

Synthesis and characterization of environmentally benign calcium-doped $\text{Pr}_2\text{Mo}_2\text{O}_9$ 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 $\text{Pr}_{2-x}\text{Ca}_x\text{Mo}_2\text{O}_{9-\delta}$ (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 $4f^2 \rightarrow 4f^15d^1$ 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.

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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 ($\text{ZrSiO}_4:\text{Pr}$) 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 ($>1273\text{ K}$) 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 $\text{Pb}_2\text{Sb}_2\text{O}_7$, 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 semi-conducting 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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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 $\text{Pr}_2\text{Mo}_2\text{O}_9$ system from an environmental point of view. The new pigments of the formula $\text{Pr}_{2-x}\text{Ca}_x\text{Mo}_2\text{O}_{9-\delta}$ (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 $\text{Pr}_{2-x}\text{Ca}_x\text{Mo}_2\text{O}_{9-\delta}$ (x ranges from 0 to 1.0) stoichiometry were prepared by corresponding oxides: Pr_6O_{11} (99.9%), CaCO_3 (99%) and $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}$ (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, $\text{Pr}_{1.9}\text{Ca}_{0.1}\text{Mo}_2\text{O}_{9-\delta}$ (10%) and $\text{Pr}_{1.4}\text{Ca}_{0.6}\text{Mo}_2\text{O}_{9-\delta}$ (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 $\text{CuK}\alpha$ radiation with a Philips X'pert Pro diffractometer. 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 $\text{Pr}_{2-x}\text{Ca}_x\text{Mo}_2\text{O}_{9-\delta}$ with different doping content of Ca, where $x = 0, 0.10$ and 0.20 , respectively. The XRD pattern of the pure $\text{Pr}_2\text{Mo}_2\text{O}_9$ 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,

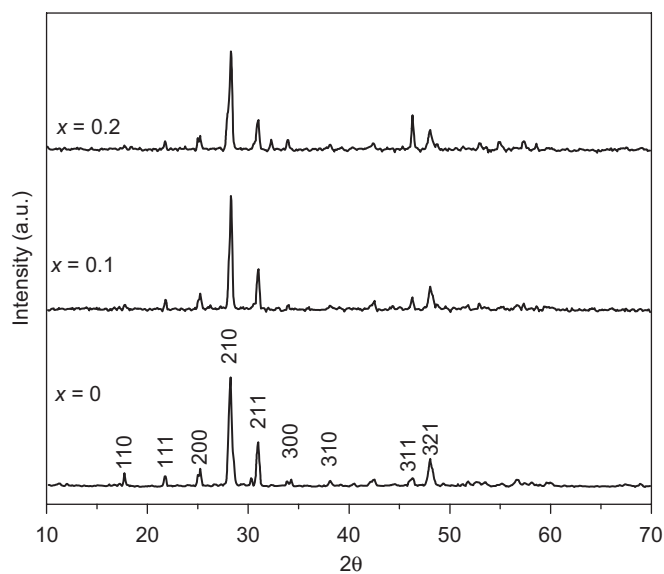


Fig. 1. XRD patterns of the $\text{Pr}_{2-x}\text{Ca}_x\text{Mo}_2\text{O}_{9-\delta}$ ($x = 0, 0.1$ and 0.2) pigments.

the lattice constant decrease first, reaches to a minimum of 0.7058 nm at 10% calcium doping content and increases to a value, which is even greater than the lattice constant of

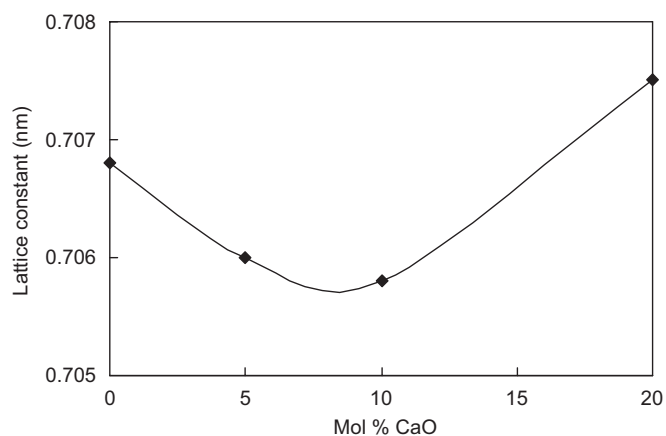


Fig. 2. Lattice constant as a function of Ca-doping content.

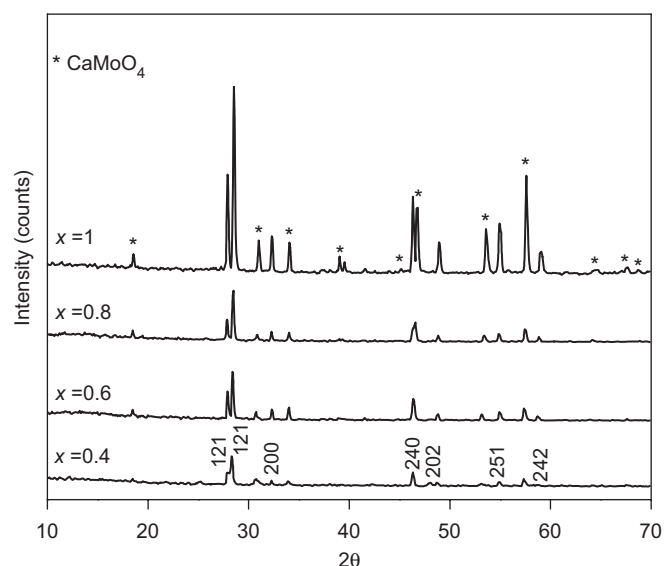


Fig. 3. XRD patterns of the $\text{Pr}_{2-x}\text{Ca}_x\text{Mo}_2\text{O}_{9-\delta}$ ($x = 0.4-1.0$) pigments.

calcium free specimen. This variation rule of lattice constant is resulted from the contribution of substitution of calcium for praseodymium and introduction of extrinsic vacancies by calcium doping, the former of which will shrink the lattice while the latter of which will expand the lattice [17]. With the increase of Ca-doping in $\text{Pr}_{2-x}\text{Ca}_x\text{Mo}_2\text{O}_{9-\delta}$ ($x = 0.4-1.0$) beyond 10%, structural transformation from cubic to monoclinic fergusonite-type (JCPDS No. 22-1180) has been noticed from the XRD patterns of the pigment samples given in Fig. 3. Further, some minor peaks appeared in the XRD patterns when the Ca concentration is greater than 10% can be indexed to CaMoO_4 . The homogeneous nature of the samples can be seen from the SEM photographs (Fig. 4) of the pigments.

The colorants with small grain size are commercially potent in pigment industries, because of their high surface area which assures high surface coverage, higher number of reflectance points and hence more scattering. The particle size distribution of the typical pigment, $\text{Pr}_{1.6}\text{Ca}_{0.4}\text{Mo}_2\text{O}_{9-\delta}$ was investigated in water as a medium and calgon as the dispersing agent. The results show a distribution with 80% of the particles being smaller than $52.43 \mu\text{m}$, 50% smaller than $22.43 \mu\text{m}$ and 10% smaller than $0.37 \mu\text{m}$. The mean particle diameter of the pigment sample was found to be $28.46 \mu\text{m}$.

The effect of calcium doping on the optical properties of $\text{Pr}_2\text{Mo}_2\text{O}_9$ based pigments was analyzed from the diffuse reflectance spectra (Fig. 5). In the reflectance spectra of the colorants, several bands in the visible region have been observed and can be assigned to the electronic transitions between $4f^2 \rightarrow 4f^15d^1$ states of Pr^{3+} . The bands in the region 440–490 (blue) and 590–625 nm (red), can be assigned based on the energy levels $^3\text{H}_4 \rightarrow ^3\text{P}_2$, $^3\text{H}_4 \rightarrow ^3\text{P}_1$, $^3\text{H}_4 \rightarrow ^3\text{P}_0$ (upper) and $^3\text{H}_4 \rightarrow ^1\text{D}_2$ and $^3\text{H}_6 \rightarrow ^3\text{P}_0$ (lower), respectively [16,19]. Weak absorptions in the blue region and strong absorptions in the red region can be observed from the reflectance spectrum of the Ca-free $\text{Pr}_2\text{Mo}_2\text{O}_9$. Thus, the pigment displays green color, since red is complementary color to green (Fig. 6). On the other hand, with increasing doping of calcium into the matrix of

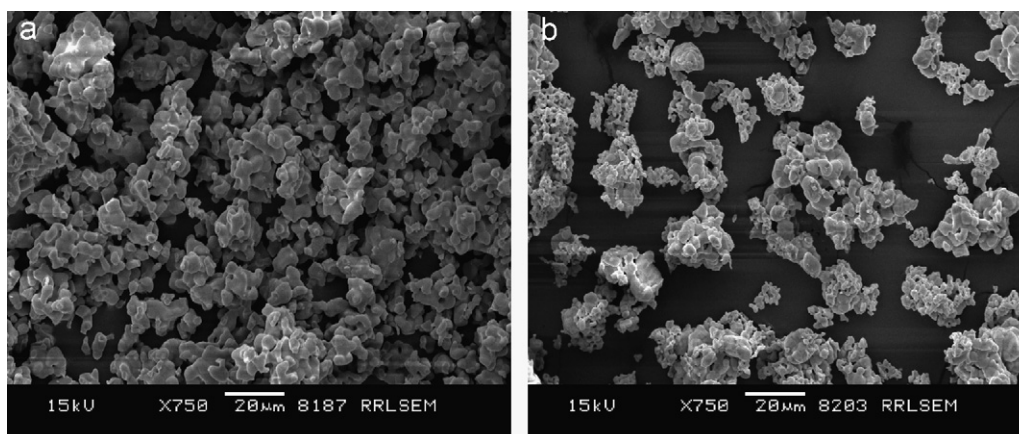


Fig. 4. SEM micrographs of (a) $\text{Pr}_{1.9}\text{Ca}_{0.1}\text{Mo}_2\text{O}_{9-\delta}$ and (b) $\text{PrCaMo}_2\text{O}_{9-\delta}$.

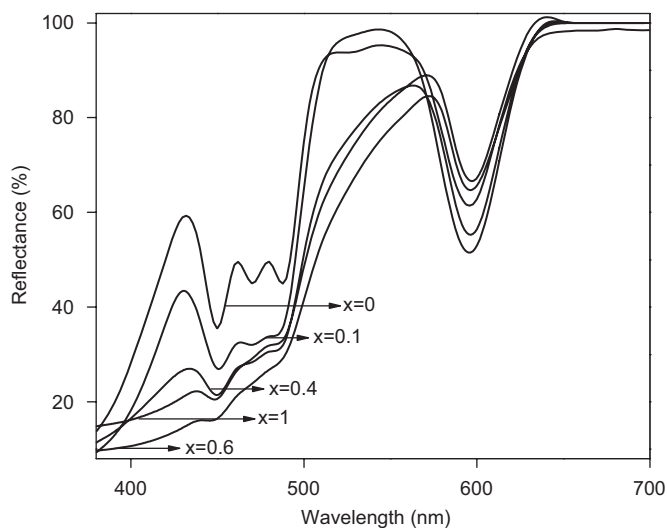


Fig. 5. Reflectance spectra of the $\text{Pr}_{2-x}\text{Ca}_x\text{Mo}_2\text{O}_{9-\delta}$ ($x = 0, 0.1-1.0$) pigments.

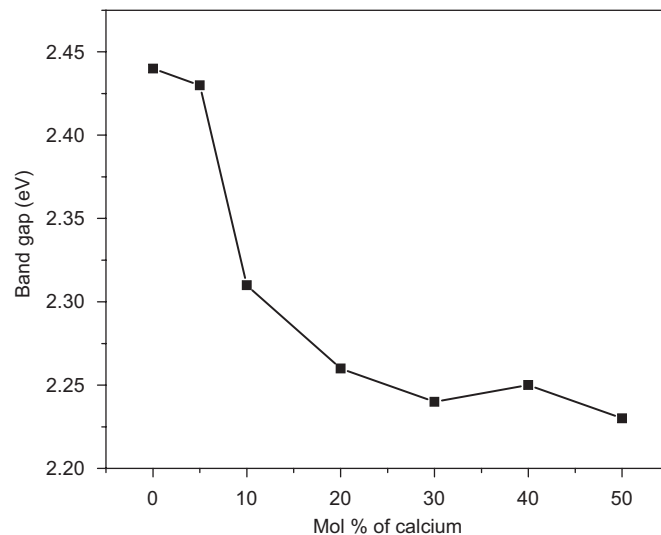


Fig. 7. Variation of band gap energy with mol% of calcium.



Fig. 6. Photograph of the $\text{Pr}_{2-x}\text{Ca}_x\text{Mo}_2\text{O}_{9-\delta}$ ($x = 0, 0.1-1.0$) pigments.

$\text{Pr}_2\text{Mo}_2\text{O}_9$, strong absorptions in the blue region can be noticed with simultaneous weakening of the absorptions in the red region. The doping of calcium for praseodymium in $\text{Pr}_2\text{Mo}_2\text{O}_9$ creates oxygen vacancies, which in turn may impart strong optical absorptions at a wavelength below 500 nm. Thus, the color of the pigment gently changes from green to yellow with increasing calcium concentration, since blue is complementary color to yellow (Fig. 6).

The CIE 1976 color co-ordinates of the pigments are summarized in Table 1. It can be clearly seen from the Fig. 7 that the band gap of the $\text{Pr}_2\text{Mo}_2\text{O}_9$ (2.44 eV) decreases with progressive doping of calcium for praseodymium (2.23 eV for $\text{PrCaMo}_2\text{O}_{9-\delta}$). The band gap was determined simply by extrapolating the linear part of the absorption curves to zero absorption [20]. 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. The increase of b^* value and decrease of $-a^*$ with the increase of dopant concentration from $x = 0$ to 0.6 in $\text{Pr}_{2-x}\text{Ca}_x\text{Mo}_2\text{O}_{9-\delta}$, indicates that color of the pigment gently changes from green to yellow. Further, at higher calcium concentrations, the yellow hue of the pigment decreases may be due to the formation of dominant phase of CaMoO_4 . The color coordinates of the present pigment, $\text{Pr}_{1.4}\text{Ca}_{0.6}\text{Mo}_2\text{O}_{9-\delta}$

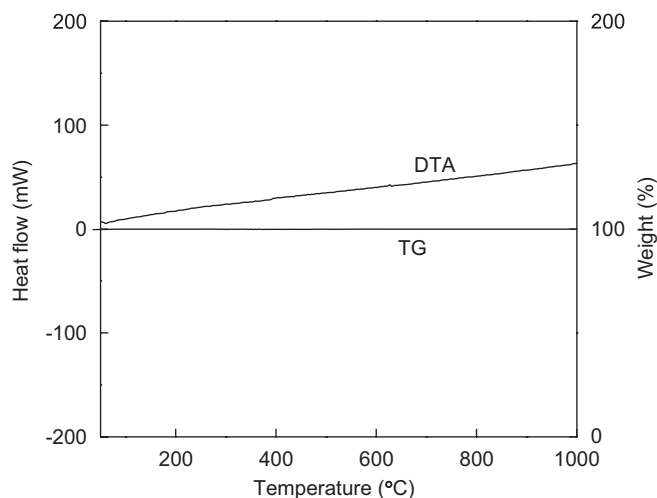
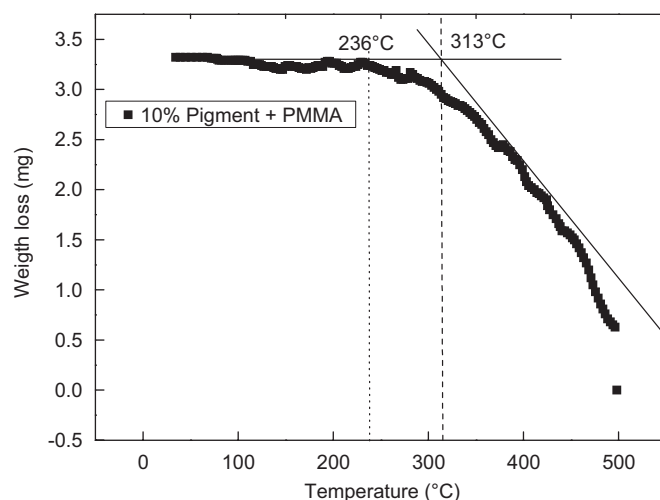
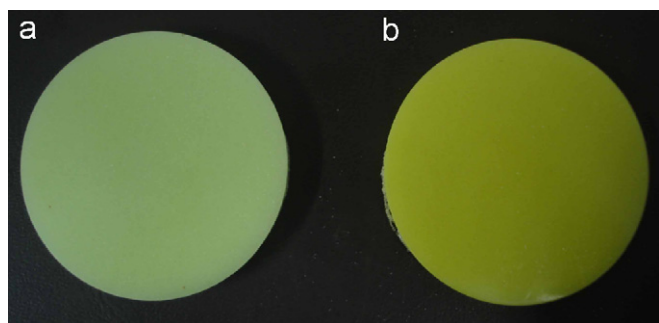
Table 1

Color coordinates and band gap (E_g) of the $\text{Ca}_x\text{Pr}_{2-x}\text{Mo}_2\text{O}_{9-\delta}$ (x ranges from 0 to 1.0) pigments

| Pigment composition | Color co-ordinates | | | Band gap (eV) |
|---|--------------------|--------|-------|---------------|
| | L^* | a^* | b^* | |
| $\text{Pr}_2\text{Mo}_2\text{O}_9$ | 87.81 | -21.57 | 37.26 | 2.44 |
| $\text{Pr}_{1.9}\text{Ca}_{0.1}\text{Mo}_2\text{O}_{9-\delta}$ | 87.48 | -22.75 | 39.56 | 2.43 |
| $\text{Pr}_{1.8}\text{Ca}_{0.2}\text{Mo}_2\text{O}_{9-\delta}$ | 88.99 | -20.34 | 45.13 | 2.31 |
| $\text{Pr}_{1.6}\text{Ca}_{0.4}\text{Mo}_2\text{O}_{9-\delta}$ | 85.12 | -12.02 | 59.69 | 2.26 |
| $\text{Pr}_{1.4}\text{Ca}_{0.6}\text{Mo}_2\text{O}_{9-\delta}$ | 81.53 | -9.01 | 59.95 | 2.24 |
| $\text{Pr}_{1.2}\text{Ca}_{0.8}\text{Mo}_2\text{O}_{9-\delta}$ | 79.18 | -6.70 | 51.97 | 2.25 |
| $\text{PrCaMo}_2\text{O}_{9-\delta}$ | 83.32 | -7.59 | 54.24 | 2.23 |
| $\text{Pr}_{1.9}\text{Ca}_{0.1}\text{Mo}_2\text{O}_{9-\delta}$ (10%) + PMMA | 79.08 | -13.88 | 35.52 | |
| $\text{Pr}_{1.4}\text{Ca}_{0.6}\text{Mo}_2\text{O}_{9-\delta}$ (10%) + PMMA | 74.99 | -5.52 | 61.05 | |

($L^* = 81.53$, $a^* = -9.01$, $b^* = 59.95$), especially yellow hue was found to be higher than that of the commercially available pigment ($L^* = 89.93$, $a^* = -3.49$, $b^* = 43.34$) Zircon Yellow (Zircon 1561: $(\text{Zr}, \text{Pr})\text{SiO}_4$ of M/s Kawamura Chemicals, Japan).

It is clear from the TG/DTA analysis, there is no loss of weight and phase transformation in the temperature range 50–1000 °C (Fig. 8). Among the series of colorants prepared, typically $\text{Ca}_{0.6}\text{Pr}_{1.4}\text{Mo}_2\text{O}_{9-\delta}$ was tested for its acid resistance and alkali resistance. A small quantity of weighed pigment sample is mixed with 2% HCl, H_2SO_4 and NaOH, and soaked for half an hour with constant stirring using a magnetic stirrer. Then, the pigment was filtered, washed with water, dried and weighed. Negligible weight loss was noticed for all the acids and alkali tested. The typical $L^*a^*b^*$ values after acid and alkali resistance tests were found to be ($L^* = 81.65$, $a^* = -9.09$, $b^* = 57.96$ and $L^* = 79.82$, $a^* = -9.83$, $b^* = 57.11$ for HCl and NaOH, respectively) same as that of the pigment powder sample. This indicates that the pigment samples are chemically and thermally stable.

Fig. 8. TG/DTA of $\text{Ca}_{0.6}\text{Pr}_{1.4}\text{Mo}_2\text{O}_{9-\delta}$ pigment.Fig. 10. TG of 10% $\text{Pr}_{1.9}\text{Ca}_{0.1}\text{Mo}_2\text{O}_{9-\delta}$ + PMMA.Fig. 9. Photograph of $\text{Pr}_{1.9}\text{Ca}_{0.1}\text{Mo}_2\text{O}_{9-\delta}$ (10%) + PMMA (a) and $\text{Pr}_{1.4}\text{Ca}_{0.6}\text{Mo}_2\text{O}_{9-\delta}$ (10%) + PMMA (b).

The coloring performance of the typically synthesized pigments ($\text{Pr}_{1.9}\text{Ca}_{0.1}\text{Mo}_2\text{O}_{9-\delta}$ and $\text{Pr}_{1.4}\text{Ca}_{0.6}\text{Mo}_2\text{O}_{9-\delta}$) was tested for its coloring application in a substrate material like PMMA. Typically, 10 wt% pigment sample was dispersed in PMMA and compressed to a cylindrical disc (Fig. 9). The color coordinates of the test pieces were measured at different locations and an average value is depicted in Table 1. The $L^*a^*b^*$ values obtained were more or less the same indicating the uniform distribution of pigment particles in the polymer matrix. The TG analysis of the pigmented polymer sample indicates that the colored polymer is thermally stable up to 236 °C (Fig. 10). The light resistance of the typical pigmented polymer ($\text{Pr}_{1.9}\text{Ca}_{0.1}\text{Mo}_2\text{O}_{9-\delta}$ (10%) + PMMA) was tested by exposing it to sunlight at various time intervals and measured the color coordinates. The $L^*a^*b^*$ values ($L^* = 79.15$, $a^* = -14.21$, $b^* = 34.09$ after 1 h; $L^* = 78.71$, $a^* = -14.21$, $b^* = 35.45$ after 4 h; $L^* = 78.62$, $a^* = -14.16$, $b^* = 35.49$ after 6 h) were found to be same as that of the unexposed sample which indicates that the pigmented polymer is resistant to light. Thus, the developed pigments may find potential applications in coloring of various plastic materials.

4. Conclusions

In summary, new environmentally secure inorganic pigments have been successfully synthesized by doping calcium into praseodymium matrix of $\text{Pr}_2\text{Mo}_2\text{O}_9$ having colors ranging from green to yellow. The band gap of these colorants gently changes from 2.44 to 2.23 eV with increasing doping of calcium. The developed pigments are found to be thermally and chemically stable and also do not contain toxic metals. Thus, the present pigments may find potential alternative to the classical toxic yellow inorganic pigments for coloring plastics and paints.

Acknowledgments

This work was supported by Council of Scientific and Industrial Research under New Millennium Indian Technology Leadership Initiative, Govt. of India. The authors wish to thank Prof. T.K. Chandrasekhar, Director, National Institute for Interdisciplinary Science and Technology, Trivandrum, India, for his constant encouragement.

References

- [1] H.M. Smith, High Performances Pigments, Wiley-VCH, Weinheim, 2002.
- [2] R.D. Swiler, US Patent 20020034644, 2002.
- [3] J.A. Badenes, M. Llusar, M.A. Tena, J. Calbo, G. Monros, J. Eur. Ceram. Soc. 22 (2002) 1981.
- [4] G.D. Nero, G. Cappelletti, S. Ardizzone, P. Fermo, S. Gilardoni, J. Eur. Ceram. Soc. 24 (2004) 3603.
- [5] K. Hill, R. Lehman, D. Swiler, J. Am. Ceram. Soc. 83 (2000) 2177.
- [6] M. Martos, B. Julian, H. Dehouli, D. Gourier, E. Cordocillo, P. Escribano, J. Solid State Chem. 180 (2007) 679.
- [7] G. Buxbaum, Industrial Inorganic Pigments, Wiley-VCH, New York, 1997.
- [8] R.D. Swiler, J.D. Terry, A.E. Axtell, US Patent 6,582,814, 2003.
- [9] M. Jansen, H.P. Letschert, Nature 404 (2000) 980.
- [10] P. Rao, M.L.P. Reddy, Dyes Pigm. 73 (2007) 292.
- [11] G. Giable, P.P. Rao, M.L.P. Reddy, Chem. Lett. 35 (2006) 1412.

- [12] N. Maso, H. Beltran, R. Munaz, B. Julian, J.B. Carda, P. Escribano, E. Cordoncillo, *J. Am. Ceram. Soc.* 86 (2003) 425.
- [13] T. Masui, S. Furukawa, N. Imanaka, *Chem. Lett.* 35 (2006) 1032.
- [14] K.J. Sreeram, S. Radhika, J.M. Devi, B.U. Nair, T. Ramasami, *Dyes Pigm.* 75 (2007) 687.
- [15] S. Furukawa, T. Masui, N. Imanaka, *J. Alloys Compd.* 418 (2006) 255.
- [16] G. George, G. Gisha, P.P. Rao, M.L.P. Reddy, *Chem. Letts.* 34 (2005) 1702.
- [17] X.P. Wang, Q.F. Fang, *Solid State Ionics* 146 (2002) 185.
- [18] R. Subasri, D. Matusch, H. Nafe, F. Aldinger, *J. Eur. Ceram. Soc.* 24 (2004) 129.
- [19] V. Sivakumar, U.V. Varadaraju, *Bull. Mater. Sci.* 28 (2005) 299.
- [20] I.H. Choi, J.I. Kim, *J. Kor. Phy. Soc.* 39 (2001) 336.