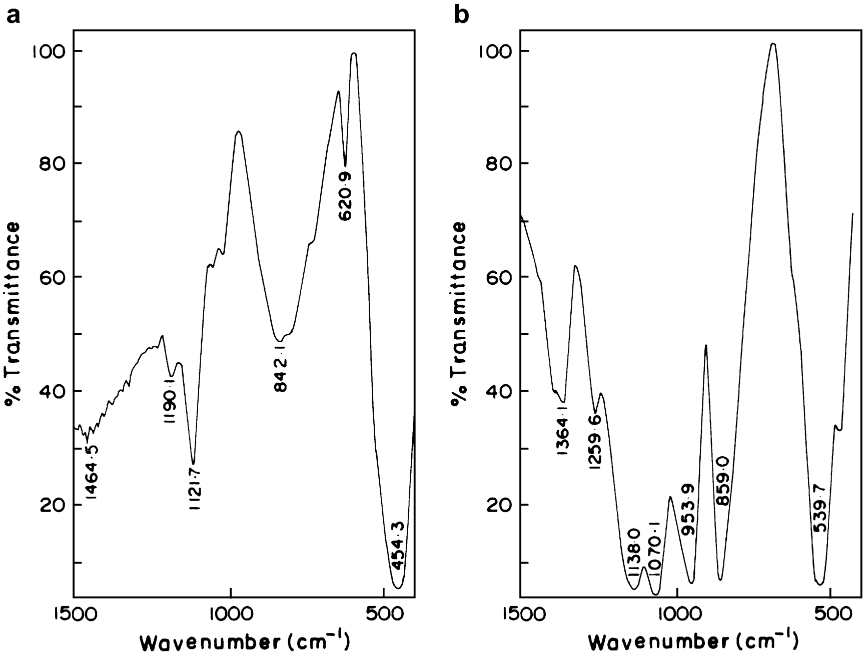

Fig. 7. FT-IR spectra of (a) Ce:Mo:P – 1.0:0.08:0.0 and (b) Ce:Mo:P – 1.0:0.08:0.6.

of 900 °C employed) to induce red shift in the optical spectrum [16]. The absorption around 590 nm could be attributed to an increase of basicity of the pigment. Other transitions observed in the photoacoustic spectra could be attributed to the O_{2P}–Mo_{3d} charge transitions. As a result of the absorption of blue light, the color of the samples is yellow because blue is a complementary color to yellow.

In the FT-IR spectra, the bands around 1138, 1070, 954 and 539 cm^{-1} are assigned to the PO_4 group in the rare earth phosphate. The bands at 1138 and 1070 cm^{-1} are due to asymmetric stretching of the P–O bonds. The band at 954 cm^{-1} is assigned to symmetric stretching vibrations of the P–O bond, while that 538 cm^{-1} is attributed to asymmetric bending modes. These bands are absent when the sample does not have a phosphate in it [17].

The pigments are expected to be cost effective as the cerium carbonate used in this study is priced at $8.8/kg and sodium molybdate at $26/kg, resulting in an overall raw material cost of $14/kg of product as against $85/kg for a praseodymium yellow pigment.

4. Conclusions

Replacement of toxic components such as lead and chromium in inorganic pigments has been sought through the development of pigments based on cerium and molybdenum. Crystalline $NaCe_{0.5}(MoO_4)$ was synthesized as a novel inorganic yellow pigment. The color of these pigments, especially the chroma was found to be dependant on the presence/absence of phosphate, with phosphate ion increasing the chroma. The yellowness of the pigment increased up to a Ce:Mo:P ratio of 1.0:0.08:0.6, subsequent to which the presence of $CePO_4$ reduced the intensity of the color. The color has been attributed to the decreasing bandgap energies and the transitions O_{2p}–Ce_{4f} and O_{2p}–Mo_{3d} involved have been analyzed with the help of photoacoustic spectroscopy. The role of phosphate in bringing about crystallinity at low temperatures as well as reducing the particle size of the pigments has been highlighted. Thus, the new pigment serves as a potential alternative to conventional yellow inorganic pigments containing toxic metal ions like lead and chromium. These pigments are expected to be cost effective as well as they employ only ions of cerium and molybdenum and can find high temperature applications.

Acknowledgements

The authors thank the Council of Scientific & Industrial Research, New Delhi, India for the financial support under the New Millennium Indian Technology Leadership Initiative (NMITLI). Authors also thank Prof. K Ramachandran of Madurai Kamaraj University, Madurai for his inputs.

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