

SOME FEATURES OF ABSORPTION AND PHOTOLUMINESCENCE OF WULFENITE (PbMoO₄) CRYSTALS

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Abstract

A description of experimental results of studying the optical absorption and photoluminescence (PL) of tetragonal (class 4/m) PbMoO₄ crystals is given. The light transmitted and reflected in the polarized radiation for both orientation (E || C₄ and E ⊥ C₄) at 300 and 77 K is measured. The spectral dependence of the absorption coefficient at the edge absorption ($\lambda \approx 0.3\text{--}0.5 \mu\text{m}$) shows that the edge absorption is determined by phonon-assisted indirect transitions.

Spectral characteristics of the absorption coefficient of crystals with two radiation polarizations in the temperature range from 77 to 300 K are investigated. The measured spectral dependence of the absorption coefficient at two orientation of polarization of light and the known theoretical dependence were combined and compared for determination the types of optical transitions in fundamental absorption of PbMoO₄ crystals. Limited energies E_g^{ind} and E_g^{dir} for E || C₄ and E ⊥ C₄ were found. A detailed investigation of the fundamental absorption of PbMoO₄ crystals is given. The direct optical edge E_g at T = 300 K is 3.28 eV and 3.36 eV for E || C₄ and E ⊥ C₄, respectively. Pure lead molybdate single crystals grown by the Czochralski method were investigated by optical absorption and PL methods. The radiative recombination mainly for interbands transitions in PbMoO₄ crystals excited with a 365-nm wavelength was observed and analyzed. All PL spectra undergo a Stokes shift and can be characterized by a large half-width.

The absorption spectra were compared with both PL and calculated emission intensity for a degenerate electron gas of the conduction band and nondegenerate hole gas in the valence band for direct transitions [1].

1. Introduction

Lead molybdate (PbMoO₄ or PM) crystals, class 4/m, are extensively employed in acousto-optic device applications because of a high acousto-optic figure of merit ($M_2 = 37 \cdot 10^{-8} \text{ s}^3/\text{g}$), low acoustic and optical loss below 1 GHz, and favorable mechanical impedance for acoustic matching. Recently, this material has been found to be useful as a scintillator for the double β decay experiment below 100 K.

The physical and optical properties of PbMoO₄ are shown below: density at 293 K $\rho = 6.95 \text{ g/cm}^3$, melting temperature of 1330°C, effective birefringence ($\lambda = 1.55 \mu\text{m}$) $\Delta n_{\text{eff}} = 0.103$, transmittance range of 0.4-5.5 μm , refractive index at 633 nm $n_o = 2.38$, $n_e = 2.25$ [2].

Crystals of lead molybdate with a diameter of up to 16 mm and a length of 60–80 mm are

grown by the Czochralsky-Kyropulos method. Lead molybdate AO elements possess low optical losses, high optical homogeneity, and stability to laser radiation. High crystal homogeneity also allows vacuum thermopressure bonding for large aperture devices.

Lead molybdate crystal features low optical losses [3], high optical homogeneity, and stability to laser radiation. The dark conductivity of PbMoO_4 crystals depends on change composition and varies from 10^{-7} to 10^{-14} s/cm [4].

The interest in the study of the optical properties of PbMoO_4 crystals is determined not only by the fundamental physical mechanism present in this material, but also by a wide range of possible applications in high speed acousto-optic devices : intensity modulators, acousto-optic deflectors and tunable filters, power spectra analyzer, ion conductors, etc.

In this work, we used PbMoO_4 crystals that belong to the space-symmetric group 4/m obtained through extraction from melt according to the Czochralski method mainly to the [100] direction having the lattice parameters $a = 5.4312 \text{ \AA}$ and $c = 12.1 \text{ \AA}$, light yellow color, tetragonal crystal type group, negative uniaxial.

The optical properties were analyzed by ultraviolet-visible (UV-Vis) absorption and photoluminescence (PL) measurement. A description of experimental results of studying the optical absorption and photoluminescence (PL) of tetragonal (class 4/m) PbMoO_4 crystals is given. The measurements of light transmitted and reflected in the polarized radiation for both orientation ($E \parallel C_4$ and $E \perp C_4$), where C_4 is the optical axis of crystal corresponding to the crystallographic [001] direction at 300 and 77 K, were performed.

In this paper, we report the results of studying the fundamental absorption and PL on PbMoO_4 crystals grown from melts of controlled stoichiometric (1 : 1) molar mixture of the constituent oxides, PbO , and MoO_3 and employing the Czochralski technique) [5]. Pure lead molybdate single crystals were investigated by optical absorption and PL methods.

2. Fundamental optical absorption

Optical measurements have many unique and attractive features for studying and characterizing crystal properties. They are contactless, nondestructive, and compatible with any transparent ambient and are useful for in-situ analysis on processing system.

In this work, we used PbMoO_4 crystals (F. 1) that belong to the space-symmetric group 4/m obtained through extraction from melt according to the Czochralsky method mainly to the [100] direction having the lattice parameters $a = 5.4312 \text{ \AA}$ and $c = 12.1 \text{ \AA}$, light white-yellow color, tetragonal crystal type group, negative uniaxial. In our study, two types of plate were used:

(1) plates in which the developed faces contained the C_4 -axis and (2) plates in which the developed faces were perpendicular to the C_4 -axis. Transmission $T(h\nu)$ and reflection $R(h\nu)$ were recorded in polarized light using a spectrophotometric setup based on an M-40 spectrophotometer and a Glan-Thompson prism in a wavelength range of 200 to 900 nm.

Measurements of optical transmission and reflection were analyzed in the standard way to yield the optical absorption coefficient α as a function of photon energy $h\nu$.

Transmission T of a thin slab of known thickness ($d \approx 10 - 40 \text{ \mu m}$) and absolute reflectivity R at nearly normal incidence in two radiation polarizations ($E \parallel C_4$ and $E \perp C_4$, where C_4 is the optical axis of crystals) were measured. The optical measurements were carried out in a range of the liquid nitrogen (77 K) to room temperature (300 K).

Figure 1b shows a probe for optical absorption studies.

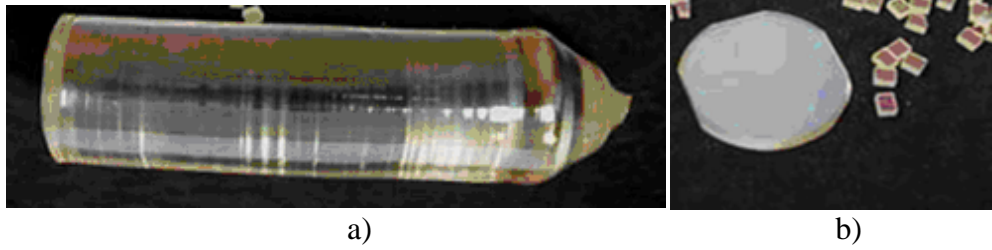


Fig. 1. Photograph^[5] of (a) a typical PbMoO₄ crystal grown by the Czochralski method and (b) the probe used for optical absorption and PL studies.

Absorption coefficient α was calculated by the following relationship [5]

$$\alpha(\nu) = \frac{(1-R)^2 e^{-\alpha d}}{1-R^2 e^{-2\alpha d}} \quad (1)$$

where ν is the light frequency and d is the thickness of the plates.

In the high-absorption range, the optical gap was evaluated from Tauc's equation

$$\alpha h\nu = B (h\nu - E_g)^{1/2} \quad (2)$$

where E_g is the energy distance between the valence and conduction band mobility edges.

In this spectral region, the extremely sharp absorption edge is best fit by (2) near the edge. The parameter B given by the slope of the plots is an interesting parameter, since it can be taken as a measure of the disorder.

Figure 2 shows plots of $(\alpha h\nu)^{1/2}$ (curve 2) versus photon energy $h\nu$ for PbMoO₄ crystals at 300 K for $E \parallel C_4$. The characteristic optical parameters $E_g^{\text{dir.}}$ (eV) present the edge of direct optical transitions of electrons from the valence to conduction band in crystals.

Fundamental optical absorption characterized by an exponential spectral dependence was observed in a variety of crystals.

The direct optical edges $E_g^{\text{dir.}}$ at $T = 300$ K are 3.28 and 3.36 eV for $E \parallel C_4$ and $E \perp C_4$, respectively. Possibilities of interpretation of the particularity of absorption spectra on the basis of the proposed band structure were examined in [6].

The calculation of the electronic structure of PbMoO₄ showed [1] that the valence and conduction bands are mainly composed of the O 2p and Mo 4d states, respectively, and the Pb state appreciably contributes to the valence band top and the conduction band bottom. In this work, the importance of the exciton transition was explained in terms of the cationic Pb 6s \rightarrow 6p excitation model taking into account the crystal-field splitting and the spin-orbit interaction of Pb 6p state in PbMoO₄ crystals. The authors of this work found that the doublet exciton band absorption at 3.6 eV shows a doublet structure with distinct dichroism.

Figure 2 (curve 1) shows that, at $h\nu < 3.2$ eV for $E \parallel C_4$, absorption coefficient α increases with photon energy loss $h\nu$ indicated by expression (2).

This behavior of absorption in PbMoO₄ crystal (curve 1) indicated that absorption in this energy range is determined by optical transitions, where the maximum valence-band energy and the minimum conduction-band energy do not occur at the same k -vector (an indirect transition appears, see [6] for details).

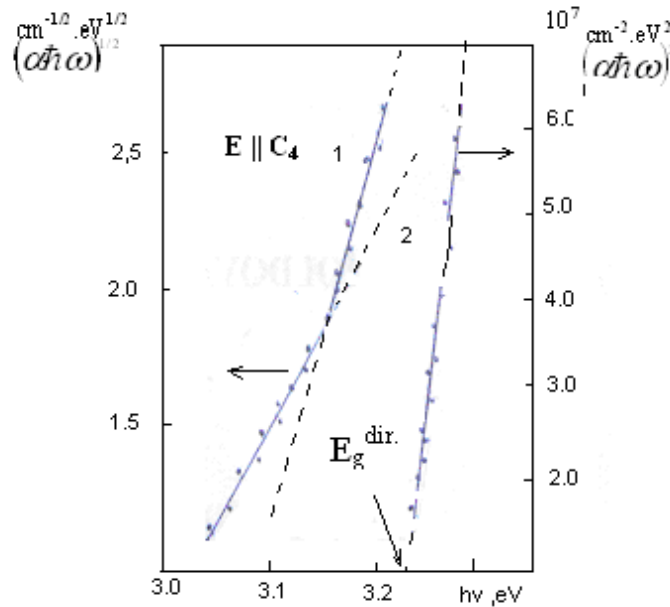


Fig. 2. Theoretical fit to the experimental absorption edge of PbMoO₄ at 300 K for $E \parallel C_4$.

In this case, the indirect-gap absorption coefficient that corresponds to the allowed indirect transition is defined by

$$\alpha_{hv} = C^{(ab)} \frac{(hv - E_g^{ind} + hv_{ph})^2}{\exp\left(\frac{hv_{ph}}{kT}\right) - 1} + C^{(em)} \frac{(hv - E_g^{ind} - hv_{ph})^2}{1 - \exp\left(-\frac{hv_{ph}}{kT}\right)} \quad (3)$$

where hv_{ph} is the energy of the phonon-assisted transition, the superscripts (ab) and (em) refer to phonon absorption and emission, respectively.

This expression is nonzero if the quantities in parentheses are positive, i.e.,

$$hv \pm hv_{ph} > E_g^{ind} \quad (4)$$

where E_g^{ind} is the indirect edge-energy interval between the valence band and the absolute minimum of the conduction band of the crystal (see the band structure from [6]).

By extrapolating the linear region of curve 1 ($(\alpha_{hv})^{1/2} \sim hv$) to value by $\alpha = 0$ in two types of polarization of radiation, the minimum energy gap E_g^{ind} was determined.

The indirect gaps E_g^{ind} are 3.08 eV and 3.16 eV for $E \parallel C_4$ and $E \perp C_4$, respectively. The interband (direct and indirect) transitions are temperature functions and decrease with its increase. The minima of interband transition were determined and the temperature dependence of the absorption edge shift was studied. The temperature coefficient of shift of E_g^{ind} is $1.8 \cdot 10^{-4}$ eV/deg. Possibilities of the interpretation of the particularity of absorption spectra on the basis of the proposed band structure were examined.

3. Photoluminescence

The luminescence study was used to obtain additional information of interband optical

transitions in the PbMoO_4 crystal. To study luminescence, it is necessary to optically pump into the absorption spectrum using high-intensity sources .

Typical sources used in luminescence spectroscopy, which have broad bands in near ultraviolet and blue regions , include usually hydrogen, xenon, or mercury (Hg) arc lamps .

High-pressure mercury (Hg) arc lamps have higher intensities than Xe arc lamps and its intensity is concentrated in sharp lines. Consequently, these lamps are mainly utilized with broadband absorbers that are crystals.

In this work, the radiative recombination was mainly studied for interband transitions in PbMoO_4 crystals.

PL measurements of wulfenite (PbMoO_4) were performed at room temperature for crystals with different size. PL was excited by 365-nm ($E_{\text{ex}} = 3.39$ eV, Hg triplet $6^3\text{P}_2-6^3\text{D}_3$) photons of an focused super-high-pressure Hg lamp beam and detected by a FEU-38 photomultiplier with associated high-voltage power supplies through a grating monochromator using the look-in technique. Luminescence spectra were recorded at a constant excitation wavelength, which resulted in the most intense emission, followed by scanning the wavelength of the monochromator emission.

These ideal light sources, monochromators, and phototubes are not available, and it is necessary to make a settlement with the selection of components and to correct the nonideal response of the luminescence spectrometer.

Generally, luminescence spectra are recorded by selecting the excitation wavelength, which results in the most intense emission, followed by scanning the wavelength of the emission monochromator. In consequence, techniques must be developed to allow for the wavelength-dependent efficiency of the emission monochromator and photomultiplier tube. In general terms, the light signal is detected using a photomultiplier tube in which the photon flux produces an electrical current proportional to the light intensity. The device is based on the photoelectric effect.

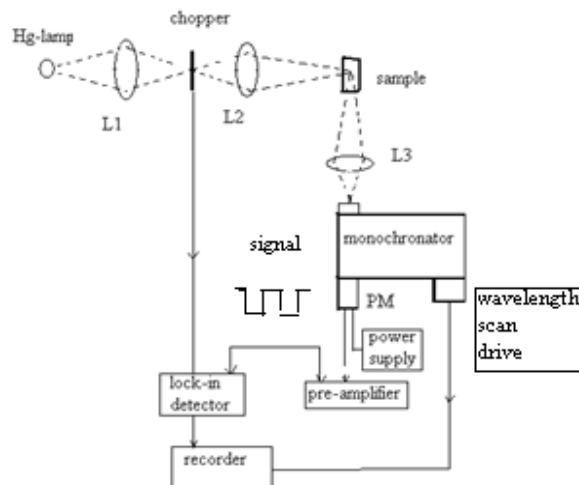


Fig. 3. Schematic of a spectrometer for measuring luminescence spectra.

The phenomena usually studied to obtain information on the optical properties of crystals are absorption and PL in a large wavelength range.

The radiative recombination mainly for interband transitions in PbMoO_4 crystals was

observed and analyzed at excitation by a 365-nm wavelength.

PL measurements of wulfenite (PbMoO₄) were performed at room temperature for crystals with different size. An intense blue-green PL band emission was observed.

Figure 4 shows the relative positions of the absorption spectra at two polarizations (for E || C₄ and E ⊥ C₄, respectively) and the PL band at 300 K. An intense blue-green PL broadened band emission was observed.

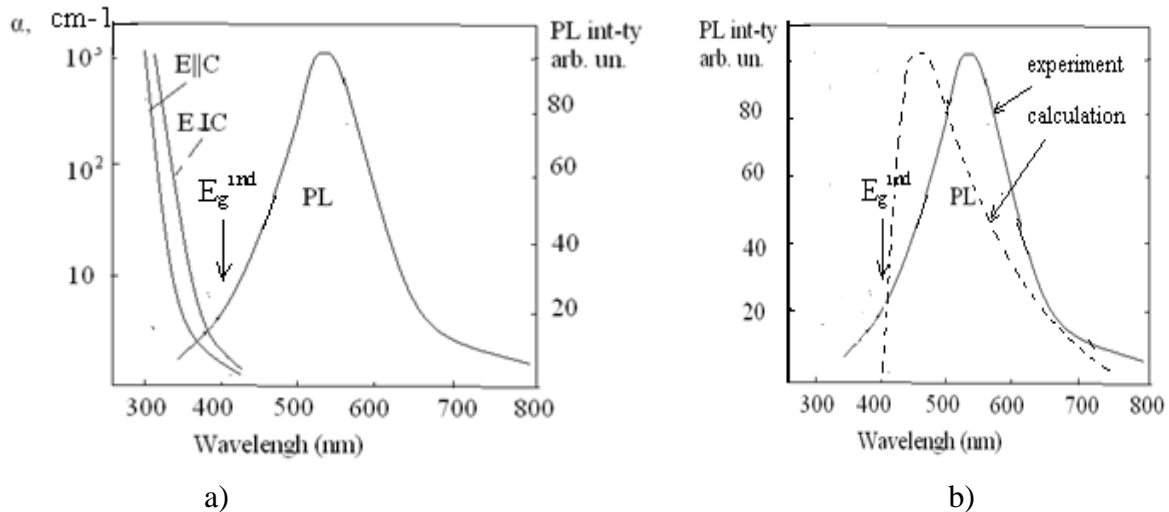


Fig. 4. (a) Relative positions of the absorption spectra at two polarizations and PL band of PbMoO₄ at 300 K excited by 365 nm ($E_{ex}=3.39$ eV) and (b) emission (solid curve) and calculated (dashed curve) spectra for a direct transition.

PL relative intensity versus wavelength shows that the illumination of crystal samples results in not only a change in the concentration of nonequilibrium free carriers by their interband transitions but also capturing in localized states.

It is evident from Fig. 4a that there are red shifts of the PL peak relatively optical band gaps. All the observed spectra in these crystals undergo a Stokes shift and can be characterized by a large band half-width and solely by E_g gap.

If spontaneous emission intensity of PL appears from recombination of nondegenerate electrons of the conduction band and nondegenerate holes of the valence band, a spectral dependence may be presented, as shown in [7], by

$$I(\nu) \sim \nu^2 (h\nu - E_g)^{1/2} \exp\left[-a \frac{h\nu - E_g}{kT}\right] \times \left\{ 1 + \left[b \frac{h\nu - E_g}{kT} - c \right] \right\} \quad (5)$$

where $a = m_c/m_c - |m_v|$, $b = |m_c|/m_c + |m_v|$, and $c = 30$ meV.

Figure 4b depicts the results of calculated PL emission intensity of PbMoO₄ according to (5).

4. Conclusions

The results of experimental studies of the spectral characteristics of the absorption coefficient of tetragonal (class 4/m) PbMoO₄ crystals are given. The light transmitted and reflected in the polarized radiation for both orientations in a temperature range of 77 to 300 K was measured. A detailed investigation of the fundamental absorption of PbMoO₄ crystals is presented.

Direct and indirect optical transitions in PbMoO₄ crystals were observed.

1. The spectral dependence of the absorption coefficient at the edge absorption ($\lambda \approx 0.3-0.5 \mu\text{m}$) showed that the edge absorption is determined by phonon-assisted

indirect transitions. Values of E_g^{dir} and E_g^{indir} and their temperature dependences for both ($E \parallel C_4$ and $E \perp C_4$) at 300 to 77 K were studied.

2. Limited energies E_g^{ind} and E_g^{dir} for $E \parallel C_4$ and $E \perp C_4$ were found.

3. Joint optical properties were analyzed by ultraviolet-visible (UV-Vis) absorption and PL measurements. A description of experimental results of studying the optical absorption and PL of PbMoO_4 crystals is given. The PL measurements of wulfenite (PbMoO_4) excited by 365 nm ($E_{\text{ex}} = 3.39$ eV, Hg triplet $6^3P_2-6^3D_3$) were performed at room temperature.

4. All PL spectra undergo a Stokes shift and can be characterized by a large band half-width and solely by E_g gap.

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