NIR emitting phosphors based on $PbMoO_4$ for modification of solar spectrum

Arpita Vyas[a], C.P. Joshi[a], S.V. Moharil[b],*

[a] Physics Department, Shri Ramdeobaba College of Engineering and Management, Katol Road, Nagpur 440013, India
[b] Department of Physics, Rashtrasant Tukadoji Maharaj Nagpur University, Nagpur 440010, India

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ABSTRACT

Molybdate luminescence is usually totally quenched at room temperature. However, molybdate anions can sensitize the luminescence of other activators like Sm^{3+}, Eu^{3+}, Tb^{3+}, Dy^{3+}, etc. These ions emit in the visible region. No emission in the Near Infrared (NIR) region that is based on sensitization by MoO_4^{-2} anion has been reported, though NIR emission has applications in several fields. In this work NIR emission is reported in $PbMoO_4$ doped with Nd^{3+} or Yb^{3+}. The emission follows excitation by near ultraviolet (nUV) light that can be absorbed by MoO_4^{-2} anion and subsequent energy transfer to Nd^{3+} or Yb^{3+}. Mechanisms of energy transfers based on cooperative energy transfer (CET) and cross relaxation followed by NIR emission are suggested. It is also suggested that $PbMoO_4$:Yb^{3+}/Nd^{3+} phosphors hold a potential for applications requiring NIR emission that can be excited by nUV light; e.g. in photovoltaics based on c-Si.

1. Introduction

PbMoO₄ also known as wulfenite [1] is a semiconductor having band gap very close to that of widely studied materials GaN and ZnO. Crystal structure had been solved quite early [2,3]. Based on semiconducting properties, $PbMoO_4$ has been studied for a variety of applications such as photocatalysis [4–6], photocatalytic water splitting for hydrogen generation [7], dye degradation [8,9], photoconductivity [10], etc. Due to its excellent chemical and thermal stability it finds use as a solid lubricant at elevated temperatures in oxidizing environments [11]. $PbMoO_4$ exhibits some interesting luminescence properties as well [5] which have been noticed quite early [12,13]. When excited with high-energy radiation (such as ultraviolet), $PbMoO_4$ shows a characteristic blue–green emission related to charge-transfer transitions within the tetrahedral $[MoO_4]$ clusters [14]. A green emission related to intrinsic transitions of the $[MoO_4]$ complex and deltahedral $[PbO_8]$ clusters in the tetragonal lattice has also been reported sometimes [15]. Defects in the crystal structure have also been held responsible for the green emission [14]. Owing to high density, short decay time and high radiation resistance, it is an attractive scintillator for studying high-energy physics [16]. $PbMoO_4$ has also been used as a host, in particular for lanthanide activators such as Eu^{3+}, Tb^{3+}, Tm^{3+} [17], etc. Based on these studies, it had been also developed as a laser host, especially for lasers based on Nd^{3+} emission [18]. However, no host to activator energy transfer has been reported, though $PbMoO_4$ absorbs UV light efficiently. In fact there are several channels for light absorption and energy transfer in $PbMoO_4$ host [19]. Being a semiconductor with band gap around 3.2 eV, there can be efficient absorption of light below 380 nm and subsequent edge emission. MoO_4^{-2} molecular ion also has absorption in near UV region. Though its emission is quenched at temperatures well below the room temperature [20,21], it can transfer energy to suitable activators. Pb^{2+} is also a well known ns^2 activator [22,23] and it can act as a sensitizer for a variety of ions like Mn^{2+} [24], Tb^{3+} [25], Gd^{3+} [26], Dy^{3+} [27,28], etc.

Uptill now most of the properties studied and applications proposed for $PbMoO_4$ are related with its semiconducting properties. Luminescence properties of $PbMoO_4$ have not been fully exploited except for few applications mentioned above. $PbMoO_4$ has strong absorption in near UV (nUV) region. If the absorbed energy can be transferred to a suitable activator, efficient phosphors can be obtained. If emission of Nd^{3+} and Yb^{3+} can be sensitized by $PbMoO_4$ host then efficient near infrared (NIR) emitting phosphors can materialize. NIR emission can be important for several applications like bioimaging [29], telecommunications [30], solar photovoltaics [31], Photodynamic therapy [32], photostimulated localized hyperthermia [33] etc. In particular, nUV/blue absorbing, NIR emitting phosphors are desired for improving performance of c-Si solar cell. Currently the commercial solar cell available in the market is the crystalline silicon solar cell with the conversion efficiency just above 15% [34] though, theoretically the maximum efficiency of c-Si solar cells can be reached

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* Corresponding author.
E-mail address: svmoharil@yahoo.com (S.V. Moharil).

up to 29%; as decided by the Shockley-Queisser limit [35]. Majority of the energy losses (over 70%) are related to the spectral mismatch of the incident solar photon energies to the energy gap (E_g = 1.12 eV for c-Si solar cell) of a solar cell [36]. Photons of low-energy are not absorbed (transmission losses) while absorption of high-energy photons with the excess energy is transformed into kinetic energy of a generated electron-hole pair, and subsequently converted to heat (thermalization loss). Effective harvesting of solar energy from ultraviolet and near infrared photons is a necessary condition for improving the efficiency of solar cells [37] which indirectly reduces the cost of electricity compared to the conventional means [38,39]. For a long time, researchers have strived to overcome the defects and limitations of solar cell. Following the predictions of Trupke et al. [40] that the efficiency of c-Si solar cell can be improved up to 38.4% by modifying the solar spectrum by a quantum cutting downconverting phosphor which converts one photon of high energy into two photons of lower energy, large number of papers have appeared on the subject [41–45].

In this paper we report energy transfer from MoO_4^{-2} anion to Nd^{3+} and Yb^{3+} in $PbMoO_4$ host resulting in NIR emission that can be useful for modifying the solar spectrum so as to match the response of c-Si solar cells.

2. Experimental

$PbMoO_4$ phosphor doped with Nd^{3+} and Yb^{3+} were prepared by solid state reaction between lead carbonate and molybdenum trioxide. $PbCO_3$ was thoroughly mixed with stoichiometric amount of MoO_3, Nd/Yb nitrate solutions in desired quantities were sprinkled on this mixture and then it was heated in the furnace in 3 steps of 300 C for 1 h, 600 C for 1 h and finally 850 C for 4 h. It was then slowly cooled to room temperature.

The crystalline phases of the synthesized samples were identified by x-ray diffraction (XRD) patterns recorded on XPERT-PRO diffractometer using Cu K_α (λ = 1.54059 Å) radiation. The NIR photoluminescence (PL) and photoluminescence excitation (PLE) spectra were measured by a Photon Technology International QM-51 NIR spectrophotometer. Reflectance spectra were recorded on Hitachi F-7000 spectro-fluorimeter by using "synchronous" mode. $BaSO_4$ was used as a reference standard.

3. Results and discussion

Formation of $PbMoO_4$ host following the solid state reaction was confirmed by XRD. In the system Pb-Mo-O there are three compounds of hexavalent molybdemnum listed in ICDD database, viz. $PbMoO_4$ (89–8706), Pb_2MoO_5 (24–0579) and Pb_5MoO_8 (87–0482). XRD pattern of the synthesized compound shows an excellent match with ICDD file 89–8706 (Fig. 1). There is no line around 25.652 that distinguishes Pb_2MoO_5 from $PbMoO_4$, and 10.659 that is characteristic of Pb_5MoO_8. Phase pure $PbMoO_4$ is thus obtained by the procedure described here. $PbMoO_4$ crystallizes in a tetragonal space group $I4_1/a$ with two formula units per primitive cell [2]. A peculiar feature of $PbMoO_4$ is the existence of two different clusters, the $[MoO_4]_2$ in tetrahedral configuration, and divalent Pb which shares corners with eight adjacent oxygen atoms, forming a $[PbO_8]_2$ configuration (Fig. 2).

Fig. 3 shows reflectance spectra for various samples. For $PbMoO_4$ (curve a), there is onset of strong absorption at about 380 nm, as indicated by a sharp drop in the reflectance. These results are in good agreement with those reported in the literature [4,14]. Absorption edge becomes more diffused in doped samples (curves b and c). There is some structure in the reflectance curve for Nd^{3+} doped sample due to f-f transitions.

Fig. 4 shows PL spectra for $PbMoO_4$ phosphor doped with Yb^{3+}. Intense emission around 982 nm corresponding to transition $^2F_{5/2} \rightarrow {}^2F_{7/2}$ can be seen for 386 nm excitation (curve a). There is
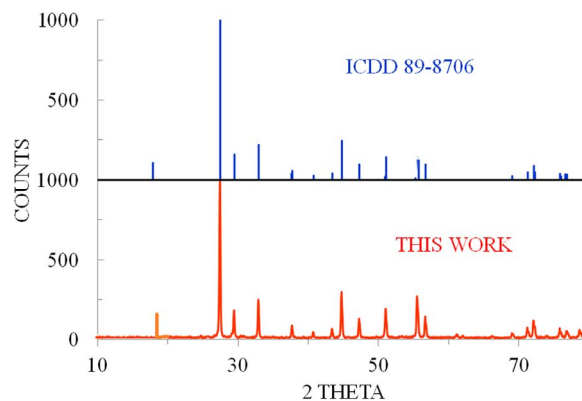

Fig. 1. XRD of $PbMoO_4$. A good match with ICDD 89–8706 is seen. There are no lines around 25.652 and 10.659 which are characteristic of Pb_2MoO_5 and Pb_5MoO_8, respectively.
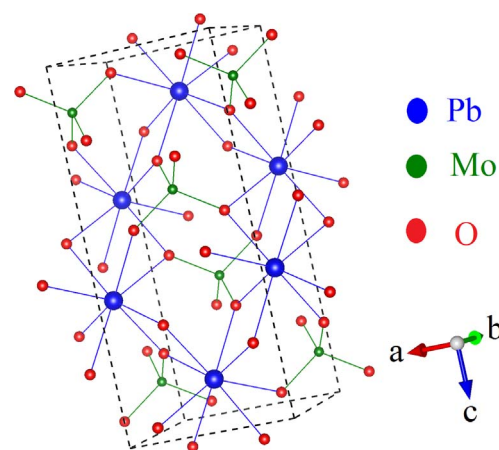

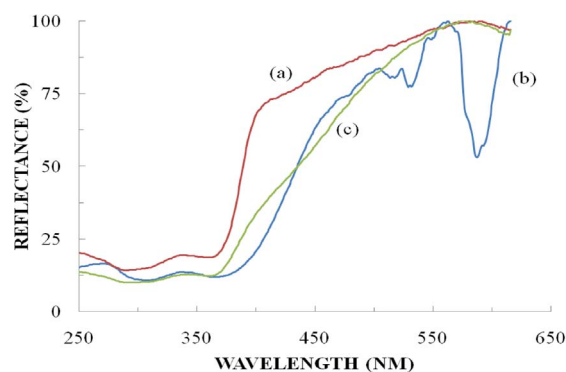**Fig. 2.** Unit cell of $PbMoO_4$ showing 8 coordinated Pb.

Fig. 3. Reflectance spectra of a > $PbMoO_4$, b > $PbMoO_4$:Nd^{3+} and c > $PbMoO_4$:Yb^{3+}.

considerable splitting due to vibronic structure. Inset shows concentration dependence of this emission. The highest PL intensity is observed for 2%. Concentration quenching is observed for higher concentrations. From this, critical distance for Yb^{3+}-Yb^{3+} energy transfer can be calculated using formula [46].

$$Rc = 2(3V/4\pi x_c N)^{1/3}$$

where x_c is the critical concentration, N is the number of cation sites in the unit cell, and V is the volume of the unit cell (357.5 Å^3). Rc comes out to be 25.8 Å.

The excitation is in form of a broad band peaking at 386 nm (curve b). This cannot be associated with Yb^{3+} which has only 2 levels viz. $^2F_{5/2}$ and $^2F_{7/2}$ separated by about 10,150 cm^{-1}. CT band of Yb^{3+}-O^{2-}