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NIR emitting phosphors based on sensitization by molybdate anion

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ABSTRACT

In this work, NIR emission is reported in Y_2MoO_6 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 with subsequent energy transfer to Nd^{3+} or Yb^{3+}. Moreover, efficient energy transfer from Nd^{3+} to Yb^{3+} was also observed. By virtue of this transfer, higher NIR emission intensities were observed for Nd^{3+},Yb^{3+} double doped phosphors. The energy transfer mechanisms based on cooperative energy transfer (CET) and cross relaxation followed by NIR emission are suggested. It is also suggested that Y_2MoO_6: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

In oxide lattices, Molybdenum forms two types of anionic complexes. More common is MoO_4^{2-} and the other is MoO_6^{6-}. In oxides, Mo^{6+} ion is usually four-coordinated. Kroger [1] has mentioned a number of luminescent molybdates containing molybdate tetrahedra, for example, $CaMoO_4$, $CdMoO_4$ and $Na_2Mo_2O_7$. Only $CaMoO_4$ has been studied in detail down to very low temperatures [2]. After the early work of Kroger [1] and Botden [3] work on molybdate luminescence gathered momentum for some time. Van Loo [4] discussed the luminescence of $PbMoO_4$. Tyner and Drickamer [5] presented a study on the pressure and temperature dependence of the decay time and the intensity of the luminescence of several molybdates. The absorption and emission spectra of the molybdate complex are at higher energies compared to those of the isoelectronic chromate complex. Owing to this fact luminescence for the molybdate has been observed more frequently than for the chromate complex. However, molybdate luminescence is characterized by a strong thermal quenching. Quite often the thermal quenching is almost total even before room temperature is reached. The decay times for MoO_4^{-2} are about 10^{-4}s [2]. There are no studies on luminescence of MoO_6^{-6} anion [6]. However it is known that absorption of MoO_6^{6-} anion is at lower energies compared to that of MoO_4^{2-} [7,8].

The luminescence of molybdate anions is not observable at room temperature. That's why there are not many applications of phosphors based on molybdate emission. In recent years, the energy transfer has been shown from molybdate group to other activators which exhibited emission at room temperature and above. Thus efficient emission from Sm^{3+} [9,10], Eu^{3+} [11–14], Tb^{3+} [15,16], Dy^{3+} [17–19] following energy transfer from molybdate ions has been reported which can be useful for solid state lighting applications. There is thus revived interest in molybdate based phosphors which work on energy transfer from molybdate group to other activators, especially rare earth ions.

There does not seem to be any report on molybdate sensitized NIR emission. NIR emission can be important for several applications like bioimaging [20], telecommunications [21], solar photovoltaics [22], Photodynamic therapy [23], photostimulated localized hyperthermia [24], etc.

Among rare earth activators, Nd^{3+} and Yb^{3+} are ideal for NIR emission. Yb^{3+} has only two energy levels separated by about 1.2 eV, corresponding emission is around 1000 nm. Since there are only 2 levels there is no branching. However, it has no optical absorption in nUV or visible region. In contrast, Nd^{3+} has a number of energy levels. The most common emissions are around 900, 1060 and 1350 nm.

We studied Y_2MoO_6 phosphor doped with Nd^{3+} and Yb^{3+} with the objective of obtaining NIR emitting phosphors with near UV excitation based on energy transfer from molybdate group to rare earth activators.

2. Experimental

Y_2MoO_6 phosphor doped with Nd^{3+} and Yb^{3+} were prepared by solid state reaction between yttrium oxalate (Indian Rare earths, 99.99% pure) and molybdenum trioxide (GR [equivalent to Analar grade] Loba). In the first step, yttrium oxalate doped with Nd^{3+} or

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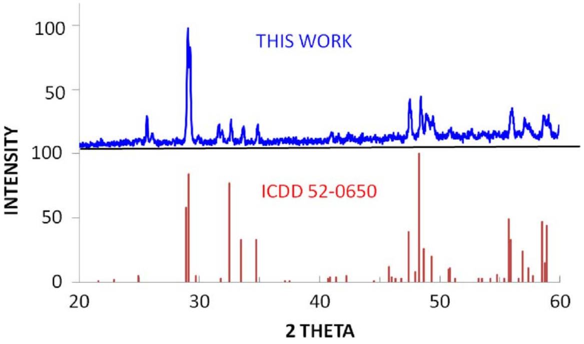

Fig. 1. XRD of Y_2MoO_6. A good match with ICDD 52–0650 is seen.

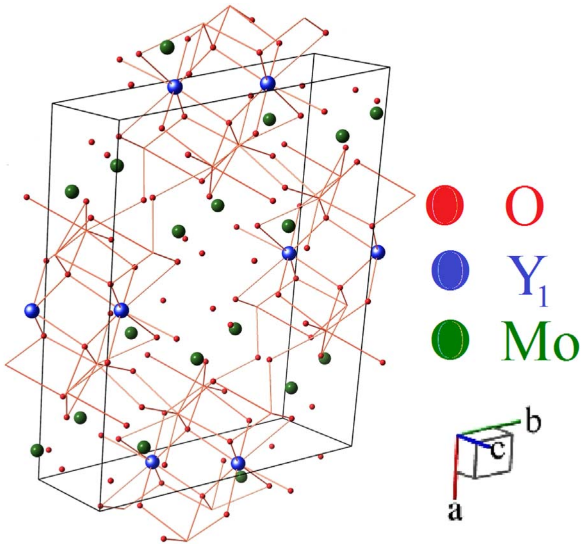

Fig. 2. 8 coordinated yttrium at Y1 site in Y_2MoO_6 unit cell.

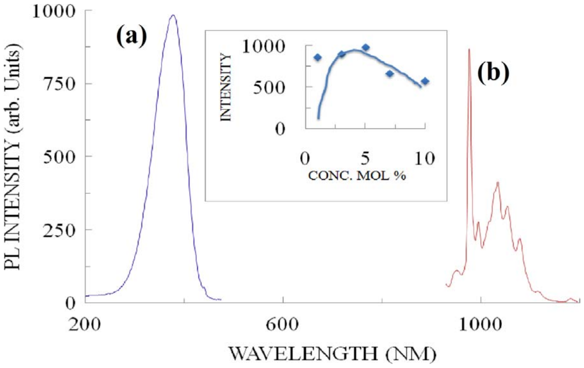

Fig. 3. PL spectra for Y_2MoO_6 phosphor doped with Yb^{3+} (5 mol%) a > Excitation for 978 nm emission b > Emission for 378 nm excitation. Inset shows concentration dependence of 378 nm emission.

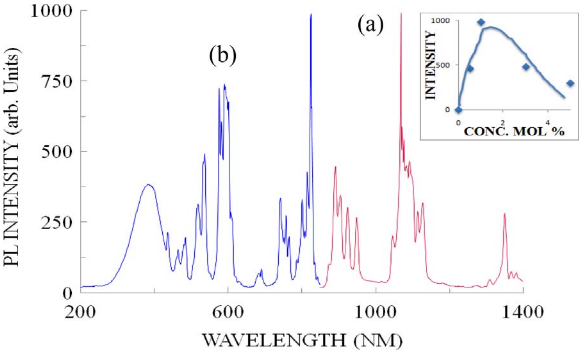

Fig. 4. PL spectra for Y_2MoO_6 phosphor doped with Nd^{3+} (1 mol%). a > Emission for 385 nm excitation b > Excitation for 1073 nm emission Inset shows concentration dependence of 1073 nm emission.

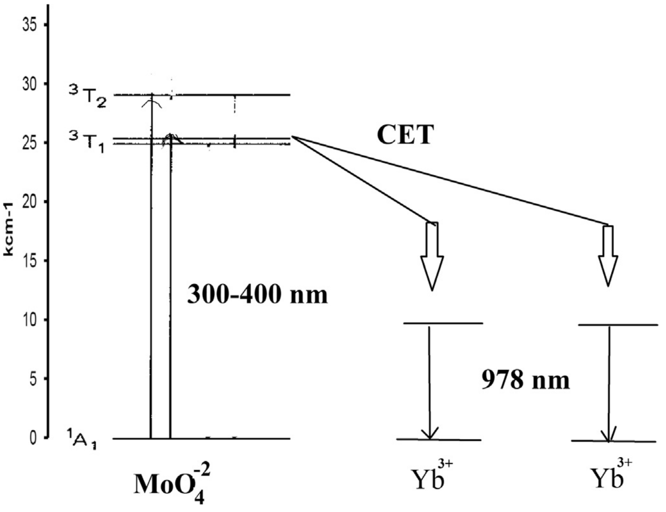

Fig. 5. Mechanism of energy transfer from $MoO_4{}^{-2}$ to Yb^{3+}.

Yb^{3+} was prepared by dissolving the corresponding oxides in dil. nitric acid. Oxalic acid solution in double distilled water was added drop wise to the nitrate solutions. The precipitate so obtained was filtered, washed and dried at 80 °C. Thus formed Yttrium oxalate doped with Nd^{3+} or Yb^{3+} was thoroughly mixed with stoichiometric amount of MoO_3 and the mixture was kept in the furnace at 1110 °C for 4 h. Then, it was slowly cooled to room temperature. The reaction temperature was chosen from the first study reported by Fournier et al. [25] who obtained $Y_2Mo_4O_{15}$ at 830 °C and found Y_2MoO_6 to be stable up to 1310 °C.

The crystalline phases of the synthesized samples were identified by x-ray diffraction (XRD) analysis. The XRD patterns were recorded on XPERT-PRO diffractometer using Cu K_α ($\lambda = 1.54059$ Å) radiation. The NIR photoluminescence (PL) and photoluminescence excitation (PLE) spectra were measured by a Photon Technology International QM-51 NIR spectrophotometer.

3. Results and discussion

Formation of Y_2MoO_6 host following the solid state reaction was confirmed by XRD. There are several phases known in the Y_2O_3-MoO_3 system. Three phases viz $YMoO_4$ (ICDD 35–1477, monoclinic) [26], Y_2MoO_6 (ICDD 52–0650, monoclinic) [27] and Y_6MoO_{12} (ICDD 30–1456, cubic) [25] are commonly studied. $YMoO_4$ formed only at high temperature (1300 °C) while Y_6MoO_{12} is formed at still higher temperature (1500 °C). As evident from Fig. 1, the observed patterns matched excellently with that of monoclinic Y_2MoO_6 (ICDD 52–0650). Phase pure Y_2MoO_6 is thus formed by the solid state reaction described here.

Y_2MoO_6 crystallizes in space group $C2/c$, with 8 formula units in the unit cell. “The structure contains four zigzag, one-dimensional MoO_5 polyhedral rows per unit cell, running through the RO_8 polyhedral framework along the [001] direction. MoO_5 form discrete units (i.e. do not share common oxygen), with Mo–O distances ranging from 1.77 to 2.24 Å, although the oxygen coordination can be extended to distances of about 3.1 Å, giving rise to strongly distorted MoO_8 scalenohedra. Thus, MoO_8 and RO_8 polyhedra are fully ordered in R_2MoO_6 compounds, which, in fact, can be considered as superstructures of fluorite (M_3O_6), containing 24 MO_2 fluorite units per unit cell” [27]. Y^{3+}