

ABSORPTION AND PHOTOCONDUCTIVITY OF PbMoO₄ CRYSTALS

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Abstract

Spectral characteristics of the fundamental absorption coefficient and photoconductivity of PbMoO₄ crystals with two polarizations in a temperature range of 77 to 300 K are investigated. The measurements of light transmitted in the polarized radiation for both orientations ($\mathbf{E} \parallel \mathbf{C}_4$ and $\mathbf{E} \perp \mathbf{C}_4$, \mathbf{C}_4 is the [001] crystallographic direction corresponding to the optical axis) of crystals are carried out.

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 indirect assisted by phonons transitions. The measured spectral dependence of the absorption coefficient at two orientations of polarization of light and the known theoretical dependence were combined and compared for determination the types of optical transitions in the fundamental absorption of PbMoO₄ crystals. Limited energies E_g^{ind} and E_g^{dir} for $\mathbf{E} \parallel \mathbf{C}_4$ and $\mathbf{E} \perp \mathbf{C}_4$ were found. A detailed investigation of the fundamental absorption of PbMoO₄ crystals is presented. A simple model of band structure of crystals is proposed.

The photoconductivity of PbMoO₄ single crystals is investigated on $\mathbf{E} \parallel \mathbf{C}_4$ and $\mathbf{E} \perp \mathbf{C}_4$ at 300 K in the fundamental absorption spectral region of 2.8 to 5.0 eV. The spectral dependence of the photoconductivity is studied and discussed in conjunction with reported optical data. The monopolar character of the photoconductivity was confirmed by investigation time-of-flight motion of carriers.

The present study reveals only the intrinsic photoconductivity in PbMoO₄ pure single crystals. Spectral responses of the photocurrent through PbMoO₄ crystals showed one spectral band in a range of 3.1 to 5.0 eV with maximums at 3.45 and 3.73 eV for $\mathbf{E} \parallel \mathbf{C}_4$ and $\mathbf{E} \perp \mathbf{C}_4$, respectively.

A good correlation of the photoconductivity bands at $\mathbf{E} \parallel \mathbf{C}_4$ and $\mathbf{E} \perp \mathbf{C}_4$ with absorption bands at also polarizations has been demonstrated. The unipolar time-of flight motion of carriers was analyzed, and drift mobility of electrons and its temperature dependence were determined.

1. Introduction

Lead molybdate (PbMoO₄) crystals, class 4/m, are widely used in acousto-optic and beam-manipulating devices. According to their band gap of ~ 3.3 eV [1-3] are among insulators. However, they exhibit dark conductivity σ and the photoconductivity $\Delta\sigma$ characteristic of semiconductors. It was grown by the Chochralski method and is currently used both acousto-optic devices and polarization-based passive components for telecommunications.

The physical and optical properties of PbMoO_4 are shown below: density at 293 K $\rho = 6.95 \text{ g/cm}^3$, melting temperature of 1330°C , effective birefringence ($\lambda = 1.55 \text{ }\mu\text{m}$) $\Delta n_{\text{eff}} = 0.103$, transmittance range of $0.4\text{--}5.5 \text{ }\mu\text{m}$, refractive index at 633 nm $n_o = 2.38$, $n_e = 2.25$ [4].

A lead molybdate crystal features low optical losses, 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 [3]. It exhibits sizeable photochromic effect—changes in optical density under irradiation in the ultraviolet or blue. This impedes the use of PbMoO_4 in the acousto-optic modulator of laser radiation. In view of this, considerable efforts have been concentrated on the study of its optical and photoelectrical properties.

The interest in the study of optical properties is determined not only by the fundamental physical mechanism present in these materials, but also by a wide spectrum of possible applications in high-speed acousto-optic devices that perform spatial, temporal, and spectral modulation of optical beam. The acousto-optical figure of merit is $M_2 = 37 \cdot 10^{-8} \text{ s}^3/\text{g}$ [4].

2. Light Absorption of Wulfenite (PbMoO_4) Crystals

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 that belong to the $4/m$ space-symmetric group obtained through extraction from melt according to the Chochralsky method mainly to the $[100]$ direction having the lattice parameters $a = 5.4312 \text{ \AA}$ and $c = 12.1 \text{ \AA}$, light yellow color, crystal type group is tetragonal, negative uniaxial. In our study, two types of plates 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 and reflection R were recorded in polarized light using a spectrophotometric setup based on an M-40 spectrophotometer and a Glan-Thompson prism.

For the transmission T of a thin slab with known thickness ($d \approx 10\text{--}40 \text{ }\mu\text{m}$), together with the absolute reflectivity R at nearly normal incidence in two radiation polarizations ($\mathbf{E} \parallel C_4$ and $\mathbf{E} \perp C_4$, where C_4 optical axis of crystals), the optical measurements were carried out in the temperature range from liquid nitrogen (77 K) to room temperature (300 K). The absorption coefficient α was calculated by the following relationship [1]

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

where ν is the light frequency and d is the thickness of plates. Measurements of optical absorption and reflection were analyzed in a standard way to yield the optical absorption coefficient α as a function of the photon energy $h\nu$.

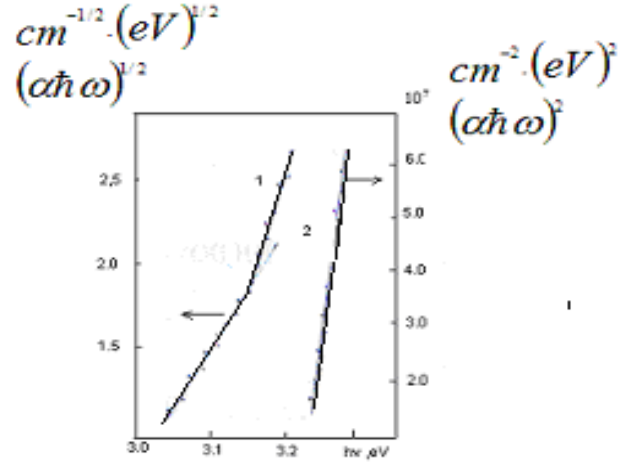


Fig. 1. Theoretical fit to the experimental absorption edge of PbMoO₄ at 300 K

Figure 1 shows the spectral variation of the absorption coefficient for PbMoO₄ plate ($d = 37 \mu\text{m}$) at the temperature 300 K. We note the extremely sharp absorption edge about 10^3 cm^{-1} , and the absorption decreases with edge at $h\nu = E_g \approx 3.0 \text{ eV}$.

In this spectral region the extremely sharp absorption edge with is fit best by the dependence near the edge

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

This increasing absorption edge (curve 1) in the PbMoO₄ crystal indicated that absorption at this energy range is determined by optical transitions were maximum valence-band energy and minimum conduction-band energy do not occur at the same \mathbf{k} -vector .

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

$$\alpha h\nu = C^{(ab)} \frac{(h\nu - E_g^{ind} + h\nu_{ph})^2}{\exp\left(\frac{h\nu_{ph}}{kT}\right) - 1} + C^{(em)} \frac{(h\nu - E_g^{ind} - h\nu_{ph})^2}{1 - \exp\left(-\frac{h\nu_{ph}}{kT}\right)}, \quad (3)$$

where $h\nu_{ph}$ is the energy of the phonon assisting in the transition, the superscripts (ab) and (em) refer to phonon absorption and emission, respectively. These expression is only nonzero when the quantities in parentheses are positive, i.e., when

$$h\nu \pm h\nu_{ph} > E_g^{ind}, \quad (4)$$

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.

By extrapolating the linear region of curve 1 by $\alpha = 0$ in two types of transitions, the minimum energy gap E_g^{ind} was determined.

As is evident, at the lowest energies, absorption coefficient α rises due to the onset of indirect absorption as seen by the $(\alpha h\nu)^{1/2}$ dependence on photon energy.

In the high-absorption range (higher energies of photons, Fig. 1, curve 2) a sharper rise of

absorption coefficient α is found where direct transitions occur at the zone center and an $(\alpha h\nu)^2$ dependence on energy is then seen. For the direct transition, the absorption coefficient is related to light frequency according to the following formula

$$\alpha h\nu = C_d (h\nu - E_g^{\text{dir}})^2, \quad (5)$$

$$\text{Coefficient } C_d = \frac{4\pi e^2 c^2 (2m_r)^{3/2} X_{cv}^2}{hn\lambda_0^3}. \quad (6)$$

Figure 2 shows the spectral variation of the absorption coefficient for PbMoO₄ crystals at a temperature of 218 and 77 K.

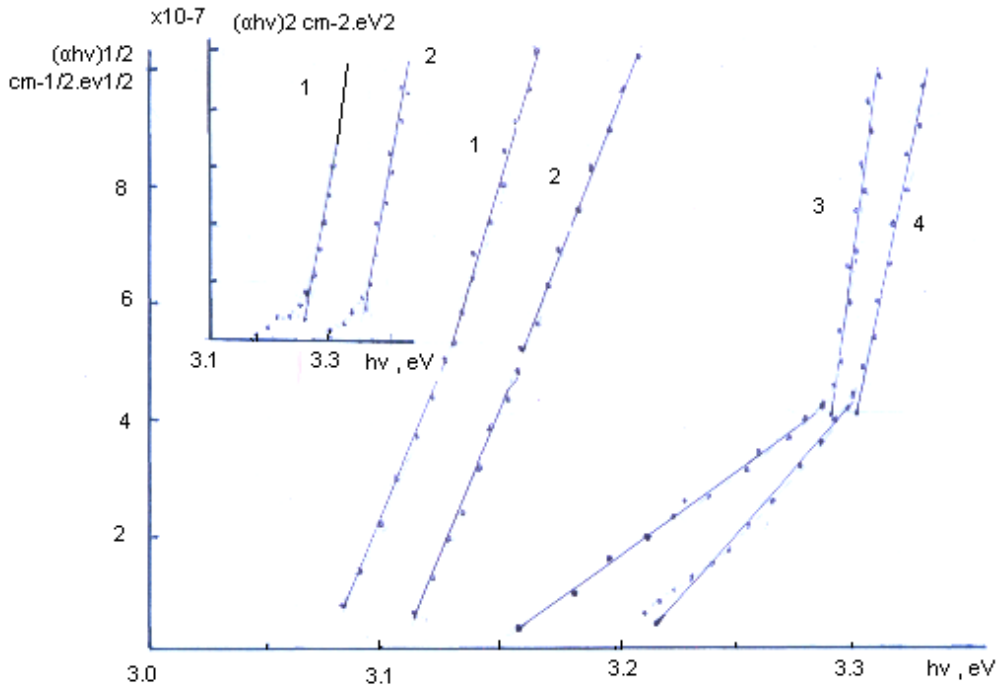


Fig. 2. Absorption edge of PbMoO₄ at 218 K (curves 1, 3) and 77 K (curves 2, 4):
 (a) $(\alpha h\nu)^{1/2}$, (1, 3) ($\mathbf{E} \parallel \mathbf{C}_4$), (2, 4) ($\mathbf{E} \perp \mathbf{C}_4$); (b) $(\alpha h\nu)^2$, (1) ($\mathbf{E} \parallel \mathbf{C}_4$), (2) ($\mathbf{E} \perp \mathbf{C}_4$).

It is evident that, at the lowest energies (Fig. 2a, (1) ($\mathbf{E} \parallel \mathbf{C}_4$), (2) $\mathbf{E} \perp \mathbf{C}_4$, T = 218 K) α rises due to the onset of the indirect absorption by the $(\alpha h\nu)^{1/2}$ dependence on photon energy. Curves 3 ($\mathbf{E} \parallel \mathbf{C}_4$) and 4 ($\mathbf{E} \perp \mathbf{C}_4$) correspond to absorption at the temperature T = 77 K.

Figure 2b shows plots of $(\alpha h\nu)^2$ versus photon energy $h\nu$ at $\alpha > 10^3$ and T = 300 K (curve 1, ($\mathbf{E} \parallel \mathbf{C}_4$), and curve 2, $\mathbf{E} \perp \mathbf{C}_4$). The absorption at this energy interval is much stronger than that of indirect absorption (see curve 2 in Fig. 1). The characteristic optical parameters E_g^{dir} are 3.28 and 3.38 eV for $\mathbf{E} \parallel \mathbf{C}_4$ and $\mathbf{E} \perp \mathbf{C}_4$, respectively.

By extrapolating the linear region of curves to the value $\alpha = 0$ for $\mathbf{E} \parallel \mathbf{C}_4$ and $\mathbf{E} \perp \mathbf{C}_4$ minimum energy gaps of 3.08 and 3.16 eV at 300 K were obtained. For indirect transitions, these minimum energy gaps E^{ind} varied with temperature and were 3.37 and 3.29 eV at 77 K for $\mathbf{E} \parallel \mathbf{C}_4$

and $E \perp C_4$, respectively. Note the large shifts of E_g^{ind} with temperature for both polarization measurements. The temperature coefficient of shift of E^{ind} is $8 \cdot 10^{-4}$ eV/deg.

3. Band structure of PbMoO₄ crystals

The model of the energy state arrangement in the PbMoO₄ crystals which provides a relevant description of optical transition is proposed schematically in Fig. 3. An E-k diagram with essential features is depicted in Fig. 3a. It is important that the minimum of the conduction band (CB) of the crystal is not directly above the maximum of the valence band (VB), but it is displaced along the k-axis (indirect-bandgap semiconductor). All the valence electrons at 0 K, therefore, fill the states (particular k_n values) in the lower E-k diagram.

In this model, the electrons with momentum k_{vb} from the valence band cannot make a direct transition from the top of the valence band to the bottom ($k = k_{cb}$) of the conduction band because this would violate conservation of momentum. This transition can still take place but as a two-step process requiring the cooperation of another particle and which can be described by second-order

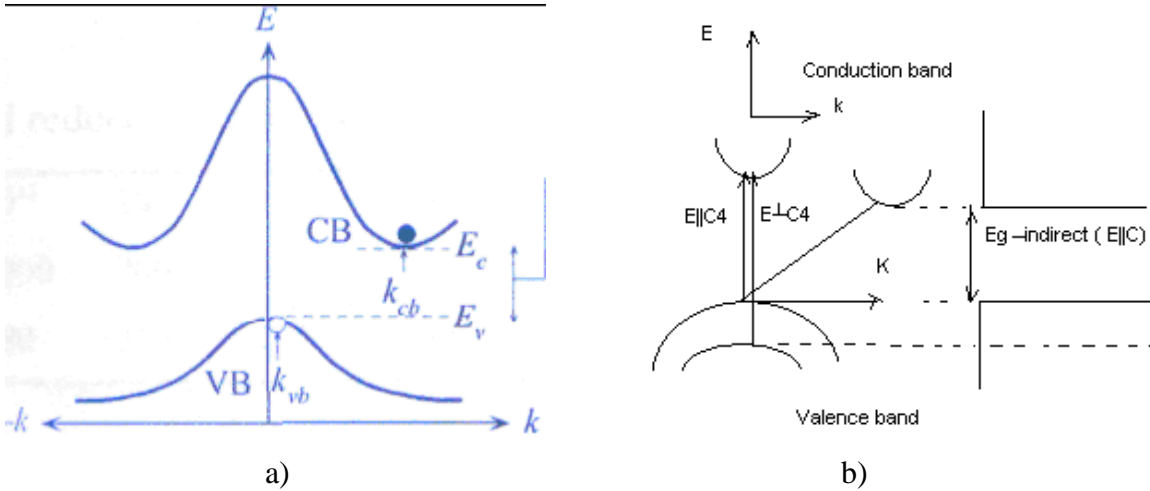


Fig. 3. A model of band diagrams of the PbMoO₄ crystals: (a) E-k diagram and (b) a simple band structure with both conduction and valence band edge.

perturbation theory. The particle most frequently involved is an interval phonon of energy $h\nu_{ph}$ which can be either generated or absorbed in the transition. The minimal-energy state in the conduction band and the maximal-energy state in the valence band are each characterized by a certain k -vector in the Brillouin zone. Therefore, if a plot of $(\alpha h\nu)^{1/2}$ versus $h\nu$ forms a straight line (Fig. 1, curve 1; Fig. 2, curves 1-4), it can normally be inferred that there is an indirect band gap which can be measured by extrapolating the line to the $\alpha = 0$ axis. On the other hand, if a plot of $(\alpha h\nu)^2$ versus $h\nu$ forms a straight line (Fig. 1, curve 2; Fig. 2b, curves 1, 2), it can normally be inferred that there is a direct band which can be measured by extrapolating the straight line to the $\alpha = 0$ axis.

According to the scheme (Fig. 3b), the 3.16-eV absorption for $E \parallel C_4$ (Fig. 1, curve 1 and Fig. 2a, curve 1) and the 3.21-eV absorption for $E \perp C_4$ (Fig. 2a, curve 2) are attributed to the indirect optical transitions from the valence bands to the minimum of the conduction bands at 300 K.

The 3.28-eV and 3.36-eV absorptions correspond to the direct transitions (arrow 2, Fig. 3; curves 1, 2, Fig. 2b) for $\mathbf{E} \parallel \mathbf{C}_4$ and $\mathbf{E} \perp \mathbf{C}_4$, respectively.

4. Photoconductivity and multiple-trapping electron transport in PbMoO_4

The photoconductivity of PbMoO_4 single crystals was investigated at 300 K in a spectral region of 2.8 to 5.0 eV. The spectral dependence of the photoconductivity was studied with indium ohmic contacts in a rectangular geometry for two polarizations ($\mathbf{E} \parallel \mathbf{C}_4$ and $\mathbf{E} \perp \mathbf{C}_4$) of light.

Spectral responses of the photocurrent through crystals (Fig. 4) show one spectral band in a range of 3.1 to 5.0 eV with maximums at 3.45 eV and 3.73 eV for $\mathbf{E} \parallel \mathbf{C}_4$ and $\mathbf{E} \perp \mathbf{C}_4$, respectively. The bands correlate with the respective bands of the absorption spectra [1] that reveal the intrinsic specificity of optical generation of carriers, i.e., band to band excitation only. The spectral positions of photocurrent maximums completely correspond to spectral rises of absorption coefficient α due to the onset of indirect absorption for both polarizations of light (see Fig. 2, curves 1 and 3 for $\mathbf{E} \parallel \mathbf{C}_4$; 2 and 4 for $\mathbf{E} \perp \mathbf{C}_4$).

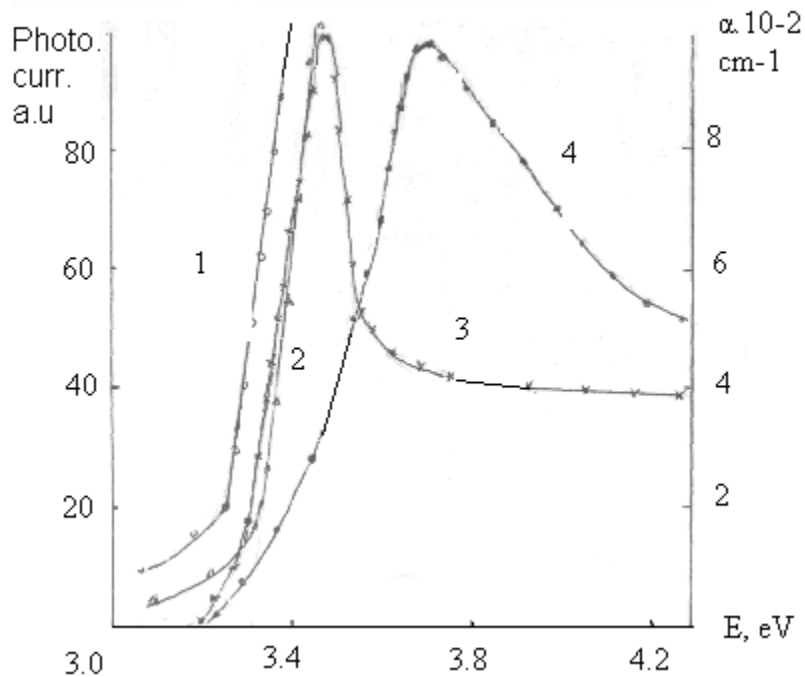


Fig. 4. Spectral dependences of absorption coefficients (1, 2) and photoconductivity (3, 4) of PbMoO_4 at 300 K: curves 1, 3 - $\mathbf{E} \parallel \mathbf{C}_4$; curves 2, 4 - $\mathbf{E} \perp \mathbf{C}_4$.

The illumination of crystal samples results not only in a change in the concentration of nonequilibrium free carriers because of their capturing in localized states, but also in a change in carrier drift mobility.

As mentioned in previous works [3, 5, 6], in dependence on the growth/charge

composition, two absorption and photoconduction bands due to Pb^{3+} and Mo^{5+} ions in PbMoO_4 crystals were shown. In the present study, the extrinsic photoconductivity in our PbMoO_4 crystals is not observed.

However, due to the large number of localized states in the gap, free carriers which appear in crystals under irradiation will be very quickly trapped in this distribution of gap states and remain trapped until they are thermally released after an average time of

$$\tau_t = \nu_o^{-1} \exp(E_t / kt) \quad (7)$$

where ν_o is the attempt-to-escape frequency (on the order of 10^{12} s^{-1} for gap states), E_t is the energy depth of the trap, k is the Boltzmann constant, and T is absolute temperature. Once free, the carrier will move with free-carrier mobility μ_o until trapped again and electrical transport is trap-limited.

The presence of distribution of localized states in crystals can be confirmed by experimental technique, i.e., by tightly-focused laser beam illumination. The experimentally accessible quantity in this case is the *drift mobility* μ_d , which differ from the free carrier mobility by the ratio of free to trapped charge, and which can be obtained in a time-of-flight transient photoconductivity experiment [7, 8] from the transit time t_T , the sample length L and the applied field E as follows:

$$\mu_d = \frac{L}{t_T E} \quad (8)$$

To extract information from measured currents, two types of photoconductive spectroscopy have been developed, one in the time and the other in the frequency domain. In this work, we will mainly use information obtained from time-domain measurements. The ultrafast dynamics of the carriers out of the equilibrium was investigated using the pulse excitation technique. The experimental set-up is shown in Fig. 5.

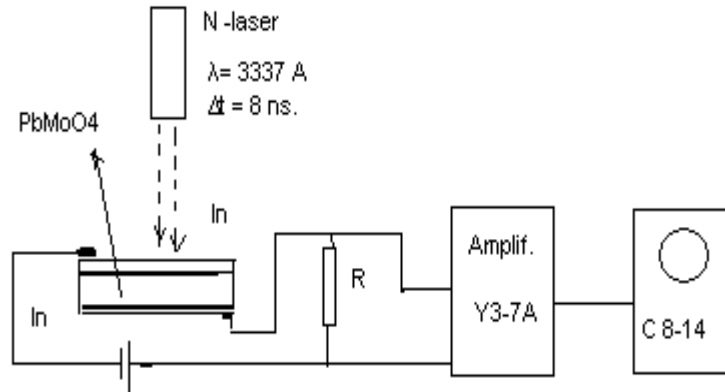


Fig. 5. Experimental set-up for recording the photo-response kinetics in PbMoO_4 crystals exposed to pulsed laser radiation.

An $8 \cdot 10^{-9} \text{ s}$ N_2 laser –beam at $\lambda = 3371 \text{ \AA}$ is focused on the sample with an area of $7 \times 5 \text{ mm}$ and a thickness of $0.3\text{-}0.7 \text{ mm}$ having $1.2\text{-}1.6 \cdot 10^{-2} \text{ cm}^{-1}$ residual absorption at $\lambda = 450 \text{ nm}$. Indium ohmic contacts were deposited onto the two faces of samples by vacuum evaporation. The transparence of top electrode $T \approx 60\%$. The optical axis C_4 of the crystal was perpendicular to the sample faces. The samples were put in the focal plane of the lens (focal length $f = 10 \text{ mm}$) in the fixed position.

The photocurrent yielded by the generation, drift and multiple trapping of free charge carries creates the signal at loading resistance R . The response of the photocurrent through the PbMoO_4 sample (load voltage $V(t)$) was measured in the constant electric field of $\sim 10^3$ V/cm using a Y3-7A large-bandwidth amplifier and was observed using a C8-14 oscilloscope. The measurements were performed in a temperature interval of 80-300 K. The present study reveals only intrinsic photoconductivity.

Time-of flight (TOF) experiments (Fig. 5) to determine the drift mobility μ_d of electrons were used. The depth of penetration of the laser beam into PbMoO_4 is $\sim 10^{-5}$ cm. Electrons optically excited by the N2-laser pulse ($h\nu > E_g$) are made move in the applied electrical field across the sample. The motion of the package of charges leads to electrical current $I(t)$. The holes generated during the absorption of the light pulse do not participate in the formation of the photoconductivity signal. This is confirmed by the lock of signal applying a positive potential to the semitransparent top electrode. The measurement of transit time τ_T used in Eq. (6) corresponds to carriers trapped in shallow states used for calculating the drift mobility μ_d .

Figure 6 represents the typical time dependence of the photoconductivity signals with different fields (curve 1- $3 \cdot 10^3$ V/cm, curve 2 - $7 \cdot 10^3$ V/cm) at 300 K. The analysis of the kinetics of photoconductivity at different fields and temperatures gives the possibility to determine the average velocity of electrons in crystal, its drift mobility, and temperature dependence. As it is known, during the Gauss charge package transfer through the crystal, the shaped character of current pulse appears. The shape of curves is determined by multiple acts of capture and release of charges by localized states. The lifetime of the electrons was determined from the relaxation of the photocurrent in perpendicular geometry and achieves $1.7 \cdot 10^{-5}$ s that is ten times more than the time of motion of charges across the sample in TOF experiments. The product of the drift mobility and times of motion is $3.4 \cdot 10^{-5}$ cm²/V and it is ten times as the same product for PbI_2 used for X-ray detection.

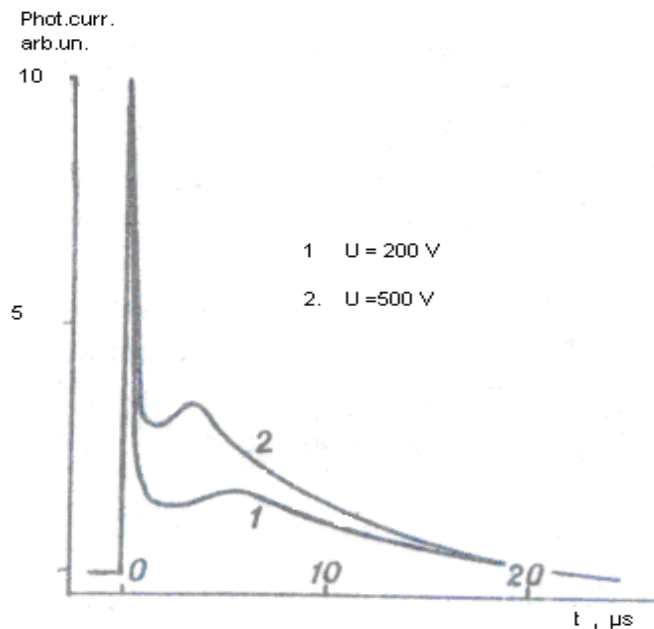


Fig. 6. Photoresponse kinetics in the PbMoO_4 crystal at 300 K after switching on the N_2 Laser excitation ($\lambda = 0.3371 \mu\text{m}$).

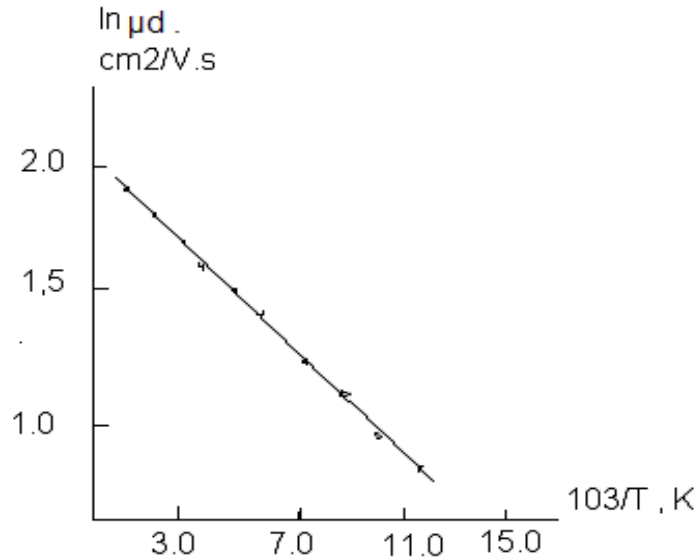


Fig. 7. Temperature dependence of the drift mobility of the PbMoO₄ crystal.

The high value of the product $\mu_d\tau_T$ of PbMoO₄ crystals and the presence of heavy Pb⁺ ions allow using the crystals for the X-ray and gamma-ray effective detection. Figure 7 indicates that the drift mobility μ_d of electrons in PbMoO₄ crystals is temperature dependent and increases with increasing temperature assuming the τ_T^{-1} dependence.

5. Conclusions

1. First of all, it is necessary to note that the lead molybdate (PbMoO₄) crystals are indirect-gap. They exhibit large direct E_g^d and indirect E_g^{indir} shifts with temperature. Also, the direct-gap absorption is much stronger than that of indirect-gap absorption.

A simple band structure model with both conduction and valence-band edge at $\mathbf{k}=0$ was proposed.

The E_g^d and E_g^{indir} for $\mathbf{E} \parallel \mathbf{C}_4$ and $\mathbf{E} \perp \mathbf{C}_4$ were determined.

2. The photoconductivity of pure PbMoO₄ is localized at $\lambda < 0.4 \mu\text{m}$ and is determined by inter-band indirect and direct absorptions and depends on light polarization.

3. The kinetics of charge motion in the PbMoO₄ crystals is controlled by capture and release by localized states. The drift mobility of electrons in crystals was measured with its temperature dependence. The high value of the product $\mu_d\tau_T$ of PbMoO₄ crystals and the presence of heavy Pb⁺ ions provide the use of the crystals for the X-ray and gamma-ray effective detection.

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