With the objective of development of optoelectronic devices, nowadays the research in this field is centred around the study of photoluminescence emission of rare earth elements present in the lattice of different oxides. Therefore, in this study we prepared samples of molybdenum trioxide doped with neodymium and erbium at concentrations of 1.0% and 2.0%, using solid state reaction technique from powders of MoO₃, Nd₂O₃ and Er₂O₃. These powders were analysed by X-ray diffraction which determined the presence of phase α-MoO₃. The morphology of the powders was examined using scanning electron microscopy, which showed that the doped samples have regular and well-defined microplates. The absorption UV-spectra revealed that the optical band gap changed slightly (3.2–3.4 eV) with the Er, Nd and Er–Nd concentrations. The photoluminescence shows emission bands at different wavelengths of the visible spectra as a function of the Er, Nd, and Er–Nd doped. The bands were centred at 748 nm and 808 nm transitions of the Nd³⁺ ions respectively. In this region and with excitation wavelength of 350 nm, strong emission lines were not observed for Er. Raman spectroscopy showed typical modes of vibration of α-MoO₃. Major changes have been noted in the case of samples doped with Er at peaks located between 350 cm⁻¹ and 580 cm⁻¹.

**Keywords:** Erbium, molybdenum trioxide, optical band gap, photoluminescence, neodymium.

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**Photoluminescence and Raman studies of α-MoO₃ doped with erbium and neodymium**

**RESEARCH ARTICLES**

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**Photoluminescence and Raman studies of α-MoO₃ doped with erbium and neodymium**

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**Keywords:** Erbium, molybdenum trioxide, optical band gap, photoluminescence, neodymium.

**MOLYBDENUM trioxide (α-MoO₃), as an intrinsic n-type II–VI semiconductor with wide band gap (~3.2 eV), has been extensively used in organic electronics as an efficient anode with interfacial layers owing to its high work function. Moreover, the MoO₃ nanostructures have also been examined as an effective photocatalyst in pollution degradation¹. MoO₃ has been used in different applications covering electro-optic to gas sensors²–⁷. Another of the exhibited characteristics of MoO₃ has been its electrochromic properties⁵. These include the reversible change in transmittance and/or reflectance, caused by the application of an externally applied DC voltage, and a change in electrical resistance of the oxide in the presence of gas. In recent years studies have been conducted on the structural, optical and electrical properties of thin films of MoO₃ doped with different elements of transitions, such as titanium and nickel, and/or cobalt³,⁴,⁷. These focus on improving the electrochromic effect through electron transitions between two kinds of metal sites with different valencies (Ti⁴⁺, Ti³⁺, Mo⁶⁺, Mo⁵⁺).

Moreover, MoO₃ has been doped with rare earths (REs) such as Er, Er–Yb and Nd ions⁵,⁶,⁸, with the objective of studying the up-conversion emission and discovering possible applications in the fields of colour display, near-infrared detectors, biological diagnosis, laser cooling and temperature sensors³–⁸. More recently, MoO₃ has been used as a hole injection layer (HIL) in organic light-emitting diodes (OLEDs)¹⁵. There are several studies available on the physical–chemical properties and applications that have MoO₃ doped and undoped; however, only few studies report evidence of the incorporation of RE ions in the lattice of MoO₃ which explains photoluminescence (PL) emission¹⁶, Raman spectroscopy, UV-Vis and scanning electron microscopy (SEM). Vila et al.¹⁷ recently reported effective RE (Er and Eu) incorporation in both MoO₃ nanostructures and bulk crystals.

**PL spectra are composed of two broad peaks at 520–570 and 640–680 nm assigned to ⁴H₁₁/₂ → ⁴I₁₃/₂ and ⁴F₉/₂ → ⁴I₅/₂ transitions of Er³⁺ ions respectively¹⁸.** For neodymium ion we have the 808 nm excitation result in strong emission at 795 nm due to the ⁴K₅/₂ → ⁴I₇/₂ transition along with other emissions from the Nd³⁺ ion¹⁹.

Therefore, in this study we present results for the photoluminescence emission of MoO₃ as a function of Er and Nd (1% and 2%) concentrations. We also discuss the Raman, X-ray, SEM, UV–Vis characteristics of this material.

**Experimental methods**

Samples of molybdenum trioxide doped with erbium and neodymium were made in atomic concentrations of 1% and 2.0% by the solid-state reaction method from Er₂O₃ (Aldrich 99.99%), Nd₂O₃ (Aldrich 99.99%) and MoO₃ (Merck 99.9%) powders. The stoichiometric amounts of oxides were mixed in isopropanol and subjected to a continuous magnetic agitation process for 8 h, followed by drying process at 80°C. Finally, each sample was subjected to a calcination process for 20 h at 550°C.
The crystalline structure of these samples was characterized with the aid of an X-ray diffractometer (XRD); Panalytical X’Pert PRO using a Bragg–Brentano geometry with CuKα radiation ($\lambda = 1.5405 \text{ Å}$) in the 2$\theta$ range (10$^\circ$–70$^\circ$) with steps of 0.02$^\circ$. A thermionic emission SEM operating at 5.0 kV (Vega3) was used to verify the morphology of the material. Raman scattering spectra were obtained in backscattering geometry JY-T64000 spectrometer for the samples, using the low-power Verdi 532 nm laser line excitation. The UV-Vis spectra were taken (Cary 5000 spectrometer; Varian) in diffuse reflection mode.

The PL measurements were performed with a monospec 27 monochromator (Thermal Jarrel AS, USA) coupled to a R446 photomultiplier (Hamamatsu photonics, Japan). A Krypton ion laser (coherent INNOVA 90 C, USA; $\lambda = 350 \text{ nm}$) was used as an excitation source.

Results and discussion

Figure 1 shows the XRD patterns of the Er$_2$O$_3$–MoO$_3$ and Nd$_2$O$_3$–MoO$_3$ systems as a function of erbium, neodymium and erbium–neodymium concentrations. The figure also establishes the fact that all crystallographic planes also belong to the orthorhombic crystallographic phase of MoO$_3$ (JCPDS 05-0508). In all the samples an orthorhombic crystallographic phase is observed with the most intense peak corresponding to the plane (040) at 2$\theta$ of 25.7$^\circ$. In the XRD patterns of molybdenum oxide mixing with the RE, there are no planes which belong to the oxides of RE. These results also establish that Er$^{3+}$ and Nd$^{3+}$ ions are integrated at the crystallographic lattice of MoO$_3$; and they can be confirmed through Raman and PL studies.

Figures 2a, 2d, and 2g show photomicrographs of erbium and neodymium oxide respectively. These two materials do not have a definite shape in their morphology. They are simple agglomerates of material.

Figure 3 shows the UV-Vis spectra of MoO$_3$ doped with Er and Nd using the solid-state reaction technique. The optical band gap was determined by extrapolation of the linear portion of the curve or tail. The band gap in the materials is related to absorbance and photon energy. Therefore, the combination of absorbance and photoluminescence measurements helps us to determine energy levels in the materials and the optical band gap. UV–Vis measurements on the six samples give the following values: (a) 3.23 eV (MoO$_3$), (b) 3.25 eV (Er 1%), (c) 3.27 eV (Nd 1%), (d) 3.25 eV (Er 2%), (e) 3.26 eV (Nd 2%) and (f) 3.32 eV (Er, Nd 1%). The energy gaps are very close; however, with simultaneously increase in erbium and neodymium, the energy gap increases.

The PL property of the samples was measured at room temperature. These materials exhibit a large optical band gap of 3.05 eV, and room temperature photoluminescence at 395 nm (ref. 25). The sample was excited with the laser line at 350 nm (3.54 eV). In Figure 4a, two peaks are observed at 442 nm (2.8 eV, blue) and 475 nm (2.6 eV, bluish-green). The transition at 442 and 475 nm may be attributed to Mo$^{5+}$ (d–d) band transition $d_{\pi}^2$–$d_{\sigma}^2$ (ref. 26). The emission spectra in Figure 4b exhibit a series of emission peaks with maxima at ~320–380 nm (UV), ~410–480 nm (blue), ~500–560 nm (green), ~600–660 nm (red) and ~700–800 nm (infrared). The first major peak at 399 nm corresponds to the radiative relaxation of electrons from the lowest unoccupied molecular orbital to the highest occupied molecular orbital energy levels. Two UV emission bands at 344 and 361 nm were observed by Huan et al. corresponding to the transitions of $^4D_{3/2} \rightarrow ^4I_{9/2}$ and $^2P_{3/2} \rightarrow ^4I_{11/2}$ or $^4D_{5/2} \rightarrow ^4I_{13/2}$. According to the energy level diagram of Nd$^{3+}$ ion, the ion emissions were found at 800 nm ($^4F_{5/2}$, $^2H_{11/2} \rightarrow ^4I_{15/2}$) and 890 nm ($^4F_{3/2} \rightarrow ^4I_{11/2}$) (ref. 29).

Figure 4c shows the typical room temperature PL spectrum of Er$_2$O$_3$. The transition at 407 nm is due to the electronic transition from $^3H_{9/2} \rightarrow ^1I_{15/2}$.
Figure 2. Scanning electron microscope (SEM) photomicrographs of molybdenum trioxide doped with neodymium and erbium using solid-state reaction method: (a) MoO$_3$, 550°C for 5 h; (b) Mo$_{0.99}$Er$_{0.01}$O$_3$, 550°C for 20 h; (c) Mo$_{0.98}$Er$_{0.02}$O$_3$, 550°C for 20 h; (d) Er$_2$O$_3$, 550°C for 5 h; (e) Mo$_{0.99}$Nd$_{0.01}$O$_3$, 550°C for 20 h; (f) Mo$_{0.98}$Nd$_{0.02}$O$_3$, 550°C for 20 h; (g) Nd$_2$O$_3$, 550°C for 5 h; (h) Mo$_{0.98}$Er$_{0.01}$Nd$_{0.01}$O$_3$, 550°C for 20 h.

Figure 3. UV–Vis spectra at room temperature: (a) MoO$_3$, 550°C for 5 h; (b) Mo$_{0.99}$Er$_{0.01}$O$_3$; (c) Mo$_{0.99}$Nd$_{0.01}$O$_3$; (d) Mo$_{0.98}$Er$_{0.02}$O$_3$; (e) Mo$_{0.98}$Nd$_{0.02}$O$_3$; (f) Mo$_{0.98}$Er$_{0.01}$Nd$_{0.01}$O$_3$, 550°C for 20 h.

$^4$F$_{3/2,5/2}$ $\rightarrow$ $^4$I$_{15/2}$, 487 nm $^4$I$_{15/2}$ $\rightarrow$ $^4$F$_{7/2}$, 524 nm $^2$H$_{11/2}$ $\rightarrow$ $^4$I$_{15/2}$ and 540 nm $^2$S$_{3/2}$ $\rightarrow$ $^4$I$_{15/2}$. In Figure 4c, an emission at 560 nm also appears as in the literature. It is expected to be the result of relaxation and emission from a higher energy level at an excited state of $^4$S$_{3/2}$ $\rightarrow$ $^4$I$_{15/2}$. The peak which appears at 680 nm is possibly related to the relaxation processes from $^4$F$_{9/2}$ $\rightarrow$ $^4$I$_{15/2}$.

Figure 4d and e shows the PL spectra of the Er-doped MoO$_3$ powders. Figure 4g and h shows the PL spectra of the Nd-doped MoO$_3$ powders. As a result of the higher
excitation energy used (350 nm) in Figure 4d and e, no emissions were observed in the range 350–800 nm, compared to other studies in which the erbium-doped molybdenum trioxide was excited by a wavelength of 378 nm at room temperature and heat-treated at 600°C. Nevertheless, due to erbium doping (less 2%) the PL peaks were not observed and the material was also heat treated at 500°C for 20 h in an air flow, a treatment similar to that of neodymium. This can be confirmed using Raman spectroscopy. Possibly, for the sample with 2% Er, the 658 nm broadband is related to defects and marks the PL of Er.

In Figure 4g four peaks appear at 442, 751, 806 and 818 nm with 2% Nd. The peak at 806 nm corresponds to the transition of the Nd3+ ion (4F5/2, 2H9/2 → 4I9/2) (ref. 32). According to the literature, absorption peaks are centred at 748 and 808 nm, which are related to the f–d transitions of Nd3+ internal ions in the crystal. The absorption bands are attributed to the (748 nm) 4I9/2 → 4F7/2 + 4S3/2 and (808 nm) 4G5/2 → 4F5/2 + 4H9/2 transition of Nd3+. In the present study, it corresponds to the 751 and 806 nm peaks. The difference in peak position may be related to defects in the material. This is indicated by the presence of neodymium in MoO3. A similar occurrence can be seen with 1% Nd in Figure 4h. Unlike erbium, changes in the photoluminescence with neodymium are more visible. For 1% of erbium and neodymium, graphs in Figure 4f and h (1% Nd) are similar, the only difference is that the peak at 754 nm disappears in Figure 4f. These small differences with the other spectra indicate that the dopant material enters the matrix (MoO3). It is possible to observe the PL for Er3+ for wavelengths of a high excitation (808 nm). However, in the present study, we have used wavelengths under 350 nm.

The irreducible representation of MoO3 with space group D2h (Pb nm) is given as

\[ \Gamma = 8A_g + 8B_{1g} + 8B_{2g} + 8B_{3g} + 4A_u + 3B_{1u} + 7B_{2u} + 7B_{3u} \]  

(1)

where A_g, B_{1g}, B_{2g} and B_{3g} are Raman-active modes. The Raman-active phonon modes can be used to estimate the structural order at a short range in the materials. Figure 5b shows a typical Raman spectrum of the α-MoO3 nanoplates. It corresponds to the atomic dispersion of an octahedron (MoO6) in the phase α-MoO3. The positions...
of these modes can be observed in: 118 (B₂g), 129 (B₃g), 160 (A₉, B₁g), 199 (B₂g), 218 (A₂), 247 (B₁g), 285 (B₂g, B₁g), 338 (B₁g, A₂), 367 (A₂), 382 (B₁g), 472 (A₉, B₁g), 667 (B₂g, B₁g), 820 (A₁, B₁g) and 995 (A₉, B₁g) cm⁻¹.

The narrow band at 995 cm⁻¹ can be assigned to the antisymmetric $\nu$(Mo = O₁) stretching. The strong band at 820 cm⁻¹ represents the symmetric $\nu$(Mo–O₃–Mo) stretching. The weak and broad bands at 667 and 472 cm⁻¹ can be assigned to the antisymmetric $\nu$(Mo–O₂–Mo) stretching (B₂g) and bending (A₉). The bands at 285 cm⁻¹ and a weak shoulder centred at 293 cm⁻¹ correspond to $\delta$(O₁ = Mo = O₁) wagging. The bands at 247 and 218 cm⁻¹ correspond to the $\delta$(O₂–Mo–O₂) scissor.

Neodymium oxide (Nd₂O₃) material has four phonons (2A₂u + 2Eu). Under room temperature, three Raman bands were observed at 295, 364 and 481 cm⁻¹ respectively (Figure 5a). Two wide shoulders were also observed in the 637 and 1076 cm⁻¹ positions. The band at 481 cm⁻¹ was assigned to the A₂u mode.

Figure 5c and d corresponds to the addition of Nd 1% and 2% respectively. In the Raman spectra for concentrations of 1% an 2% (Nd³⁺), major changes are not observed. It is difficult to identify vibrational modes in the fluorescent emissions that overlap the Raman spectrum in the lattice area with the 514 nm (ref. 30). In order to excite the samples in the present study, a green laser (532 nm) was used. This may be a possible justification of why not many changes are observed in the Raman spectrum of MoO₃ with neodymium doping.

Figure 6a shows spectra obtained from Er₂O₃ using a 532 nm excitation. The bands at 232, 262, 381, 484, 522, 565, 606, 653, 725, 746, 831, 983 and 1071 cm⁻¹ correspond to the Raman bands for Er₂O₃. Figure 6b corresponds to MoO₃, and the Raman modes have already been explained in Figure 5b. Figure 6c and d corresponds to the spectra of molybdenum trioxide doped with erbium 1% and 2% respectively. The Er³⁺ ions in the material MoO₃ induce partial structural amorphization of the samples as evidenced by the spectra in the region between 370 and 580 cm⁻¹. The three peaks that appear in the Raman spectra for the two erbium concentrations are wide. This is an indication that Er ions are incorporated into the material. In the case of PL (Figure 4), this effect had not been observed. However, in Figure 6c and d these new peaks indicate the effects of erbium doping. These new peaks appear at positions 401, 416, 456, 485 and 550 cm⁻¹.

Conclusion

In the present work, the incorporation of Er and Nd to MoO₃ was studied, by means of the comparison of the Raman spectra and the PL emission, of the doped and undoped samples. These measurements made with excitation line of 350 nm, show a band centred at 443 nm for MoO₃ doped with Er, at 806 nm for samples doped with Nd, and at 803 nm for samples doped with Er-Nd: these are different from emission band of the oxides, centred at 442 nm (MoO₃), and emission band between 400 and 600 nm in neodymium and erbium oxide. These results suggest that MoO₃ doped with the Er and Nd can be used to develop middle infrared optical devices. Moreover, Raman spectra excited at 532 nm, showed major changes in low-frequency modes with increased doping of Er. Three new peaks at 400, 480 and 550 cm⁻¹ were observed. These results suggest that the erbium ions be incorporated into the MoO₃ causing defects in their lattice. XRD shows the orthorhombic phase in the doped samples. SEM measurements showed that the doping of Er and Nd favours the growth of grains, with a more defined and regular shape compared to the MoO₃ sample. However, the energy band gap of the samples increases with the concentration of Er and Nd compared to the pure sample of MoO₃.


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