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Phenomena induced by UV irradiation in PbMoO_4 single crystal

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ABSTRACT

Electrical properties and optical absorption of PbMoO_4 single crystal were studied after UV irradiation. Anomalies of permittivity ϵ and conductivity σ were detected and attributed to the dipole centers induced by UV light. It was proposed that dipole centers were created by photoelectrons trapped by Mo within oxygen tetrahedra distorted by an oxygen vacancy V_{O} . At high temperatures conductivity was nearly insensitive to UV irradiation. Additional optical absorption was observed in PbMoO_4 single crystal after UV irradiation. It was argued that transfer of photoelectrons from lead to molybdenum groups was responsible for the photochromic effect found.

KEYWORDS

Dielectric permittivity; lead molybdate crystal; optical density spectra; UV light irradiation

1. Introduction

Lead molybdate (PbMoO_4) is one of the most intensively studied representatives of the scheelite crystal family. PbMoO_4 crystals attract close attention of technologists, researchers and engineers owing to their applications in various fields of technology and, in particular, acousto-optics. Lead molybdate is characterized by wide spectral range, high acousto-optical parameters, low acoustic and optical losses at low frequencies and favorable mechanical impedance for acoustic matching [1]. Unique combination of properties provides broad prospects for the practical use of PbMoO_4 in a family of acousto-optical devices including diffraction modulators of light, acousto-optical waveguides, acoustic wave sensors, scanning microscopes and others [2–4]. Another important area of lead molybdate application is the manufacture of solid-state Raman lasers for systems of the Lidar type (laser radar), since this material acts both as an active laser medium and as a Raman converter [5,6]. Lead molybdate (as well as lead tungstate, PbWO_4) crystals demonstrate the strongest effect of stimulated Raman scattering among crystals with quasi-molecular anions. It provides high conversion efficiency caused by interaction of laser active ion (Nd^{3+} , Yb^{3+}) with the vibration modes of $(\text{MoO}_4)^{2-}$ anions [7]. In addition, lead molybdate is considered a promising cryogenic scintillator for the experimental search of dark matter and neutrinoless double β decay of ^{100}Mo [8–10].

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Crystal structure of PbMoO_4 has tetragonal symmetry (C_{4h}^6 space group [11]) and is formed by PbO_8 eight-vertex polyhedra and slightly distorted MoO_4 tetrahedra. Each oxygen ion from surrounding of lead belongs to one of the adjacent MoO_4 tetrahedra. The point symmetry of Pb as well as Mo site is S_4 .

It is known that optical quality of PbMoO_4 crystals is highly dependent on purity of initial chemical reagents, crystal growth method and heat treatment conditions. As a rule PbMoO_4 single crystals are characterized by relatively low radiation hardness and light yellow coloration. These shortcomings restrict more extensive commercial application of PbMoO_4 in acousto-optic and scintillator devices.

Usually it is assumed that as-grown PbMoO_4 crystals have certain deficiency of Mo and Pb due to high volatility of molybdenum and lead oxides. Cationic deficiency is compensated by oxygen vacancies, that leads to disorder of Schottky type. The vacancies of host ions can trap electrons or holes, which create the states within bandgap with the width about $\sim 3.4\text{ eV}$ (see [12] and the references therein). Such centers change optical properties, and, in particular, could be responsible for coloration of the crystals. Comprehensive study of the structural point defects, such as ion vacancies, associated complexes, color centers, etc, can help to understand the nature of the phenomena causing low radiation hardness and coloration of PbMoO_4 single crystals. As it was shown earlier, doping and using non-stoichiometric charge for crystals growth make it possible to control the content of the defects affecting optical characteristics of lead molybdate [13,14]. The detailed information on the centers responsible for photoinduced phenomena in PbMoO_4 is of particular interest.

Recently [15,16] the nature of the light induced defects in PbMoO_4 was studied in details by using EPR and thermally stimulated luminescence (TSL). Three centers Mo1, Mo2 and Mo3 induced with light ($\lambda = 420\text{ nm}$, $T = 35\text{ K}$) were found. These centers represent electrons (e^-) trapped at the $(\text{MoO}_4)^{2-}$ complexes with different surroundings in nearest Pb sites. Nevertheless, all these centers were thermally stable only at low temperature and were destroyed on heating in the interval from 40 K to 120 K. This temperature range is too far away from an interval of desirable operating conditions for devices using PbMoO_4 as functional material. It is of interest to investigate the proper and light induced centers that affect the physical properties of lead molybdate crystals at moderate temperatures.

The purpose of the paper is to study electrical properties and optical absorption in PbMoO_4 single crystals irradiated with UV light. The observed photoinduced phenomena are discussed on the basis of the previous investigations of proper defects and light induced centers in PbMoO_4 crystal [14–16].

2. Experimental results and discussion

The single crystals of lead molybdate were grown from the melt by the Czochralski technique in air. The obtained crystals had a diameter up to 35 mm and a length about 50 – 60 mm. They were free from macroscopic inclusions (gas bubbles, cracks) and had a weak yellow color.

Permittivity ε and conductivity σ were measured in AC field on the samples prepared as plane-parallel plates with dimensions $5 \times 5 \times 1\text{ mm}^3$. The main planes of the samples

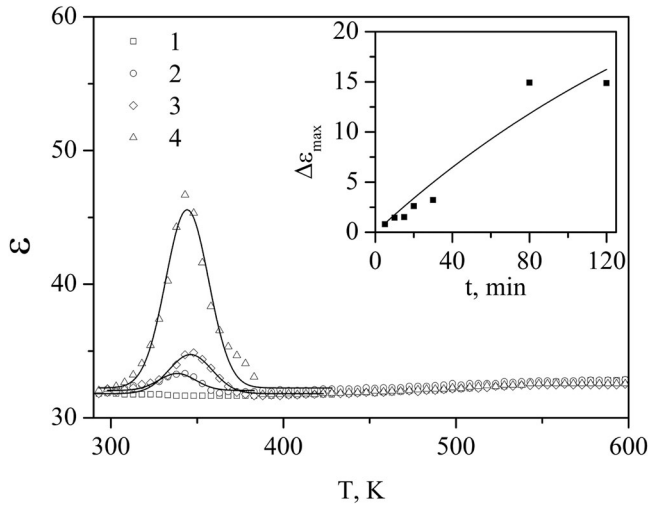


Figure 1. Permittivity dependencies $\epsilon(T)$ for PbMoO_4 crystal irradiated with UV light at $T=290$ K during the following exposure times t : 1 – 0, 2 – 10, 3 – 30, 4 – 80 min. Measuring field frequency was $f=1$ kHz. The inset shows permittivity peak magnitude $\Delta\epsilon_{max}$ vs exposure time t .

were cut parallel to (001) and coated with platinum electrodes. The measurements were carried out by bridge method at fixed frequency ($f=1$ kHz). Temperature of the samples was varied in the interval 290–700 K.

Isothermal annealing of the short-circuited samples at 700 K for 10 min was performed before each measuring cycle. Such procedure was used in order to eliminate dependence of electrical properties on the sample pre-history, similar to observed earlier in double lead molybdate Pb_2MoO_5 [17]. After annealing the samples were cooled to room temperature and irradiated through the side faces by using UV light of Hg ball lamp (wavelength of the principal line was about 366 nm). Permittivity and conductivity were measured on heating runs carried out with the rate 8 K/min.

The optical density spectra were measured at 295 K on PbMoO_4 double polished plates using “Specord -UV-VIS” spectrophotometer. The thickness of the samples was about 10–12 mm. The polished planes were oriented perpendicular to the optical axis. The photochromic coloration was observed after irradiation by light of Hg lamp during 5–30 h. Annealing of the samples was carried out at 700–950 K in air for 20 h.

2.1. Photodielectric effect

Figures 1 and 2 show the temperature dependencies of ϵ and σ for PbMoO_4 crystal irradiated at $T=290$ K for different exposure times. It can be seen that irradiation leads to appearance of $\epsilon(T)$ and $\sigma(T)$ maximums near $T\sim 340$ K. One should note that UV light induced ϵ and σ anomalies could be detected on the first heating run only and disappeared for the subsequent temperature cycling. The permittivity peak magnitude $\Delta\epsilon_{max}$ corrected for the background is plotted in the inset to Fig. 1 as a function of exposure time t . One can see that $\Delta\epsilon_{max}$ increases for longer times t and higher irradiation doses respectively. The dependence $\Delta\epsilon_{max}(t)$ was described in the assumption of exponential saturation, the relaxation time was estimated as 200 min.

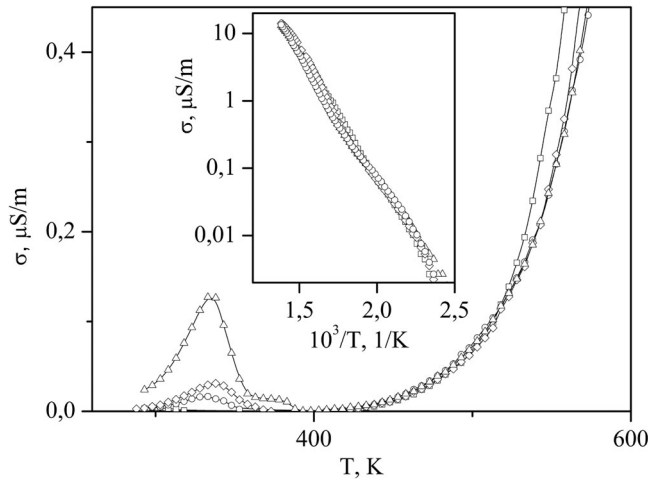


Figure 2. Conductivity dependencies $\sigma(T)$ for PbMoO_4 crystal irradiated with UV light during the times indicated in the caption to Fig. 1. The inset shows Arrhenius plot of σ vs $(1/T)$ for $T > 400$ K.

For the exposure times used, temperature dependences of conductivity σ are plotted in Fig. 2. The broad maximums of $\sigma(T)$, detected in the irradiated crystals, correspond to dielectric anomalies in Fig. 1. As shown in the inset to Fig. 2, upon further heating ($T > 400$ K) the dependences $\sigma(1/T)$ in Arrhenius scale are linearized and practically do not depend on exposure time.

The character and magnitudes of $\varepsilon(T)$ and $\sigma(T)$ anomalies give evidence that UV irradiation generates centers with electric dipole moment. Reorientations of the dipole centers in AC external field give rise to $\varepsilon(T)$ peaks (Fig. 1). Displacement currents cause maximums in $\sigma(T)$ dependences (Fig. 2). After annealing at 700 K ε and σ peaks disappeared as a result of thermal destruction of dipole centers. The dipole centers can be regenerated by following UV irradiation which performed at $T = 290$ K.

It should be noted that $\varepsilon(T)$ anomalies represent nearly symmetrical peaks (Fig. 1) which significantly differ from typical Debye-type stepwise temperature behavior [18]. This difference can be explained by the thermal decay of the dipole centers. It becomes noticeable in the same temperature range where $\varepsilon(T)$ anomalies were detected in the experiment. In fact, the dipole centers concentration decreases on heating that leads to more abrupt falling down of the high temperature wing of ε anomalies (Fig. 1).

The experimental data available allow discuss nature of the dipole centers, induced with UV light. Three types of the molybdenum complexes Mo1, 2, 3, found in PbMoO_4 recently [15,16], were thermally destroyed in the range 40–120 K. Hence, Mo1, 2, three cannot be responsible for the UV light induced ε and σ anomalies (Figs. 1 and 2) which were observed at much higher temperatures. Additional information can be taken from earlier works where photoinduced centers in isomorphous lead tungstate PbWO_4 crystal were studied [19–21]. In fact, it was pointed out [15,16] that the light induced centers in PbMoO_4 and PbWO_4 were similar in nature, since their EPR spectra were described by very close spin – Hamiltonian parameters. One can hope, that the models of the photoinduced centers in PbWO_4 [19–21] can be applied to interpret the data on PbMoO_4 .

In particular, it was shown, that irradiation of PbMoO_4 ($\lambda = 420$ nm at $T = 35$ K [15]) and $\text{PbWO}_4:\text{Mo}$ ($\lambda = 260\text{--}330$ nm at $T < 50$ K [20]) generated photoelectrons trapped by molybdenum ions in regular (PbMoO_4) or irregular ($\text{PbWO}_4:\text{Mo}$) sites: $e^- + (\text{MoO}_4)^{2-} \rightarrow (\text{MoO}_4)^{3-}$. These polaron centers were shallow (the depth was about $E_t = 0.05$ eV below the conduction band bottom) and thermally destroyed on heating above 40–50 K. $(\text{MoO}_4)^{3-}$ centers destruction resulted in disappearance of EPR spectrum and TSL glow. The released electrons partially recombined with holes and partially were captured by other deeper traps. Among such traps there were centers thermally stable up to 180–190 K ($E_t = 0.55$ eV). It was supposed that these centers were formed by oxygen vacancy V_{O} and neighboring Pb ion capturing an electron: $\text{Pb}^+ - V_{\text{O}}$. The deepest photoinduced centers ($E_t = 0.9$ eV) were stable up to room temperature and even above. Very detailed analysis of the EPR spectra anisotropy gave evidence that such centers could be associated with tungsten (molybdenum) – oxygen tetrahedron distorted by vacancy V_{O} and stabilized by the unknown defect in neighboring Pb site: $(\text{W}(\text{Mo})\text{O}_3)^- - A_{\text{Pb}}$ [20].

Accounting the EPR and TSL data in [15,16,19–21], the dipole defects, induced with UV light and giving rise to the maximums of ε and σ (Figs. 1 and 2) can be attributed to photoelectrons captured by molybdenum atoms within tetrahedra distorted by oxygen vacancy $(\text{MoO}_3)^-$. An additional neighboring defect A_{Pb} in lead sublattice stabilizes such complexes similarly to the situation in PbWO_4 . Distorted $(\text{MoO}_3)^-$ tetrahedron acquires electric dipole moment produced by excess charges of photoelectron captured by Mo and oxygen vacancy V_{O} . Thermally activated V_{O} hopping through the vertices of $(\text{MoO}_3)^-$ complex is accompanied by reorientation of the dipole moment. In AC external field such reorientations give rise to ε and σ anomalies shown in Figs. 1 and 2.

Apparently, that reorientations of $(\text{MoO}_3)^-$ dipoles cause dielectric losses and contribute to conductivity peaks observed around 340 K (Fig. 2). One can see that for $T > 400$ K behavior of $\sigma(1/T)$ becomes nearly independent on the time of UV irradiation. Therefore excited by UV light electrons do not participate in charge transfer because they are captured by other traps or recombined with holes.

It should be noted that there are other possible traps for photoelectrons. For instance, $\text{Pb}^+ - V_{\text{O}}$ centers which were found in PbWO_4 [20]. Dipole moment of such centers could be reoriented by hopping of captured electrons between structurally equivalent lead sites. But in PbWO_4 these F^+ centers were stable only below 180 K. Consequently in PbMoO_4 existence of such F^+ centers above room temperature seems unlikely.

2.2. Photochromic effect

The optical density spectra of nominally pure lead molybdate single crystal before and after UV irradiation are shown in Fig. 3. The crystal was irradiated and optical spectra were measured at room temperature. One can see that after irradiation the optical absorption increased significantly. This effect was reversible. Annealing in air at 700–950 K for 20 h eliminated the absorption induced by UV irradiation. The inset to Fig. 3 shows the additional optical density caused by irradiation. Two wide absorption bands with maximums near 24,000 and 17,300 cm^{-1} can be distinguished.

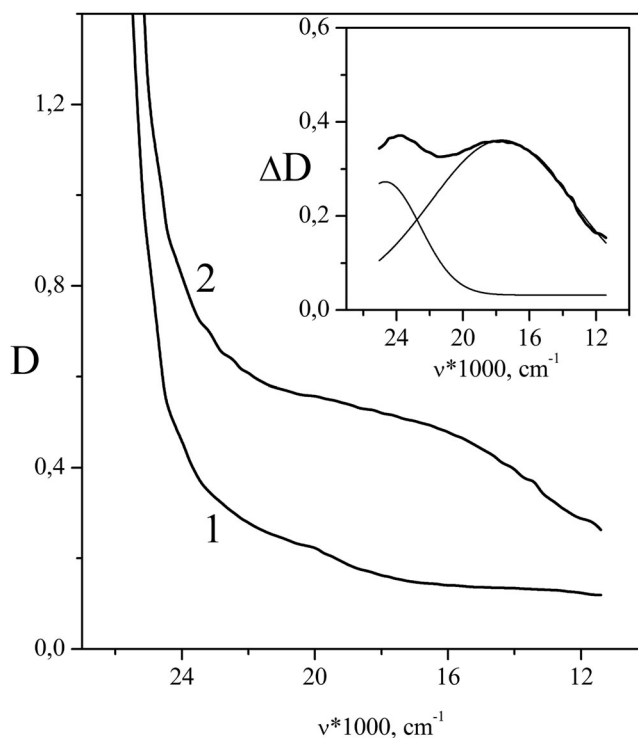


Figure 3. Optical density spectra of PbMoO_4 crystal: 1 – before UV exposure; 2 – after UV exposure. The difference between 1 and two spectra consists of two absorption bands near $24,000$ and $17,300\text{ cm}^{-1}$ (the inset). The thickness of the samples was about 10.2 mm .

Photochromic effect in PbMoO_4 single crystals most likely is caused by charge exchange between cations by means of redox reactions. Earlier [14,22] a number of experiments were performed in order to analyze the influence of dopants, deviations from composition stoichiometry, irradiation by UV light and high-temperature annealing on the color centers in PbMoO_4 . Two absorption bands in spectrum of UV irradiated PbMoO_4 crystals (the inset to Fig. 3) can be associated with creation of Mo^{5+} ($17,300\text{ cm}^{-1}$) and Pb^{3+} ($24,000\text{ cm}^{-1}$) in accordance with Ballmann model [23,24]. The investigations of the optical absorption do not give enough information to resolve the structure of such centers in details. However, the formation of Mo^{5+} as a result of various processes in PbMoO_4 was repeatedly observed by EPR [15,16,24,25]. Presence of oxygen vacancies in the vertices of Mo-O tetrahedra favors electron capturing and formation of Mo^{5+} centers [26].

Appearance of Pb^{3+} hole centers or participation of lead electronic states in the creation of the emission centers was proposed by some authors to interpret luminescence in PbMoO_4 caused by UV excitation [11,27,28]. It was suggested that photoluminescence was due to radiative transitions in $(\text{MoO}_4)^{2-}$ complexes and transfer of an electron from Pb^{2+} ions to adjacent molybdenum groups [11,28]. Van Loo offered formation of a $\text{Pb}^{3+} - \text{Mo}^{5+}$ glow centers created by UV irradiation [27]. The participation of lead ions in such centers was confirmed by experiments and calculations in [15],

which showed the significant (of about 40%) mixing of lead orbitals into the ground state of the molybdenum complex.

It has to be noted that electrical activity may be expected for certain UV light induced centers which participate in the photochromic processes. The question is whether the same centers are electrically and optically active and contribute to the anomalies of ε and σ (Figs. 1, 2) as well as optical density spectra (Fig. 3), or these centers are different in nature and generated by UV irradiation independently. If the vacancies V_O are involved into formation of UV light induced centers, heat treating $PbMoO_4$ crystals in various atmospheres (oxygen, inert gases, vacuum) and at different temperatures should give additional information on the nature of the photoinduced centers and could help to answer the question above.

3. Conclusions

Electrical properties as well as optical absorption were studied in $PbMoO_4$ single crystals irradiated at $T = 290$ K with UV light. Appearance of $\varepsilon(T)$ and $\sigma(T)$ anomalies around 340 K was found after UV irradiation. It was inferred that UV light irradiation generated the centers with electric dipole moments. Dipole centers were associated with photoelectrons captured by Mo ions within oxygen tetrahedra distorted by V_O . Thermally activated V_O hopping through the vertices of $(MoO_3)^-$ complexes was accompanied by reorientation of the dipole moments and gave rise to the observed ε and σ anomalies. After isothermal treating at 700 K the dipole centers were decomposed and light induced anomalies of $\varepsilon(T)$ and $\sigma(T)$ disappeared.

Besides that UV irradiation changed optical density spectra and caused photochromic effect. Two wide absorption bands with peaks near 24,000 and 17,300 cm^{-1} appeared. We associate this effect with photoinduced transfer of the electrons from lead to molybdenum complexes.

References

- [1] W. A. Bonner and G. J. Zydzik, *J. Cryst. Growth* **7** (1), 65 (1970).
- [2] V. Hinkov and I. Hinkov, U.S. Patent No. 6204952 (1998).
- [3] W. Jau-Sheng and T. Yung-Hsin, U.S. Patent No. 9690164 (2016).
- [4] Y. Shimada *et al.*, U.S. Patent No. 9261689 (2014).
- [5] D. Welford *et al.*, U.S. Patent No. 9905992 (2018).
- [6] M. B. Kosmyna *et al.*, *Acta Phys. Pol. A* **124** (2), 305 (2013). doi:10.12693/APhysPolA.124.305
- [7] V. N. Baumer *et al.*, *Func. Mater.* **17** (4), 515 (2010).
- [8] Y. G. Zdesenko *et al.*, *Instrum. Exp. Tech.* **39**, 364 (1996).
- [9] S. Pirro *et al.*, *Phys. Atom. Nuclei* **69** (12), 2109 (2006). doi:10.1134/S1063778806120155
- [10] L. L. Nagornaya *et al.*, *IEEE Trans. Nucl. Sci.* **NS-56**, 2513 (2009). doi:10.1109/TNS.2009.2022268
- [11] M. R. D. Bomio *et al.*, *Polyhedron* **50** (1), 532 (2013). doi:10.1016/j.poly.2012.12.001
- [12] S. Nedilko *et al.*, *Opt. Mater.* **36** (10), 1754 (2014). doi:10.1016/j.optmat.2014.03.019
- [13] I. P. Volnyanskaya *et al.*, *Phys. Solid State* **57** (7), 1399 (2015). doi:10.1134/S1063783415070355
- [14] T. M. Bochkova *et al.*, *Phys. Solid State* **45** (2), 244 (2003). doi:10.1134/1.1553525

- [15] M. Buryi *et al.*, *J. Lumin.* **192**, 767 (2017).
- [16] M. Buryi *et al.*, *J. Lumin.* **205**, 457 (2019). doi:[10.1016/j.jlumin.2018.09.052](https://doi.org/10.1016/j.jlumin.2018.09.052)
- [17] M. P. Trubitsyn and I. P. Volnyanskaya, *Visnik Dnipropetrovs'kogo Unìversitetu. Seriâ Fizika, Radioelektronika* **17** (16), 70 (2009).
- [18] Y. M. Poplavko, *Physics of Dielectrics* (NTUU "KPI": Kyiv, Ukraine, 2015) (in Ukrainian).
- [19] V. V. Laguta *et al.*, *J. Phys.: Condens. Matter.* **10** (32), 7293 (1998). doi:[10.1088/0953-8984/10/32/020](https://doi.org/10.1088/0953-8984/10/32/020)
- [20] V. V. Laguta *et al.*, *Phys. Rev. B.* **67**, 205102-1 (2003). doi:[10.1103/PhysRevB.67.205102](https://doi.org/10.1103/PhysRevB.67.205102)
- [21] V. V. Laguta *et al.*, *Phys. Rev. B.* **71** (23), 235108-1 (2005). doi:[10.1103/PhysRevB.71.235108](https://doi.org/10.1103/PhysRevB.71.235108)
- [22] T. M. Bochkova *et al.*, *Ukr. J. Phys.* **48** (2), 128 (2003) (in Ukrainian).
- [23] W. Ballmann, *Krist. Tech.* **15**, 367 (1980).
- [24] W. Ballmann, *Krist. Tech.* **15**, 585 (1980).
- [25] E. G. Reut, and A. I. Ryskin, *Optika i Spectroscopiya* **35** (5), 862 (1973) (in Russian).
- [26] M. Tyagi *et al.*, *Phys. Stat. Sol. A.* **207** (8), 1802 (2010). doi:[10.1002/pssa.200925625](https://doi.org/10.1002/pssa.200925625)
- [27] W. Van Loo, *Phys. Stat. Sol. A.* **28** (1), 227 (1975). doi:[10.1002/pssa.2210280126](https://doi.org/10.1002/pssa.2210280126)
- [28] D. A. Spassky *et al.*, *Radiat. Meas.* **38** (4–6), 607 (2004). doi:[10.1016/j.radmeas.2004.03.019](https://doi.org/10.1016/j.radmeas.2004.03.019)