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Effects of rare earth substitution on the optical properties of Bi₂MoO₆ for coloring applications



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ABSTRACT

A new class of colored inorganic compounds, BiREMoO₆ (RE = Pr, Nd, Sm, Tb and Yb) has been synthesized by a solid state route. The substitution of different rare earths for Bi^{3+} in Bi_2MoO_6 produces visible light responsive compounds by gently red shifting the absorption edge to low energy side. The visible light absorption is based on the charge transfer transitions from O_{2p} valence band to conduction band made of primary Mo_{4d} and secondary Bi_{6p} . The substitution of RE^{3+} introduces partially occupied 4*f* electronic levels in between the band gap and the position of 4*f* level depend on the number of *f* electrons which allows tuning the band gap. Thus the rare earth substitution provides an opportunity to tailor the band gap of Bi_2MoO_6 from 2.99 eV to 2.19 eV. The developed compounds exhibited different shades of yellow hue and demonstrated good coloration to plastics.

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1. Introduction

Bismuth molybdates, having the general chemical formula $Bi_2O_3 \cdot nMoO_3$, where n = 3, 2, 1, and their metal ion doped analogs have attracted much attention for several years because of their catalytic application in the area of selective oxidation/oxidative dehydrogenation or ammoxidation of lower olefins [1-4]. Recently, bismuth molvbdates have also been demonstrated to exhibit visible-light driven photocatalytic activity [5,6]. Many studies about the effects of the crystallinity, size, and morphology on the photocatalytic property of Bi₂MoO₆ synthesized by the hydrothermal process have been carried out [7]. Bismuth mixed oxides with the Aurivillius structure are represented by $(Bi_2O_2)^{2+}(A_{n-1}B_nO_{3n})$ (A = Ba, Bi, Pb; B = Ti, Nb, W, Mo). The γ -Bi₂MoO₆ with the Aurivillius structure has been found to possess unique layered structure in which perovskite slabs of corner-sharing, distorted MoO_6 octahedra are sandwiched between $(Bi_2O_2)^{2+}$ layers [6]. Shimodaira et al. have reported the photocatalytic activity of Bi₂MoO₆ and found that among the various bismuth molybdates, AS-Bi₂MoO₆ (AS-Aurivillius) with a corner sharing structure of MoO₆ octahedra possessed low band gap influenced by the octahedral coordination of oxygen ions to a molybdenum ion [6]. Compared with Bi₂WO₆ (2.77 eV), Bi₂MoO₆ with a narrower band gap (2.63 eV) has the ability to harness more sunlight [8]. Visible light absorption of Bi_2MoO_6 was revealed to be due to the transition from the valence band consisting of the O_{2p} orbitals to the conduction band primarily derived from Mo_{4d} orbitals in MoO_6 octahedra and the secondary Bi_{6p} orbitals [6].

Oxo salts of bismuth (III) exhibit interesting properties as ionic conductors, yellow pigments and selective oxidation catalyst [9–11]. Pigments on the base of Bi₂O₃ seem to be interesting, because they provide interesting color hues from yellow to orange [12]. Intense colors of these pigments are based on the incorporation of doped Ln (lanthanide) ions into the host lattice of Bi₂O₃ [12–16]. The mixed pigment $4BiVO_4 \times 3Bi_2MoO_6$ exhibit brilliant greenish yellow to reddish yellow shades [17]. To exploit materials for optoelectronic applications, it is essential to tune the optical band gap which can be done by way of doping with various metal ions. Band gap tailoring at the ultraviolet end and visible region of the solar spectrum is of considerable interest for large area optical coatings. Generally, the band gap transition is mainly related to M-d (metal d orbitals) and O-p (oxygen p orbitals) states, but the localized character of RE 4f levels would make contribution to tune the band gap. Zou et al. have reported the modification of band structure by controlling the ionic radius (r_R^{3+}) in Bi₂RNbO₇ photocatalysts and the dependence of band gap on the rare earth f bands have been well explained [18]. Optical and electronic properties of a series of novel rare earth bismuth tungstate compounds have been recently reported [19]. Liu et al. have reported formation of solid solution as the feasible method to

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adjust the conduction band and valence band to obtain a visible light driven photocatalyst by synthesizing BiYWO₆ [20]. The rare earths, Yb and Er have been used in the fiber for realizing optical switching to reduce the switching power [21,22]. A low band gap material like Bi₂MoO₆ offers wide scope of tuning the band gap by substituting different metal ions to produce various shades. The strongly localized f shell in rare earth metals which determines the similar chemical and physical properties of the lanthanides can influence the band structure of bismuth molybdate. The band gap change depends on the number of *f* electrons of the substituted rare earth ion. In the present study, new series of rare earth based compounds, BiREMoO₆ (RE = Pr, Nd, Sm, Tb and Yb) have been prepared. The influence of RE *f* bands on the optical property of Bi₂MoO₆ has been investigated through optical absorption studies and band structure analysis. Their color properties, as possible potential yellow inorganic pigments have been investigated for coloration of plastics.

2. Experimental

2.1. Materials and methodology

Compositions based on BiREMoO₆ (RE = Y, Pr, Sm, Nd, Tb and Yb) were prepared from the corresponding oxides: Bi_2O_3 , Pr_6O_{11} , Sm_2O_3 , Nd_2O_3 , Tb_4O_7 , Yb_2O_3 , and MoO_3 (99.9%) supplied by M/s Sigma–Aldrich. Stoichiometric proportions of the chemicals were weighed and were thoroughly wet mixed in an agate mortar with acetone as the wetting medium for 1 h and dried in an air oven. This process of mixing and drying was repeated thrice to obtain a homogeneous mixture. Bi_2MoO_6 was calcined at $1100 \,^\circ$ C for 6 h, BiPrMoO_6 was calcined at 950 $\,^\circ$ C for 9 h and BiREMoO₆ (RE = Nd, Tb and Yb) were calcined at 1000 $\,^\circ$ C in air. The calcination 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. Characterization techniques

The crystalline nature and phase purity of the samples were investigated using powder X-ray diffractometer with Ni-filtered Cu-K α (K α_1 = 1.54060 Å, K α_2 = 1.54443 Å), radiation using a PANalytical Philips X'pert Pro diffractometer. Data was collected over a 2θ range from 10° to 90° . The morphology of the synthesized samples was recorded on a scanning electron microscope JEOL JSM-5600 model, with an acceleration voltage of 15 kV. The diffuse reflectance of the powdered pigment samples were measured (200-780 nm) with a UV-vis Spectrophotometer (Shimadzu UV-2450 with an integrating sphere attachment, ISR-2200) using barium sulphate as the reference. The color coordinates were determined by coupling analytical software (UVPC Color Analysis Personal Spectroscopy Software V3, Shimadzu) to the UV-2450 spectrophotometer. The CIE 1976 *L***a***b** colorimetric method was used, as recommended by the Commission Internationale de l'Eclairage (CIE).

Among the pigment compositions prepared, the typical pigment sample BiTbMoO₆ was dispersed in polymer matrix like PMMA to test their coloring performance. The pigment, BiTbMoO₆ (10 wt%) was ultrasonicated in an alcohol-water (1:4) mixture for 10 min to ensure complete dispersion of the pigment particles. A viscous solution of PMMA (90 wt%) was made using a conventional electrical coil heater. The pigment dispersion was slowly added with stirring and converted to a thick paste. The paste after 2 h curing was compressed uniaxially into a form of cylindrical disk using a hydraulic press 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 color coordinates of the pigmented compacts were examined to assess the coloration.

3. Results and discussion

3.1. Structural studies

The powder XRD patterns of Bi₂MoO₆ and BiREMoO₆ (RE = Pr, Nd, Sm, Tb and Yb) are presented in Fig. 1. Bi₂MoO₆ crystallizes with a monoclinic phase with the space group P21/c and all the reflections are indexed as per the JCPDS data base number 00-033-0208. For BiREMoO₆, all the diffraction peaks could be attributed to a monoclinic BiREMoO₆ type structure with different space groups depending on the rare earth element. Crystallographic analysis reveals that the BiTbMoO₆ and BiYbMoO₆ compounds belong to the monoclinic system with space group P2/c. Both BiPrMoO₆ and BiNdMoO₆ crystallize with monoclinic crystal lattice (space group C2/c). The formation of monoclinic BiSmMoO₆ (space group C2) can be judged from the diffraction pattern.

3.2. Morphological analysis

The primary particles of the pure Bi₂MoO₆ exhibited a mixture of relatively elongated rod shapes, in which the average length was $25 \,\mu\text{m}$ and were agglomerated. SEM analysis (Fig. 2) of Bi₂MoO₆ and BiREMoO₆ (RE = Pr, Nd, Sm, Tb and Yb) reveals the changes in the morphology from long rod type to small irregular shaped particles. Rare earth substitution in Bi₂MoO₆ is found to decrease the particle size. As seen from the morphological analysis, it can be concluded that the substitution of smaller rare earth elements in Bi₂MoO₆ significantly influences the crystal growth and prefers morphology entirely different from the rod shaped structure of the host material. Even though all the compounds crystallize in the monoclinic crystal system, Bi₂MoO₆ and BiREMoO₆ fall under different space groups depending on their lattice type. This might have caused the change in morphology with the substitution of rare earth ions. The effective solid solution formation was checked by energy dispersive spectrophotometer (EDS) analysis attached with TEM. Fig. 3 shows the EDS analysis of selected samples BiNdMoO₆, BiTbMoO₆ and BiYbMoO₆ and identifies the presence of all the expected elements. The stoichiometric formula calculated from the semiquantitative EDS results are in close agreement with the theoretical formulae. This also further confirms the homogeneity of the phase formed.



Fig. 1. Powder X-ray diffraction patterns of Bi_2MoO_6 and $BiREMoO_6$ (RE = Pr, Nd, Sm, Tb and Yb) compounds. S.G refers to space group. For $BiREMoO_6$, all the diffraction peaks could be attributed to a monoclinic $BiREMoO_6$ type structure with different space groups depending on the rare earth element.



Fig. 2. SEM photographs of Bi₂MoO₆ and BiREMoO₆ (RE=Pr, Nd, Sm, Tb and Yb). Substitution of different rare earth metal ions in Bi₂MoO₆ changes the morphology of the particles from long rod type particles to small irregular shaped particles.

3.3. Optical properties

The colors of Bi₂MoO₆ and BiREMoO₆ are presented in Fig. 4. Bi₂MoO₆ exhibits a pale yellow color. Tb and Yb substitution in Bi₂MoO₆ leads to yellow color whereas Pr substitution produces greenish yellow color. Light green and light yellow colors were obtained for Nd and Sm substituted Bi₂MoO₆, respectively. Fig. 5 shows the combined absorption spectra of Bi₂MoO₆ and BiREMoO₆ (RE = Pr, Nd, Sm, Tb and Yb). For oxides containing RE³⁺, there is strong optical absorption in the near-UV region based on O_{2p}–Mo_{4d} charge transfer transition. The absorption edge typically extends into the visible region to give various color shades with different rare earths. The optical absorption edge critically depends on the rare earth element (RE³⁺) present in the samples. Bi₂MoO₆ absorbs below 400 nm with a sharp edge at ~400 nm. Rare earth substitution significantly shifts the absorption edge to low energy side. BiSmMoO₆ and BiNdMoO₆ show a sharp absorption edge at around 450 nm, with characteristic absorption bands at about 523, 587, 682 and 750 nm for BiNdMoO₆. The spectra of BiPrMoO₆ show several well-resolved bands attributed to the *f*–*f* transitions of the Pr³⁺ ions. BiPrMoO₆ displays greenish yellow hue as it absorbs in blue and red region of the visible spectrum. More red shift was observed for BiYbMoO₆ and BiTbMoO₆ with steep absorption edge at ~500 nm. Tb and Yb substituted bismuth molybdates absorb blue light efficiently and the compounds exhibit yellow hue. The band gap energy is decreased with the substitution of RE³⁺ in Bi₂MoO₆ from 2.99 to 2.19 eV (Table 1).

The reflectance and absorbance of a material can be affected by a combination of factors such as mean particle size, particle size distribution, particle shape, particle porosity, packing density, surface texture, its chemical composition, and wavelength. Rare earth substitution in Bi_2MOO_6 is found to decrease the particle size and change the morphology from long rod type to small irregular shaped particles. Even though the particle morphology changes



Fig. 3. EDS analysis of BiREMoO₆ (RE = Nd, Tb and Yb) pigments and identifies the presence of all the expected elements.



Fig. 4. Photographs of Bi_2MoO_6 and $BiREMoO_6$ (RE=Pr, Nd, Sm, Tb and Yb) compounds. Tb and Yb substitution in Bi_2MoO_6 leads to yellow color whereas Pr substitution produces greenish yellow color. Light green and light yellow colors were obtained for Nd and Sm substituted Bi_2MoO_6 , respectively. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

with substitution of rare earth metal ion, the expected increase in reflectance is not observed and instead absorbance is found to increase in the visible region. This may be attributed to the band gap engineering in the charge transfer transitions of bismuth molybdate by the intermediate *f* orbitals of different rare earth metal substituent which overrules the effect of particle size effect.

3.4. Band gap engineering in BiREMoO₆ (RE = Pr, Nd, Sm, Tb and Yb)

The band gap energy of BiREMoO₆ calculated from UV–vis absorption spectra (Fig. 5) indicates a sudden decrease in band gap with red shift in the absorption edge of Bi_2MoO_6 . Pure Bi_2MoO_6



Fig. 5. Absorbance spectra of Bi_2MoO_6 and $BiREMoO_6$ (RE = Pr, Nd, Sm, Tb and Yb). The substitution of different rare earths for Bi^{3+} in Bi_2MoO_6 produces visible light responsive compounds by gently red shifting the absorption edge to low energy side. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

Table 1

Color co-ordinates and band gap of Bi_2MoO_6 and $BiREMoO_6$ (RE = Pr, Nd, Sm, Tb and Yb). The band gap decreases with the incorporation of RE^{3+} into the Bi_2MoO_6 matrix.

Sample	Color c	Color co-ordinates					
	L*	<i>a</i> *	b^*	С*	h°		
Bi ₂ MoO ₆	93.4	-4.3	11.5	12.2	69.4	2.99	
BiPrMoO ₆	84.3	-12.6	49.1	50.7	104.4	2.47	
BiNdMoO ₆	74.2	4.7	8.25	9.49	60.3	2.51	
BiSmMoO ₆	91.2	-7.4	39.5	40.2	100.6	2.54	
BiTbMoO ₆	79.1	16.0	61.6	63.3	75.4	2.19	
BiYbMoO ₆	78.3	17.7	58.8	61.4	73.4	2.20	

showed a clear absorption edge at around 400 nm, and the corresponding band gap energy is 2.99 eV. This can be explained by the reported band structure of the AS-Bi₂MoO₆, where O_{2p} forms the valence band and the conduction band is derived from the Mo_{4d} orbitals and the Bi_{6p} orbitals [6]. The contribution of each orbital is not equivalent, although the LUMO consisted of hybrid orbitals of Mo_{4d} and Bi_{6p} orbitals. The Mo_{4d} orbitals mainly contributed to the LUMO rather than the Bi_{6p} orbital. Visible light absorption of AS-Bi₂MoO₆ was revealed to be due to the transition from the valence band consisting of the O_{2p} orbitals to the conduction band derived from the primary Mo_{4d} orbitals in MoO₆ octahedra and the secondary Bi6p orbitals. The band structure model of BiREMoO₆ (RE = Pr, Nd, Sm, Tb and Yb) can be illustrated schematically as shown in Fig. 6. As shown in the schematic diagram, the band gap is therefore the difference in energy between the top of the O_{2p} band and the bottom of the Mo_{4d} band for Bi2MoO6. Red shifted absorption edge observed for RE substituted bismuth molybdate depends on the partly filled RE 4f shell.

Shift of optical absorption edge towards lower energy side is continued from Sm to Pr compounds, suggesting that the filled 4f levels are positioned between the O_{2p} valence band and $Mo_{4d} + Bi_{6s}$ conduction band. The variation of E_g can be explained by the energy of the RE 4f levels lowering in energy with an increasing occupation of 4f electrons. Prokofiev et al. have studied periodicity in the optical band gap variation of Ln sesquioxides [23]. According to their report, the occupied 4f band in Ce₂O₃, Pr₂O₃, and Tb₂O₃ lies above the O_{2p} band, and thus, 4f–5d transition may determine the



Fig. 6. Band structure models of Bi_2MoO_6 and $BiREMoO_6$ (RE = Pr, Nd, Sm, Tb and Yb). The band gap is therefore the difference between the top of the O_{2p} band and the bottom of the Mo_{4d} band for Bi_2MoO_6 . Red shifted absorption edge observed for RE substituted bismuth molybdate depends on the partly filled RE 4*f* shell. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

band gap energy. The RE 4f energy level gradually becomes lowered with an increase of their atomic number, finally lying in the valence band, which results in a monotonic increase of band gap energy from Ce_2O_3 to Sm_2O_3 . Considering this, we can assume the band structure of BiSmMoO₆ to be composed of valence band consisting of the O_{2p} orbitals and the conduction band primarily derived from the Mo_{4d} orbitals in MoO_6 octahedra and the secondary Bi_{6p} orbitals. Occupied Sm 4f⁵orbitals are overlapped with the valence band. Correspondingly, the band gap is reduced to 2.54 eV from 2.99 eV with the substitution of Sm^{3+} . But the Nd $4f^3$ and Pr $4f^2$ filled levels are still raised in energy due to the lower number of 4f electrons. For BiNdMoO₆the band gap is still lowered to 2.51 eV as Nd $4f^3$ level lies just above the O_{2p} valence band. Similar band structure with partially filled Pr $4f^2$ orbital located within the band gap above the valence band can be assumed for BiPrMoO₆. Thus the highest occupied level is formed by Sm 4f overlapped with O_{2p} for BiSmMoO₆ or by filled Pr 4f lying above the O_{2p} bands for BiPrMoO₆.

Tb and Yb substituted compounds show minimum band gap values compared to other rare earth compounds in contrast to the increased number of 4f electrons. For Ce, Pr and Tb the energy of 4f-5d transition is lower than for the rest of the lanthanides. It is the transition that determines the absorption edge E_{g} of these oxides (4f band lies above valence band) [23]. This explains the lower E_g values of Tb compound. As soon as the *f*-band enters into the 2p band, the E_g values become constant. The 4f ground state energy levels trend for Pr³⁺, Nd³⁺, Sm³⁺ and Tb³⁺ in the current system is in agreement with the Dorenbose theory [24,25]. However, for Yb³⁺ the observed band gap points out a higher ground state energy level than the other lanthanides, which is not in accordance with the expected trend. It is to be mentioned here that Tb³⁺ is a 'hole trap' and Yb³⁺ is an 'electron trap'. Due to this Yb³⁺ tend to Yb²⁺ in the system. For the divalent lanthanides the 5d levels will be close to the bottom of the conduction band and the ionization energy E_{dC} is minimal for Yb^{2+.} As a consequence, this positions the 4f ground level of Yb^{2+} to much below the conduction band, which is much above the 4f ground levels of other trivalent rare earths (Pr³⁺, Nd³⁺, Sm³⁺ and Tb³⁺). This difference in RE 4f levels and the corresponding difference in the band gaps lead to different color, as can be seen from Table 1.



Fig. 7. Photograph of BiTbMoO₆ (10%) dispersed in PMMA. The test piece exhibits uniform distribution of pigment particles in the polymer matrix.

Table 2

 $L^*a^*b^*Ch^\circ$ values of pigmented polymer compact BiTbMoO₆ (10%) dispersed in PMMA after exposure to sunlight.

Exposure time (h)	L*	a*	b*	С	h°
0	80.98	13.2	63.12	64.48	78.18
1	77.50	15.20	58.55	60.49	75.44
2	78.28	15.66	59.53	61.56	75.28
5	83.50	17.40	62.14	64.53	74.34
12	81.98	16.13	60.38	62.49	75.04
24	80.65	17.02	61.72	64.02	74.58
48	80.19	16.08	62.74	64.76	75.62

3.5. Color characterization

The CIE 1976 color co-ordinates of the powdered compounds are summarized in Table 1. The brightness (L^*) is slightly lowered with the introduction of rare earth metals but a^* (redness) value is found to escalate. The *b*^{*} value corresponding to yellow chromaticity depends on the identity of the RE³⁺ element. From Table 1, it follows that the *b*^{*} coordinate has a wide interval of values ranging from 11.5 to 61.6. This is also reflected in its chroma value (C^*) which gets enhanced from 12.2 to 63.6. The richest yellow hue was obtained for BiTbMoO₆ and BiYbMoO₆ compounds. The color shade is shifting from off white for Bi₂MoO₆ to light yellow color for BiSmMoO₆, greenish yellow for BiPrMoO₆ and bright yellow color for Tb and Yb containing bismuth molybdate. The hue angle values of the samples lie in the yellow region of the cylindrical color space (h° = 70–105 for yellow) [26]. The color co-ordinates of the yellow compounds BiTbMoO₆ and BiYbMoO₆ sample are found to be higher than that of the powder BiVO₄ (L^* = 68.0, a^* = 16.5, $b^* = 42.35$) reported elsewhere in the literature [27].

3.6. Coloration of plastics

The coloring performance of the typically synthesized samples, BiTbMoO₆ was tested for its coloring application in a substrate material like PMMA. Typically, 10 wt% pigment samples were dispersed in PMMA and compressed to a cylindrical disc (Fig. 7). The color co-ordinates of the test pieces were measured at different locations. The average $L^*a^*b^*$ values (L^* = 80.98, a^* = 13.2, b^* = 63.12) obtained were similar indicating the uniform distribution of pigment particles in the polymer matrix. The light resistance of the typical pigmented polymers was tested by exposing it to sunlight at various time intervals and measured the color coordinates. The $L^*a^*b^*$ values of pigmented compact were found to be nearly same as that of the unexposed sample which indicates that the pigmented polymer is resistant to light (Table 2). Thus, the developed compounds may find potential application in the coloring of various plastic materials as yellow pigments.

4. Conclusions

A series of novel rare earth substituted bismuth molybdate compounds, BiREMoO₆ (RE = Pr, Nd, Sm, Tb and Yb) have been synthesized and elucidated the role of RE 4*f* levels on the optical properties of Bi₂MoO₆. It is observed that the substitution of rare earth metals for bismuth in Bi₂MoO₆ red shifted the absorption edge. This leads to yellow color for Sm, Yb and Tb and greenish yellow color for Pr and light green color for Nd. Rare earth ion dependence of the band gap is governed by the position of energy level of RE 4*f* levels in the band structure, which lowers with increasing occupation of *f* electrons in RE³⁺. The partially occupied 4*f* levels close to the valence band edge decreases the band gap of Bi₂MoO₆ and produces various color shades. The position of 4*f* band depends on the number of *f* electrons in RE and hence is the

variation of band gap. The developed compounds demonstrated good coloration to plastics with effective light resistance.

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