



The structural and optical studies of titanium doped rare earth pigments and coloring applications



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ABSTRACT

Structural and optical investigations were performed on solid-state synthesized Pr_2MoO_6 doped with titanium at different compositions with a goal of preparing environmentally secure yellow pigments as alternate to classical toxic inorganic pigments. The systematic substitution of Pr^{3+} for Ti^{4+} in Pr_2MoO_6 matrix helps the band gap tuning of the pigment which results in the change of color from yellow to greenish-yellow and the band gap changes from 2.17 eV to 2.31 eV. The typically designed pigment samples have been evaluated for their mass tone/hiding power. The coloring performance of the developed yellow Pr_2MoO_6 pigment was evaluated by incorporating it into a polymer substrate material. The ceramic pigments obtained have been found to be interesting alternatives to the existing classical toxic inorganic pigments for applications on surface coating and coloring of plastics.

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1. Introduction

Inorganic pigments contribute to the enjoyment, beauty, and functionality of the objects we bring into the world. To ensure that their benefits far outweigh their liabilities, research efforts are directed toward the development of environmentally acceptable pigments that do not release any toxic materials into the environment during their production, use, or disposal. In the recent past, a good number of environmentally benign inorganic pigments have been designed and developed for commercial use which include yellow bismuth vanadate, red cerium sulphide, praseodymium-zircon yellow, vanadium-zirconia yellow, tin-vanadium yellow, chromates of alkaline earth metal ions, and lead antimonate, cadmium yellow, and nickel-antimony doped rutile phase TiO_2 . Among these inorganic yellow pigments, the toxicity [1] of chromium(VI), cadmium and lead based yellow pigments restricts their commercial usage; and praseodymium-zircon yellow, vanadium-zirconia yellow which are even if most popular in the market of yellow inorganic pigments, they have some limitations in bulk coloration porcelain stoneware at high temperature [2,3]. Thus serious need arises to search for environmentally friendly and economically viable materials for the replacement of toxic inorganic yellow pigments.

Recently, many rare earth-based inorganic yellow pigments have been proposed by several researchers [4,5]. Accordingly, the major objective of the present investigation is to develop environmentally secure inorganic yellow-green pigments with high temperature stability to replace the toxic ceramic pigments, currently used in the pigment industry. In the present study, a series of new colorants having the general formula $\text{Ti}_x\text{Pr}_{2-x}\text{MoO}_{6+\delta}$ (x ranges from 0 to 0.6) were synthesized by solid-state reaction of the respective oxides and characterized by UV-Visible spectroscopy. The typical designed pigment samples have also been evaluated for their surface coating applications. The thermal and chemical stabilities of the pigments and their application for coloring plastics have also been investigated.

2. Experimental

2.1. Materials and methodology

Several compositions based on $\text{Ti}_x\text{Pr}_{2-x}\text{MoO}_{6+\delta}$ (x ranges from 0 to 0.6) stoichiometry were prepared by the corresponding oxides and salt: Pr_6O_{11} (99.9%), TiO_2 (99%) and $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}$ (99.9%) supplied by Sigma Aldrich. The required precursor oxides and salt were mixed in a stoichiometric ratio, transferred to an agate mortar and homogenized by wet milling in acetone solvent for 10 min. Residual acetone was removed by evaporation and the resultant powders were calcined in platinum crucibles in a

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Nabertherm electric furnace at an optimized temperature (1000 °C) and time (3 h) in air atmosphere, followed by auto-cooling inside the furnace. The heating of the furnace was programmed to increase the temperature at 5 °C/min. The thermal treatment process was repeated three times with intermittent grinding to ensure the completion of reaction and to improve the color properties. To refine and homogenize the particle size after calcinations, the resulting products were ground in an agate mortar and utilized for the determination of their optical properties.

2.2. Methodology adopted for coloration of plastic materials

Poly (methyl methacrylate) (PMMA; S.D. Fine Chemicals, India) was utilized as a binder phase for fabricating the pigmented compact. The typical pigment samples, Pr₂MoO₆ (5 wt.%) and (10 wt.%) were ultrasonicated (Vibronics, 250 W, India) in an alcohol/water (1:4) mixture for 10 min to ensure the complete dispersion of the pigment particles. The pigment dispersion was then added to pre-prepared 90 wt% PMMA (S.D. Fine Chemicals, India and average M_w ~350,000) containing viscous solution, which was made by dissolving it in 10 wt% of Acralyn cold curing liquid (Asian Acrylates, India) over a conventional electrical coil with vigorous stirring and then it converted into a thick paste. The temperature used for processing the PMMA was 70–80 °C. Then obtained thick viscous paste after 2 h of curing, was compressed uniaxially into a form of cylindrical disc using a hydraulic press (Lawrence & Maya, India) at a pressure of 25 MPa. Further both sides of the pigmented polymer disc 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. Development of paint formulation

The typical pigment samples Pr₂MoO₆ and Ti_{0.6}Pr_{1.4}MoO_{6+δ} were ground, sieved to obtain the particles in the range of 25–45 μm and analyzed for their mass tone/hiding power. For this, a standard commercial paint composition consisting of a long oil alkyd as a binder, oleic acid as a plasticizer and aluminum stearate as a rheological agent was used. A paint formulation, consisting of 20 g (~27 wt.%) pigment, 50 g (~68 wt.%) resin, 3 g (~4 wt.%) plasticizer and 0.5 g (~0.7 wt.%) rheological agent, were mixed along with mineral turpentine in a ball mill for 60 min [6,7]. The paint formulation thus developed was used for coating.

2.4. Characterization techniques

The phase purity of the calcined pigment samples were determined using powder X-ray diffraction in a diffractometer (Philips X'pert Pro) employing Ni-filtered Cu Kα ($\lambda = 0.154060$ nm) radiation. Thermo-gravimetric (TG) and differential thermal analyses (DTA) were performed in a Pyris Diamond TG/DTA. The particle size distribution of the typical pigment sample was investigated in water medium with Sodium Hexametaphosphate as the dispersing agent using the Laser Scattering Size in uppercase Analyzer (CILAS 930).

The diffuse reflectance of the powdered pigment samples were measured in the wavelength range 380–700 nm using a UV–vis Spectrometer (Shimadzu UV-2450 with an integrating sphere attachment, ISR-2200) using illuminant D₆₅, 10° standard observer and measuring geometry d/8°. The CIE 1976 colorimetric method was used to analyze the color coordinates of the designed pigments, as recommended by Commission Internationale de l'Éclairage (CIE).

3. Results and discussion

3.1. Powder X-ray diffraction analysis

Fig. 1 depicts the XRD patterns of the pigments Ti_xPr_{2-x}MoO_{6+δ} (x ranges from 0 to 0.6) calcined at an optimized time (9 h) and temperature (1000 °C). The XRD pattern of Pr₂MoO₆ shows the characteristic reflections of the tetragonal structure - JCPDS No: 024-0913 and all the major reflections are clearly visible in the pattern [8]. The intense and sharp peaks found in the diffraction pattern reveal the crystalline nature of the compound. With the increase of Ti⁴⁺-dopant concentration in Ti_xPr_{2-x}MoO_{6+δ} ($x > 0.1$) beyond 2.5%, structural transformation from tetragonal Pr₂MoO₆ to tetragonal TiPr₂MoO₈ (JCPDS No: 049-0601) has been observed from the XRD patterns of the pigment samples, which is well supported with the literature [9]. The ionic radius of Ti⁴⁺ is 0.068 nm, which is smaller than that of Pr³⁺ (0.112 nm); hence after Pr³⁺ was partially substituted by Ti⁴⁺ in Pr₂MoO₆, the crystal lattice would be partially distorted due to cation deficiency may accommodated in the structure on one of two ways: one may be due to cationic vacancies and the other due to the excess of oxygen in the interstitial positions, giving Ti_xPr_{2-x}MoO_{6+δ}. Further, it is also clear from the XRD pattern of the pigments when $x = 0.6$, only tetragonal TiPr₂MoO₈ has been formed.

3.2. Particle size analysis

The crystallite size is 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 of Pr₂MoO₆ varies in the range 21–77 nm. The particle size distribution obtained from Cilas of the typical pigment; Ti_{0.6}Pr_{1.4}MoO_{6+δ} investigated shows a distribution with 80% of the particles being smaller than 32.61 μm, 50% smaller 14.79 μm and 10% smaller 0.37 μm. The mean particle diameter of the pigment sample was found to be 17.80 μm.

3.3. Effect of titanium doping on the optical properties of Pr₂MoO₆ pigments

The effect of titanium doping on the color of Pr₂MoO₆ based pigments was analyzed from the diffuse reflectance spectra (Fig. 2)

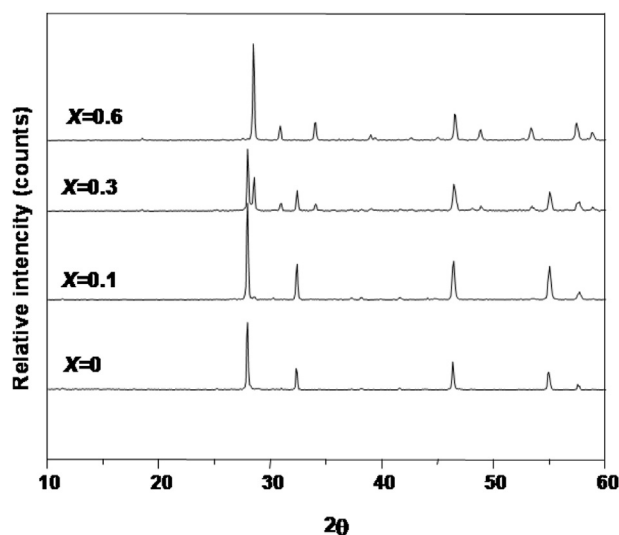


Fig. 1. XRD patterns of the Ti_xPr_{2-x}MoO_{6+δ} ($x = 0$ –0.6) pigments.

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