Optical and electrical properties of MoO$_2$ and MoO$_3$ thin films prepared from the chemically driven isothermal close space vapor transport technique

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Abstract
Chemically—driven isothermal close space vapour transport was used to prepare pure MoO$_2$ thin films which were eventually converted to MoO$_3$ by annealing in air. According to temperature-dependent Raman measurements, the MoO$_2$/MoO$_3$ phase transformation was found to occur in the 225 °C–350 °C range while no other phases were detected during the transition. A clear change in composition as well as noticeable modifications of the band gap and the absorption coefficient confirmed the conversion from MoO$_2$ to MoO$_3$. An extensive characterization of these two pure phases was carried out. In particular, a procedure was developed to determine the dispersion relation of the refractive index of MoO$_2$ from the shift of the interference fringes of the used SiO$_2$/Si substrate. The obtained data of the refractive index was corrected taking into account the porosity of the samples calculated from elastic backscattering spectrometry. The Debye temperature and the residual resistivity were extracted from the electrical resistivity temperature dependence using the Bloch–Grüneisen equation. MoO$_3$ converted samples presented a very high resistivity and a typical semiconducting behavior. They also showed intense and broad luminescence spectra composed by several contributions whose temperature behavior was examined. Furthermore, surface photovoltage spectra were taken and their relation with the photoluminescence is discussed.

Keywords: transition metal oxides, optical properties, phase transformation, photoluminescence

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(Some figures may appear in colour only in the online journal)

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1. Introduction

Molybdenum forms different oxides of formula MoO$_3$–$x$ with $x$ ranging from 0 to 1. The most oxidized compound in the family, MoO$_3$, presents an orthorhombic structure, has n-type conductivity and a band gap of approximately 3.0 eV [1]. In the case of the MoO$_2$, the most reduced compound in the family, the stable phase presents a monoclinic structure. A metallic behavior, as predicted by theoretical calculations [2], has been observed in MoO$_2$ although an optical band gap has been frequently found in its absorption spectra [3]. Among other important applications, both MoO$_2$ and MoO$_3$ present very interesting properties as catalysts, while oxygen deficient MoO$_x$ is being widely used as hole transporter layer in either inorganic or organic solar cells. A comprehensive account of the applications of molybdenum oxides can be found elsewhere [4].

Molybdenum oxides prepared with different techniques such as thermal evaporation [5] sputtering [6, 7] or pulsed laser deposition [8] for example, typically referred as MoO$_x$ in the literature, are composed by a mixture of different phases. This complicates the task of associating any measured property with a given phase, and has caused a large dispersion in the reported values for some properties of these oxides. In a previous work, we have developed a method for obtaining pure MoO$_2$ thin films by a chemically driven isothermal close space vapor transport technique (CD-ICSVT) using MoO$_3$ as the precursor [9]; thin films and flakes were obtained by controlling the growth conditions.

In the present manuscript we studied the conversion of the as-grown MoO$_2$ films to MoO$_3$ by annealing in air and determined the temperature range in which this conversion occurs. The possibility of preparing both MoO$_2$ and MoO$_3$ pure phases provides us an excellent opportunity for the study and comparison of their properties. So, we present an extensive characterization of the electrical and optical properties of pure MoO$_2$ and MoO$_3$ samples which includes measurements of elastic backscattering spectrometry (EBS), electrical resistivity as a function of temperature, UV–VIS transmission and reflectance, surface photo-voltage (SPS), photoluminescence (PL) and Raman spectroscopies. Results are discussed and compared with those reported in literature for samples grown by other techniques whenever this was possible.

2. Experimental details and characterization

MoO$_2$ thin films were grown by the CD-ICSVT technique [9] in which a substrate is located at the same temperature and a few millimeter above a small amount of MoO$_3$ powder under a reductive gas flow at atmospheric pressure. Beyond its simplicity and compatibility with continuous processing, this technique has the advantage of producing pure MoO$_2$ samples instead of MoO$_x$ mixtures. MoO$_2$ thin films were grown at 570 °C onto SiO$_2$/Si or fused silica substrates under a flow of a H$_2$:Ar (1:5) gas mixture at a rate of 25 ml min$^{-1}$ at atmospheric pressure. Some as-grown MoO$_2$ samples were converted into MoO$_3$ by oxidation in two different ways: (i) using rapid thermal annealing at 400 °C for 1 min (similar annealings in N$_2$ gas did not lead to any change in the sample properties, while similar annealings in air at higher temperatures promoted, together with the phase transformation, a partial sublimation of the film) or (ii) during Raman spectra acquisition as a function on temperature.

Raman spectroscopy was performed with a confocal optical microscope coupled to a modular Raman spectrometer from Horiba (iHR320). The light source was a continuous wave diode-pumped solid-state laser with a wavelength of 473 nm (Cobolt Inc.), TEM 00, and linearly polarized, which was focused onto the sample with a 50 × microscope objective lens, NA 0.5; a power of 2.8 mW in front of the objective entrance was used. The Raman signal was dispersed into the spectrometer with a grating of 2400 lines mm$^{-1}$, then, a thermoelectrically cooled charge-coupled detector (Synapse, Horiba Inc.) was used to collect the Raman spectra. The temperature was varied between 50 °C and 500 °C using a Linkam station THMS600 under ambient conditions. X-ray diffraction (XRD) was used to study the structure of the films. Measurements in the $\theta–2\theta$ configuration were carried out with a Panalytical X-Pert Pro diffractometer and using CuK$_{\alpha1}$ radiation.

To study the optical properties of the films, reflection and transmission spectra measurements in the 200–900 nm range were carried out in a Jasco V-560 UV–VIS double-beam spectrophotometer provided with an integrating sphere. PL measurements were carried out using the 325 nm wavelength He–Cd laser line (maximum output power of 16 mW) as excitation source. The sample emission was focused into an Acton SpectraPro 2500i spectrograph and detected by a photomultiplier tube. All the spectra were corrected taking into account the spectral response of the system. SPS was performed at room temperature in a lab-made automated experimental setup; comprising a halogen lamp coupled with a grating monochromator, a lock-in amplifier and an optical chopper [10]. The sample was located between a transparent indium–tin–oxide (ITO) electrode and a copper plate which acts as a sample holder and the bottom ground electrode [11]. Then, the surface photovoltage (SPV) signal measured as a function of incident photon energy provided the SPV spectra.

EBS were obtained using alpha particles detected at a scattering angle of 170° with alpha particles beams of three different energies of 2000, 3057, and 4268 keV in order to study the Rutherford scattering and also to promote resonant nuclear reactions with oxygen and carbon. The analysis of the EBS was performed using the computer code SIMNRA 6.06 [12]. Values from non-Rutherford cross section for carbon and oxygen were generated using Sigma Calc 1.6 [13] while those for Si were provided by the file ASICH93A.RTR available in the SIMNRA computer code.

High resolution scanning electron microscopy images were obtained by using an FE-SEM Hitachi S-4700 microscope. Resistivity measurements were carried out from 77 to 340 K in van der Pauw configuration for MoO$_2$ while resistance measurements in MoO$_3$ used a two-probe arrangement.
3. Transformation from MoO$_2$ to MoO$_3$ by annealing in air

Diffractograms for an as-grown sample and a sample annealed at 400 °C for 1 min in air, both grown onto SiO$_2$/Si substrates are shown in figure 1. The calculated reference patterns from monoclinic MoO$_2$ (space group P121/c1, 14) and orthorhombic MoO$_3$ (space group Pbmm, 62) are shown as well in the figure. They were used to identify the indexes of the different peaks in the diffractograms. As can be noted, the pure MoO$_2$ as-grown sample was transformed to MoO$_3$ by the annealing in air. Raman spectra for samples with the same characteristics, but grown onto fused silica substrates, are shown in figure 2(a) in which the type of the identified vibration modes are indicated in the irreducible representation notation. The most notorious modifications after the annealing are the emergence of the peaks at 820 and 995 cm$^{-1}$, characteristic of MoO$_2$. This reflects the phase change from MoO$_2$ to MoO$_3$ during the annealing process and confirms the results of the XRD analysis. The peaks at 820 and 995 cm$^{-1}$, labeled as $A_2$ in figure 2(a), correspond with stretching modes of single and double Mo–O bonds in MoO$_3$ [15]; the rest of the peaks in the spectra of the annealed sample can also be assigned to MoO$_3$ characteristic modes. On the other hand, the characteristic MoO$_2$ peak at 744 cm$^{-1}$, labelled as $B_{3g}$ is a stretching mode of the Mo–O bond.

UV–VIS transmission spectra for the same samples are shown in figure 2(b). Significant changes in the transmission (that could be observed to the naked eye) and in the optical band gap, as consequences of the annealing, were observed. To determine the band gap from absorbance measurements, $(a\nu)^2$ versus $\nu$ Tauc plots are typically used in which $a$ is the absorption coefficient and $\nu$ the photon energy. The exponent $n$ is $\frac{1}{2}$ or 2 for indirect allowed or direct allowed transitions, respectively.

Although a large amount of research work has been devoted to the study of MoO$_3$ properties, in the known of the authors, there are not conclusive experiments indicating the indirect or direct character of MoO$_3$ band gap. In the supplementary material (stacks.iop.org/JPhysCM/31/295703/mmedia), we present an account (not exhaustive) of different reports in the literature showing that authors have used indistinctly one or other criterion. Absorbance measurements are helpful for estimating the band gap of the materials but not for deciding its direct or indirect character. In fact, Tauc plots with any of the two exponents can be adjusted to the same experimental data, affording different values of the band gap. Theoretical calculations [16] based in the density functional theory, have indicated that the conduction band minimum is located at the $\Gamma$ point and the valence band maximum at the $R$ point of the Brillouin zone, respectively, suggesting an indirect nature of the band gap. Guided by these theoretical work and in view of the lack of conclusive experimental reports, we have used $n = \frac{1}{2}$, corresponding to an indirect transition, in our band gap calculation for MoO$_3$. The $h\nu$ intercept of the linear region of the Tauc plot (in the inset of figure 2(b)), indicates a band gap of 2.92 eV for the annealed (MoO$_3$) samples. This result is in good agreement with the value of near 3.0 eV typically reported in the literature [1, 17] for this material, when an indirect band gap is considered. To allow comparisons, we also calculated the band gap of MoO$_2$ by supposing a direct band gap ($n = 2$ in the Tauc plot). In this case, the obtained value was 4.2 eV (the corresponding Tauc plot is presented in the supplementary material).

Regarding the MoO$_2$ band gap, we obtained values of 1.83 and 3.44 eV when indirect or direct criteria ($n = \frac{1}{2}$ or 2)
for the band gap transition were used. It is worth to comment that a clear absorption edge should not be expected since a metallic behavior has been predicted from theoretical band structure calculation. However, besides our present result, several authors have reported the existence of a band gap for reduced molybdenum oxides. For example, band gap values of 2.4 and 2.7 eV have been reported in reduced MoO3 thin films although those samples really contained a mix of different MoOx (2 < x < 3) phases [5]. In another report [3], a band gap of 4.22 eV was found for MoO2 considering n = 2 in the Tauc plot. Our result confirms the presence of an optical band gap for pure MoO2. The existence of an optical band gap in a material in which the Fermi level crosses electronic bands, as in the present case, is puzzling and deserves more experimental and theoretical investigations. A decrease in the transmission is observed for longer wavelengths in MoO2, probably due to free electron absorption, which seems to confirm the mixed metallic/semiconductor structure character of this material.

To study the evolution of the phase transition, Raman spectra were measured as a function of temperature. As it can be noticed in figure 3, the phase transition is observed in the range between 225 °C–350 °C. The spectrum at the top was measured after cooling the sample. The normalized spectra are shifted in vertical for illustration purpose only. (Spectra for the complete set of temperatures are shown in the supplementary material.)

Figure 3. Temperature evolution of Raman spectra. The transition from MoO2 to MoO3 is observed in the range between 225 °C–350 °C. The spectrum at the top was measured after cooling the sample. The normalized spectra are shifted in vertical for illustration purpose only. (Spectra for the complete set of temperatures are shown in the supplementary material.)

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4. Refractive index of MoO2

Reflectance spectroscopy in the UV–VIS region is a useful tool for determining the optical properties and thickness of thin films. Even when the absolute value of the reflectance is
hard to be measured (i.e. because of sample size), fitting the position and relative amplitude of interference fringes allows the determination of the refractive index when the thickness is known. In general, interference fringes only arise for relatively transparent films in which the radiation entering at the external surface can reflect at the internal interface and return to the external surface without significant loss of intensity. Then, due to the absorbing character of MoO$_2$, only very thin films present appreciable transmission, but at the same time, the appearance of interference fringes is excluded in this case, because the small optical path difference introduced by the film. We have devised the following approach to measure the refractive index of MoO$_2$. Very thin MoO$_2$ films, in the range of tens of nanometers were grown onto SiO$_2$/Si substrates, which present their own interference fringes due to the relatively large thickness and transparence of the SiO$_2$. The very thin MoO$_2$ films grown on top of these substrates do not show interference fringes of their own, but they induce a noticeable shift of the substrate’s fringes. This effect is illustrated in figure 5(a) in which the reflectance spectra of the SiO$_2$/Si substrate and that of the grown MoO$_2$/SiO$_2$/Si structure are shown. Then, simulating the reflectance spectra of thin MoO$_2$ films on top of the SiO$_2$/Si substrate by the transfer matrix procedure, considering two-layer interference, and fitting the induced spectral shift for a sample of known thickness, the refractive index can be determined. Figure 5(b) shows the effect of the increasing MoO$_2$ layer thickness on the simulated reflectance spectra of a SiO$_2$(305 nm)/Si substrate. The interference fringes are clearly shifted even for MoO$_2$ layers less than 2 nanometers thick. The inset in figure 4(b) details the evolution of the interference maximum initially in the pristine SiO$_2$ (305 nm)/Si substrate at 435 nm as a function of MoO$_2$ thickness.

In order to determine the (complex) refractive index of the MoO$_2$ layers and its dispersion relation, using the above procedure, the reflectance spectrum of a MoO$_2$/SiO$_2$ (305 nm)/Si structure of known MoO$_2$ thickness was simulated and fitted to the experimental measurement. The actual MoO$_2$ layer thickness was determined by cross-sectional SEM (figure 6(a)); the well-known values of SiO$_2$ and Si refractive indexes were introduced into the simulation as well. In the inset of figure 6(a), a micrograph of the rough MoO$_2$ surface is presented. Figure 6(b) shown the experimental and simulated reflectance spectra of the 100 nm MoO$_2$ layer grown on a SiO$_2$(305 nm)/Si substrate, while in figure 6(c) the real and imaginary parts of the refractive index of MoO$_2$ obtained from this fitting procedure are shown. Again, the goal of this simulation was to properly fit the position and height of the interference fringes, not their absolute intensity value.
A remarkably low refractive index at the red edge of the spectrum is observed in figure 6(c). Taking into account that the refractive index obtained by this method corresponds to an effective refractive index of the MoO₂ film, such a low value suggests a low MoO₂ density due to the porosity of the layer, in accordance with the results of EBS measurements commented above. The steep increase in the extinction coefficient and the anomalous dispersion of the refractive index below 400 nm suggest the presence of an absorption edge as observed in transmission measurements above.

The effective refractive index of porous MoO₂, \( n_{\text{eff MoO}_2} \), can be approximated, using effective medium theory [19], as a combination of the refractive indices of the MoO₂, \( n_{\text{MoO}_2} \), and air, \( n_{\text{air}} \):

\[
 n_{\text{eff MoO}_2} = n_{\text{air}} p + n_{\text{MoO}_2} (1 - p).
\]

Here, \( p \) represents the porosity, i.e. the void fraction of the total volume. From this equation, and using the porosity determined by the EBS spectra, the refractive index of MoO₂ was calculated. The corrected refractive index is shown in figure 7 together with that obtained before the correction. Also, the MoO₃ refractive index is shown for comparison.

In the only previous report found in the literature, the refractive index of electro-deposited MoO₂ [20] was measured at a wavelength of 632.8 nm. The authors determined values ranging between 1.7 and 2, depending on the morphology and thickness of the films. Our measured dispersion relation...
The determined dispersion relation of the effective refractive index of MoO₂ allowed the estimation of the layer thickness of the films from simple reflectance measurements (using the inverse process than that described above for determining the refractive index from a sample with known thickness). For two relatively thick samples with thickness of 65 and 120 nm (measured by profilometry) this method yields values, of 50 and 100 nm, respectively, which represents a relatively good agreement between both methods.

5. Temperature dependence of the electrical parameters

5.1. Electrical resistivity and Bloch–Grüneisen (BG) parameters of MoO₂

A very low resistivity in the $10^{-4}$ Ω cm range was typically determined by the four probe method for the as-grown MoO₂ samples. The dependence of the resistivity with temperature from 77 K to RT is shown in figure 8(a) in which a typical metallic behavior with an approximately linear increase of resistivity at high temperatures was observed. The temperature dependence of the resistivity for metals is commonly described by the BG integral equation:

$$\rho(T) = \rho_0 + K \frac{T^n}{T_D^{n+1}} \int_0^{\frac{T}{T_D}} \frac{x^n \, dx}{(e^x - 1)(1 - e^x)}$$

in which $\rho_0$ is the residual low temperature resistivity, $K$ is a constant proportional to the electron–phonon coupling constant, $T_D$ is the Debye temperature and the exponent $n$ can take the values 2, 3 or 5 depending on the electron dispersion mechanism. The $\rho - T$ curve was fitted quite well using the above equation and $C$ and $T_D$ as fitting parameters. $\rho_0$ was taken as the low temperature resistivity and different values of $n$ were tried. As a result of the fitting procedures the following values were obtained: $\rho_0 = 4.4 \times 10^{-5} \, \Omega \, \text{cm}$, $T_D = (617 \pm 6) \, \text{K}$, $C = (8.5 \pm 1.5) \times 10^{-5} \, \Omega \, \text{cm} \, \text{K}$ and $n = 5$. Attempts to use $n = 2$ or 3 returned unrealistic high values of $T_D$. This is a very clear metallic behavior with the electron dispersion limited by the electron–phonon interaction. The value of the high temperature limit of the slope of the $\rho - T$ curve [21], $\beta = C / 4T_D^4$, was calculated as 0.34 $\mu \Omega \cdot \text{cm} \cdot \text{K}^{-1}$. In [22] the source-drain resistance of a MoO₂–MoS₂ heterostructures was found to increase with temperature in a way similar to the BG behavior; they found $T_D = 709.3 \, \text{K}$ and $n = 2$. But the resistivity was not measured and the material was not pure MoO₂.

Other authors have reported the metallic behavior of MoO₂ [23] but, in the best of our knowledge, our report is the first one of the BG parameters of MoO₂. For comparison, values of $\rho_0$, $T_D$ and $\beta$ reported in the literature for different materials are shown in table 1. As it can be observed, the resistivity of MoO₂ is almost two order of magnitude larger than common metals like silver or copper but is smaller than transparent conductive oxides like ITO or ZnO:Al. The temperature coefficient and the Debye temperature are higher for MoO₂ with respect to the metals but is smaller than those of ITO, ZnO:Al and In₂O₃. These transparent conductive oxides present also a metallic behavior but they have a clear band gap in the band structure, since the Fermi level does not cross electronic bands as in the case of MoO₂.

5.2. Temperature dependence of the resistance in MoO₃

In contrast to MoO₂, the samples converted to MoO₃ were found to be highly resistive. This made it impossible to obtain reliable values of the resistivity using a four probes measurement as in the Van der Pauw technique; a two probe one was used instead. Although in this kind of measurement the contact resistance can induce overestimated values for the resistivity, the temperature behavior of the sample resistance can still afford valuable information. Figure 8(b) shows the temperature dependence of the resistance of a MoO₃ film. A decrease of the resistance with increased temperature is observed in all the temperature range as an indication of semiconductor behavior. In the inset, the Arrhenius plot shows the presence of four regions in which the resistance is proportional to $\exp(E_A/kT)$ (k is the Boltzmann constant and T the absolute temperature) with activation energies $E_A$ of 0.45, 0.22 and 0.054 and 0.023 eV, respectively. Such a behavior should be explained, according the Petritz model [24], by the presence of potential barriers due to inter-crystallite oxide material in a polycrystalline semiconductor. But, in the case of MoO₃, the inter-crystallite material cannot be more oxidized than the bulk of the crystallites, since MoO₃ is the more oxidized of all molybdenum oxides. Of course, this do not exclude the formation of an energy barrier in the inter-crystalline region due to surface states, for example. However, it is well known that oxygen vacancy defect band gap states are present in the proximity of the conduction band of MoO₃ [25]. For this reason, we consider most probable that the Arrhenius behavior in our samples is due to the ionization of these states with the emission of electrons to the conduction band. Further support to
this assumption should be given in the next paragraph with the analysis of the thermal behavior of the PL.

### 6. PL and SPV of MoO₂ samples converted to MoO₃

While MoO₂ thin films did not show appreciable PL at any temperature, a strong and broad emission was observed in samples annealed to MoO₃. Typical PL spectra at 12 K and RT are shown in figures 9(a) and (b) (all the spectra can be accessed at the supplementary information). The spectrum was fitted with six Gaussian contributions located at 400.9 (3.09), 410.6 (3.02), 427.2 (2.90), 463.4 (2.68), 527.7 (2.35), and 618.0 (2.0) nm (eV) in the 12 K spectrum. Several MoO₃ samples were measured and their spectra were fitted with relatively similar contributions. Other authors [31] ascribe the blue emissions ranging from 400 to 470 nm to near band gap emissions, and associate the rest of the emission bands to defects states in the band gap. In an effort to elucidate the origin of the different emission bands we studied the evolution of the PL with temperature. The behavior of the integrated area and the energy position of the PL peaks are shown in figures 9(c) and (d).

With increasing temperature, the intensity of the peaks remains relatively constant up to around 140 K, then it starts to decrease exponentially (except the peak at 527.7 nm whose intensity increase and the peak at 618.0 nm that remains practically unchanged). This temperature dependence of the peaks intensity causes an overall green shift of the RT luminescence as shown in figure 9(b). The activation energy of the luminescence quenching is of around some tens of meV (27, 42.4, 52, 21.3 meV for peaks P1, P2, P3 and P4, respectively). The wavelength position of the peaks, even those in the blue region of the spectrum, is practically constant with temperature. Since near band gap PL peaks positions are expected to decrease with increasing temperature following the band gap temperature behavior, the above result indicates that all the observed emissions are originated by defects band gap states, in contrast with the assumption in [31]. It is interesting to note that, with increasing temperature, both the conductivity and the quenching of the PL are activated. The ionization of band gap defect states assumed in the previous paragraph to justify the thermal behavior of the resistance, will explain also the quenching of the luminescence. That is, if luminescence is due to recombination from carriers in the band gap states, the release of these carriers to the conduction band will both inhibit the luminescence and increase the conductivity.

To study the influence of the band gap defect states in the electrical properties, SPV spectrum was measured at RT in the range 350–600 nm. SPS technique relies on the measurement of the change in the surface potential as a result of the redistribution of charges due to the external illumination. The absorbed photons induce the formation of free carriers via band-to-band transitions and/or release captured carriers via trap-to-band transitions. A typical SPV spectrum measured at room temperature is displayed (black line) in figure 8(b). As can be observed, a SPV response exists in the all PL.
emission range. This confirms that PL is originated in band gap defect states. The fact that no appreciable SPV response was observed above 3 eV seems to exclude the presence of a direct band gap at near 4.0 eV, this would support our previous assumption of the indirect character of the band gap in MoO$_3$.

7. Conclusions

Pure MoO$_2$ and MoO$_3$ thin films have been obtained: MoO$_2$ by using chemically driven close space vapor transport and MoO$_3$ by annealing in air the as-grown MoO$_2$ films. The MoO$_2$/MoO$_3$ phase transition was found to occur in the 225 °C–350 °C range. We reported an optical band gap for pure MoO$_2$ of 1.83 eV assuming an indirect transition; this value seems to be more realistic than others reported in the literature, due to the absence of mixed phases in our material. After the simulation of substrate interference fringes shift resulting from the deposition of MoO$_2$, the dispersion relation of the refractive index of MoO$_2$ is reported in this paper by the first time. The measured value was corrected considering the porosity of the samples estimated by Rutherford backscattering spectra.

Electrical resistivity measurements as a function of temperature confirmed the metallic character of MoO$_2$ and allowed to fit the BG equation to extract the relevant parameters as the Debye temperature, the residual resistivity, and the high temperature limit of the $\rho - T$ curve slope. Although a metallic behavior had been previously observed in MoO$_2$, our fit of the BG formula allowed determining the Debye temperature of the material. The PL of the samples converted to MoO$_3$ was measured as a function of temperature. A broad wide spectra producing white luminescence was observed at low temperature and fitted with six Gaussian contributions. With increasing temperature, the higher energy peaks partially quenched and the color of the overall luminescence changed to green. The energy position of the peaks, comprising those with energies in the blue region, near the band gap, remain practically constant. This indicates that all the observed peaks are originating from defect states in the band gap.

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