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Near-infrared Reflecting Yellow Inorganic Pigments Based on Molybdenum-doped Yttrium Cerate: Synthesis, Characterization, and Optical Properties

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A new series of yellow inorganic pigments possessing high near-infrared (NIR) reflectance (91–96% at 1100 nm), based on molybdenum-doped yttrium cerate was synthesized by traditional solid-state route. The band gap of the designed pigments changes from 3.01 to 2.44 eV, displaying colors ranging from ivory-white to yellow. The coloring mechanism is attributed to the O_{2p}–Mo_{4d} charge-transfer transition. The pigments are environmentally benign and effectively confer their NIR reflectance properties to a roofing material like asbestos.

Pigments possessing the ability to confer high solar reflectance have received considerable attention in recent years.[1] The inorganic class of NIR reflective pigments are mainly metal oxides and is primarily employed in two applications: (i) visual camouflage and (ii) reducing heat build up on the surface of a building roof. More than half of solar radiation consists of near-infrared radiation (52%), the remaining being 43% visible light and 5% ultraviolet radiation.[2] Both UV and IR radiation, being invisible to the human eye, have no direct influence on the color of an object. However, all radiations, whether visible or invisible, will increase the temperature of an object when absorbed by it. Overheating due to solar radiation negatively affects comfort in the built environment and contributes substantially to electrical consumption for air conditioning and release of green house gases.[3]

A pigment which has strong reflections in the NIR region (780–2500 nm) can be referred to as a "cool" pigment. However, most of the NIR reflective inorganic pigments particularly yellow (e.g., cadmium yellow, lead chromate, chrome titanate yellow, etc.) contain toxic metals, and hence their consumption is being limited. Quite a few NIR reflective inorganic pigments have been reported recently; mostly as patents, which is an indication of their vast potential applications. Replacing conventional pigments with environmentally benign cool pigments that absorb less NIR radiation can yield colored coatings similar in color but with higher NIR reflectance. The current manuscript reports on a new series of NIR reflective yellow inorganic pigments with general formula $Y_2Ce_{2-x}Mo_xO_{7+\delta}$ (x ranges from 0 to 0.5) synthesized by traditional solid-state route. The designed pigments exhibit colors ranging from ivory white to yellow and possess high NIR reflectance. Further, these pigments are environmentally benign and effectively impart their NIR reflectance properties to roofing material like asbestos.

Powder samples of the present system, $Y_2Ce_{2-x}Mo_xO_{7+\delta}$ (x ranges from 0 to 0.5) were synthesized using Y_2O_3 (99.9%), CeO_2 (99.9%), and $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$ (99.9%) as starting materials at an optimized temperature of 1500 °C for 18 h in air atmosphere (heating rate: 5 °C min^{-1}). The synthesized samples were characterized by powder X-ray diffraction (Philips X'pert Pro) with Ni-filtered Cu Kα ($\lambda = 0.15406$ nm) radiation. The diffuse reflectance of the powdered pigment samples was measured (380–780 nm) with a UV–vis spectrometer (Shimadzu UV-2450 with an integrating sphere attachment, ISR-2200) using $BaSO_4$ as a reference. The CIE 1976 $L^*a^*b^*$ colorimetric method was used to describe the color parameters. The near-infrared reflectance of the powdered pigment samples as well as the pigment coated asbestos was measured with a UV–vis–NIR spectrophotometer (Shimadzu, UV-3600 with an integrating sphere attachment) using poly(tetrafluoroethylene) (PTFE) as a reference. The particle size was investigated using a laser scattering particle size distribution analyzer (CILAS 930 Liquid). The thickness of the pigment coating on asbestos sheet was measured employing a LEICA DMRX optical microscope.

The XRD pattern of $Y_2Ce_2O_7$ given in Figure 1 shows several weak cubic type (C-type) superstructure peaks in addition to the diffraction peaks of the cubic fluorite (F)-type phase. The peaks corresponding to C-type phase are too close to F-type phase and, hence, are difficult to resolve, whereas peaks at higher 2θ values are slightly distorted indicating the possible coexistence of two phases.[4] The doping of Mo^{6+} for Ce^{4+} in $Y_2Ce_2O_7$ vanishes the C-type phase and only shows reflections of F-type phase. The introduction of Mo^{6+} up to 7.5 mol % into $Y_2Ce_2O_7$ slightly expands the lattice, which is evident from the

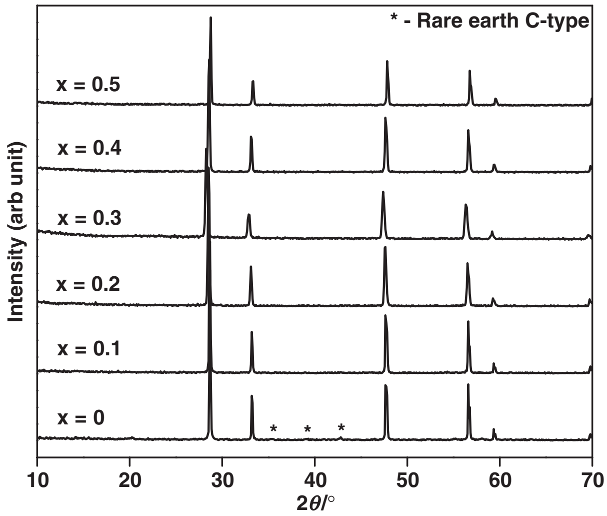

Figure 1. XRD patterns of $Y_2Ce_{2-x}Mo_xO_{7+\delta}$ (x ranges from 0 to 0.5) pigments.

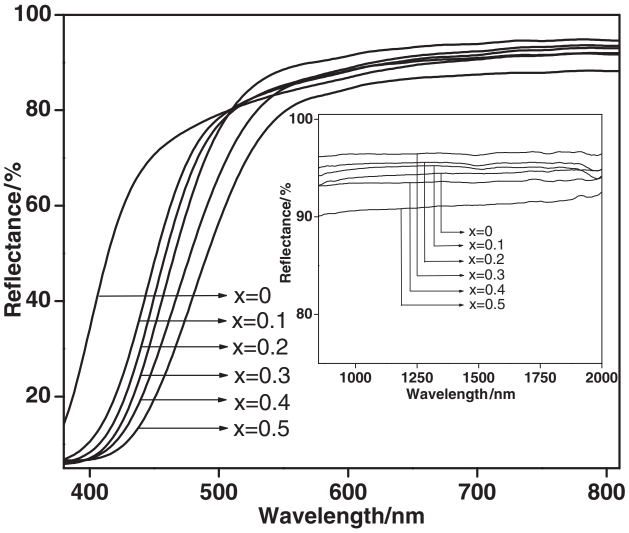

Figure 2. Diffuse reflectance spectra of $Y_2Ce_{2-x}Mo_xO_{7+\delta}$ ($x = 0$ to 0.5) pigments (NIR reflectance shown in the inset).

marginal shift in XRD patterns to lower 2θ angle. However, the cell parameter value of $Y_2Ce_2O_7$ (1.0773 nm) has not been affected with the doping of small amounts of Mo^{6+}. On the otherhand, higher doping amounts of Mo^{6+} (>5 mol %) shrinks the lattice and shifts the XRD patterns to higher angle side. The cell parameter value has been decreased to 1.0747 nm with the substitution of 12.5 mol % of Mo^{6+} (Table S1).[7] The ionic radius of Mo^{6+} (0.059 nm) is smaller than Ce^{4+} (0.097 nm), and hence a decrease in lattice parameter is expected. Particle size analysis of the typical yellow pigment, $Y_2Ce_{1.5}Mo_{0.5}O_{7+\delta}$ reveals a mean diameter of 10.62 µm.

As can be seen from the diffuse reflectance spectra of $Y_2Ce_{2-x}Mo_xO_{7+\delta}$ (x ranges from 0 to 0.5) pigments given in Figure 2, there is a strong absorption at 410 nm for $Y_2Ce_2O_7$ which is originated from charge-transfer transitions between O_{2p} valence and Ce_{4f} conduction bands of Ce^{4+} resulting in its ivory-white color. The reflectance spectra also reveal a significant shift in the absorption edges toward higher wavelengths (from 410 to 506 nm) for the molybdenum-doped samples in comparison with the parent compound. Doping of Mo^{6+} for Ce^{4+} in $Y_2Ce_2O_7$ results in a systematic decrease in band gap from 3.01 to 2.44 eV with increase in dopant concentration. As a result, the color of the pigment samples change from ivory-white to yellow (Figure S1).[7] The red shift in wavelength and the consequent decrease in band gap can be attributed to the O_{2p}–Mo_{4d} charge-transfer transitions.[5]

The NIR reflectance of $Y_2Ce_{2-x}Mo_xO_{7+\delta}$ (x ranges from 0 to 0.5) yellow powder pigments are shown in the inset of Figure 2. $Y_2Ce_2O_7$ possess an NIR reflectance of 94% at the 1100 nm region. Substitution of Mo^{6+} for Ce^{4+} up to 7.5 mol % initiates a slight increase in NIR reflectance up to 96%. However, a further increase in dopant concentration to 12.5 mol % decreases the NIR reflectance to 91%. As can be seen from the figure, all the compositions show high NIR reflectance. This indicates the potential use of these pigments as cool colorants.

The chromatic properties of the $Y_2Ce_{2-x}Mo_xO_{7+\delta}$ powder pigments are given in Table 1. As evident from the increase in b^* values, the yellowness of the pigment increases with systematic increase in Mo^{6+} concentration in $Y_2Ce_2O_7$. The hue angles ($h°$) of the pigments in the present study are found to be in the yellow region of the cylindrical color space ($h° = 70$–105 for yellow).[6]

Table 1. The color coordinates (±0.1) of the $Y_2Ce_{2-x}Mo_xO_{7+\delta}$ (x ranges from 0 to 0.5) powder pigments and band gap values

Pigment composition	Color coordinates					E_g /eV
	L^*	a^*	b^*	C^*	$h°$	
$Y_2Ce_2O_7$	95.2	−0.8	11.1	11.2	94	3.01
$Y_2Ce_{1.9}Mo_{0.1}O_{7+\delta}$	94.6	−7.3	32.0	32.8	103	2.66
$Y_2Ce_{1.8}Mo_{0.2}O_{7+\delta}$	95.4	−8.4	38.5	39.4	102	2.62
$Y_2Ce_{1.7}Mo_{0.3}O_{7+\delta}$	96.2	−9.4	46.0	46.9	102	2.57
$Y_2Ce_{1.6}Mo_{0.4}O_{7+\delta}$	91.1	−7.2	53.6	54.1	98	2.49
$Y_2Ce_{1.5}Mo_{0.5}O_{7+\delta}$	90.2	−4.5	62.4	62.6	94	2.44

Among the synthesized pigment samples, the typical pigment $Y_2Ce_{1.5}Mo_{0.5}O_{7+\delta}$ which exhibits better chromatic properties was chosen to prepare NIR reflecting coatings in a two-step process on a building roofing material like asbestos. In the first step, a small strip of asbestos is precoated with an inexpensive white pigment that is highly reflective to NIR light. In the second step, the designed pigment is applied to the precoated substrate material. The NIR reflectance spectrum of $Y_2Ce_{1.5}Mo_{0.5}O_{7+\delta}$ coated with varying thickness over a base coat of TiO_2 on a roofing material like asbestos is shown in Figure S2.[7] The spectrum clearly reveals a low reflectance of 38% (at 1100 nm) for bare asbestos. Application of the pigment on the asbestos surface increases its reflectance properties substantially. It is also observed that NIR reflectance increases with thickness of the pigment coatings. The yellow pigment over TiO_2 base coat exhibited an NIR reflectance of 83.2, 85.4, and 86.8% (at 1100 nm), respectively, for 360, 407, and 472 µm thickness.

Chemical and thermal resistance studies of the pigment were done using the typical pigment $Y_2Ce_{1.5}Mo_{0.5}O_{7+\delta}$ and found that the pigment was chemically (Table S2) and thermally stable (Figure S3).[7]

In summary, novel yellow inorganic pigments with NIR reflectance have been synthesized as environmentally benign cool colorants. The ability of the pigment to confer high NIR reflectance onto a roofing material like asbestos was also discussed.

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