Synthesis and Characterization of Environmentally Benign Nontoxic Pigments: $RE_2Mo_2O_9$ (RE = La or Pr)

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New inorganic pigments based on rare earth molybdenum mixed oxides: $RE_2Mo_2O_9$ (RE = La or Pr) have been synthesized with a goal of preparing environmentally secure colorants. Characterizations using XRD, UV–vis spectroscopy, and CIE 1976 color coordinates assessment reveals the formation of compounds displaying colors: white for $La_2Mo_2O_9$ and yellow-green for $Pr_2Mo_2O_9$. The prepared pigments consisting of nontoxic elements and further found to be thermally and chemically stable.

Inorganic pigments are widely used in various applications such as paints, inks, plastics, rubbers, ceramics, enamels, and glasses. Unfortunately, majority of the colorants currently employed for the above applications contain toxic metals (e.g. Cr, Co, Cd, Hg, Pb, etc.) that can adversely affect environment and human health if critical levels are exceeded.[1] Thus serious need arises to search for environmentally friendly and economically viable materials for the replacement of toxic inorganic pigments.

Transition metals are used as a chromophore in a vast number of mixed metal oxide pigments.[2,3] In contrast, rare earths are used quite sparingly in inorganic pigments.[4–6] The intense coloration of rare earth based materials can arise from mostly charge-transfer interactions between a donor and acceptor with the metal ions playing generally the role of an acceptor. Dopants based on rare earth elements in mixed oxide systems offer an unique opportunity to tune the color response through the manipulation of energy gaps and delocalization phenomena in conduction and valence bands. This phenomenon offers wide scope for designing of colorants for specific applications. Recently, rare earth–transition metal oxide materials, having the general formula: $(RE_xTM)O_y$, where RE is rare earth, TM is transition metal, x ranges from 0.08 to 12 and y ranges from $x + 1$ to $2x + 2$, have been reported as novel inorganic pigments for use in plastics, paints, coatings, glass enamels, and other materials with various advantages over the traditional pigment formulations.[7] Recently, Masui et al. reported environmentally-friendly yellow pigments based on amorphous cerium tungstate and cerium silicates.[8,9] However, till date, to our knowledge no reports have been seen on the preparation and characterization of mixed metal oxide pigments, involving molybdenum and rare earth oxides. In the present study, new yellow-green and white pigments having the formula $RE_2Mo_2O_9$ (RE = La or Pr) have been synthesized by solid-state reaction of the respective oxides.

La_2O_3 (99.9%) or Pr_6O_{11} (99.9%) and $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$ (99.9%) were thoroughly mixed in the stoichiometric ratio in agate mortar with a pestle. The mixture was calcined at 900 °C for 6 h in air. The obtained powders were characterized by means of X-ray powder diffraction (XRD) using Ni filtered Cu Kα1 radiation with a Philips X'pert Pro diffractometer. Morphological analysis was performed by means of scanning electron microscope with a JEOL JSM-5600LV SEM. Optical reflectance of the powder was measured with UV–vis spectrophotometer (Shimadzu, UV-2450) using barium sulphate as a reference. Color coordinates were determined using CIE-LAB 1976 color scales.

The XRD patterns of $La_2Mo_2O_9$ and $Pr_2Mo_2O_9$ pigment samples are given in Figure 1. The intense and sharp peaks found in the diffraction patterns reveal the crystalline nature of the powders. Both the XRD patterns of the compounds are in good agreement with the powder X-ray diffraction file: PDF No. 28-0509. $La_2Mo_2O_9$ crystal exhibits two polymorphs, a low temperature monoclinic α-phase and high temperature cubic β-phase, with a reversible phase transition around 580 °C.[10] The structure of α $La_2Mo_2O_9$ was described as distorted cubic form of β structure with $2 \times 3 \times 4$ super lattice. The particle size was calculated from Debye Scherrer formula, $D = 0.9\lambda/\beta\cos\theta$, where D is the particle size, λ is the wave length of X-ray used, β and θ are the half width of X-ray diffraction lines and half diffraction angle of 2θ. The crystallite size was found to be 21–77 nm for the $La_2Mo_2O_9$ and 25–73 nm for $Pr_2Mo_2O_9$. The homogeneous and crystalline nature of the sample has also been noticed from the SEM photographs of $La_2Mo_2O_9$ and $Pr_2Mo_2O_9$ pigments.

Figure 2 shows the reflectance spectra of the pigments. High reflectance of the $La_2Mo_2O_9$ pigment lies in a broad region of 450–800 nm with maximum reflectance 93.16% at a wavelength of about 780 nm. Color coordinates data are listed in Table 1. The pigment shows very high lightness value $L^* = 95.39$ with a^* (−ve) and moderate b^* (+ve) value. The obtained chromaticity coordinates (x, y) lies very close to the white point in the chromaticity diagram. The representative picture of the pigment is shown in Figure 3a.

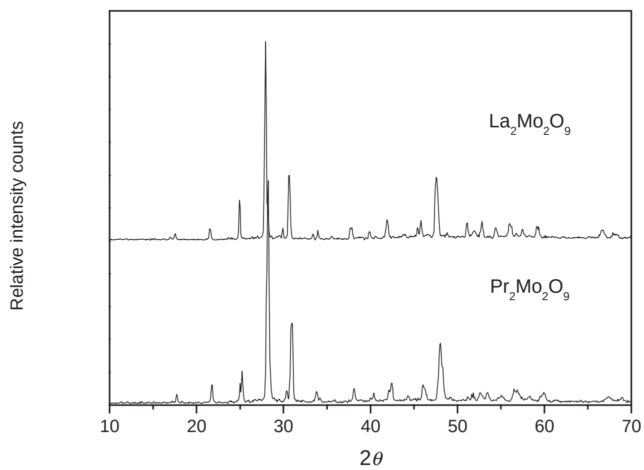

Figure 1. Powder XRD patters of the pigments.

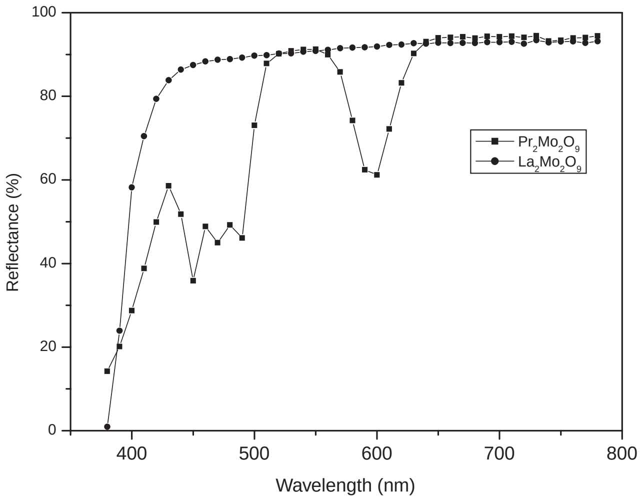

Figure 2. Reflectance spectra of the pigments.

(a) **(b)**

Figure 3. Photographs of the pigments.

Table 1. Color coordinates of $RE_2Mo_2O_9$ (RE = La or Pr) Pigments

Composition	Color coordinates			Color
	L^*	a^*	b^*	
$La_2Mo_2O_9$	95.39	−0.98	3.03	White
$Pr_2Mo_2O_9$	89.95	−15.25	24.66	Yellowish green

In the reflectance spectra of the $Pr_2Mo_2O_9$, several absorption bands in the visible region have been observed and can be assigned to the electronic transition between $4f^2 \rightarrow 4f^1\ 5d^1$ states.[11] There are bands around 448, 475, 488, 591, and 605 nm, which can be assigned based on the energy levels $^3H_4 \rightarrow {}^3P_2$, $^3H_4 \rightarrow {}^3P_1$, $^3H_4 \rightarrow {}^3P_0$, $^3H_4 \rightarrow {}^1D_2$ (upper) and $^3H_4 \rightarrow {}^1D_2$ (lower), respectively. Absorptions of the visible light around 448–500 nm (blue) and 591–605 nm (red) corresponds to appearance of yellow and green colors, because yellow and green are complementary colors to blue and red, respectively. The pigment shows lightness value $L^* = 89.95$, color coordinates with medium a^* (−ve) and b^* (+ve) values. The color coordinates lies in the yellow green region of the chromaticity diagram. The pigment exhibits yellowish green hue as can be seen from the Figure 3b.

TG/DTA analysis of $Pr_2Mo_2O_9$ pigment highlights that there is no loss of weight and phase transformation in the temperature range (50–1000 °C). Acid and base resistance of the pigments were tested and found these pigments are chemically resistant towards various mineral acids (HNO_3, HCl, or H_2SO_4) and alkalis (NaOH).

In summary, new inorganic white and yellow-green pigments: $La_2Mo_2O_9$ and $Pr_2Mo_2O_9$ have been synthesized and the properties of the pigments suggest that these products have potential to be used as environmental-secure pigments for surface coating applications.

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References and Notes

This manuscript contains pigment photograph(s). Please visit our website; http://www.csj.jp/journals/chem-lett/ for the available photograph(s).

1 "High Performances Pigments," ed. by H. M. Smith, Wiley-VCH, Weinheim (2002).
2 D. Huguenin, F. Pettini, and T. Seguelong, U.S. Patent 5,560,772 (1996).
3 A. Niesert, R. Sievers, A. Siggel, K. Langer, and M. Jansen, *Solid State Sci.*, **6**, 1149 (2004).
4 P. Sulcova and M. Trojan, *Dyes Pigm.*, **40**, 87 (1998).
5 B. Gonzalvo, J. Romero, F. Fernández, and M. J. Torralvo, *J. Alloys Compd.*, **323–324**, 372 (2001).
6 P. Prabhakar Rao and M. L. P. Reddy, *Dyes Pigm.*, **63**, 169 (2004).
7 R. Swiler Daniel, J. D. Terry, and A. Axtell Enos, U.S. Patent 6,582,814 (2003).
8 T. Masui, S. Furukawa, and N. Imanaka, *Chem. Lett.*, **34**, 1322 (2005).
9 T. Masui, H. Tategaki, and N. Imanaka, *J. Mater. Sci.*, **39**, 4909 (2004).
10 S. Tsai, M. J. Hsieh, J. C. Tseng, and H. Y. Lee, *J. Eur. Ceram. Soc.*, **25**, 481 (2005).
11 F. Kao and T. Chen, *J. Solid State Chem.*, **156**, 84 (2001).

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