UV irradiation effect on the electrical properties of Pb$_2$MoO$_5$ single crystal

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DOI:1026565/2222-56172018-29-09

Electrical properties of double lead molybdate Pb$_2$MoO$_5$ single crystal were studied in AC field (f=1 kHz) after irradiation with UV light (290 K). It was found that UV irradiation caused appearance of maximums on permittivity ε and conductivity σ temperature dependences, which were observed around 530 K. The anomalies of ε and σ vanished after annealing at 700 K and could be restored by subsequent UV irradiation performed at room temperature. The magnitude of ε and σ peaks increased for higher exposition time. Above 600 K conductivity σ was practically independent on irradiation. It is proposed that photoelectrons induced by UV light, are trapped by Mo located within the oxygen tetrahedrons with vacancy VO in one of the vertexes. The dipole moments of (MoO$_3$)$^-$ groups reorient at VO hopping through the tetrahedron vertexes. Annealing at 700 K thermally decomposes (MoO$_3$)$^-$ complexes. For $T > 600$ K behavior of $\sigma(T)$ is determined by conduction currents and nearly insensitive to UV irradiation. At high temperatures the photoelectrons do not contribute to conductivity since they are bound in (MoO$_3$)$^-$ centers, recombine with holes or re-captured by more deep traps.
Keywords: dielectric relaxation and loss, UV light irradiation, double lead molybdate crystal.

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Електричні властивості монокристалів подвійного молібдату свинцю Pb$_2$MoO$_5$ вивчалися в змінному полі (f=1 кГц) після опромінення ультрафіолетовим світлом (290 K). Виявлено, що УФ опромінення призводить до появи максимумів на температурних залежностях діелектричної проникності ε і провідності σ, які спостерігаються поблизу 530 K. Аномалії ε і σ зникають після відпалу при 700 K і можуть бути відновлені наступним УФ опроміненням, який проводився при кімнатній температурі. Величини піків ε і σ збільшуються для більш тривалих часів експозиції. Вище 600 K провідність σ практично не залежить від опромінювання. Передбачається, що фотоелектрони, індуковані УФ світлом, захоплюються Мо, що знаходяться в кисневих тетраедрах з вакансією VO в одній з вершин. Дипольні моменти (MoO$_3$)$^-$ груп переорієнтуються при стрибках VO по вершинах тетраедра. Відпал при 700 K призводить до термічного руйнування (MoO$_3$)$^-$ комплексів. При $T > 600$ K поведінка $\sigma(T)$ визначається струмами провідності і є майже нечутливою до УФ-опромінення. При високих температурах фотоелектрони не дають вкладу в провідність, оскільки вони пов'язані в (MoO$_3$)$^-$ центрах, рекомбінують з дірками або повторно захоплюються більш глибокими пастками.
Ключові слова: діелектричні релаксація і втрати, опромінення УФ світлом, кристали подвійного молібдату свинцю.

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Электрические свойства монокристаллов двойного молибдата свинца Pb$_2$MoO$_5$ изучались в переменном поле (f=1 кГц) после облучения ультрафиолетовым светом (290 K). Обнаружено, что УФ облучение приводит к появлению максимумов на температурных зависимостях диэлектрической проницаемости ε и проводимости σ, которые наблюдаются вблизи 530 K. Аномалии ε и σ исчезают после отжига при 700 K и могут быть восстановлены последующим УФ облучением, которое проводилось при комнатной температуре. Величины пиков ε и σ увеличиваются для более длительных времен экспозиции. Выше 600 K проводимость σ практически не зависит от облучения. Предполагается, что фотоэлектроны, индуцированные УФ светом, захватываются Мо, находящимися в кислородных тетраэдрах с вакансией VO в одной из вершин. Дипольные моменты (MoO$_3$)$^-$ групп переориентируются при прыжках VO по вершинам тетраэдра. Отжиг при 700 K приводит к термическому разрушению (MoO$_3$)$^-$ комплексов. При $T > 600$ K поведение $\sigma(T)$ определяется токами проводимости и почти нечувствительно к УФ-облучению. При высоких температурах фотоэлектроны не вносят вклада в проводимость, поскольку они связаны в (MoO$_3$)$^-$ центрах, рекомбинируют с дырками или повторно захватываются более глубокими ловушками.
Ключевые слова: диэлектрические релаксация и потери, облучение УФ светом, кристаллы двойного молибдата свинца.

Introduction

Because of monoclinic structure, double lead molybdate Pb_2MoO_5 crystal is optically biaxial and considered as the perspective material for applications in acousto-optic devices [1, 2]. Nevertheless, light yellow coloration and low optical strength hinder its commercial usage. Obviously, that these shortcomings are caused by the structural defects. Accounting high volatility of molybdenum and lead oxides, certain Mo and Pb deficiency can be expected in as-grown crystals. Cationic deficiency causes corresponding Schottky type disorder in oxygen sub-lattice. Acting as the traps for electrons and/or holes, the vacancies of the host ions can create the states within bandgap that modifies optical properties and leads to coloration and photochromism. Growing the crystals with certain non-stoichiometry and doping with heterovalent impurities can be the effective ways to reduce the content of undesirable defects. The information on the local structure of the defects, which degrade optical properties of Pb_2MoO_5, is of great importance.

Up to now there are only a very few works devoted to investigations of optical [2], acoustic [3], and dielectric [4] properties of Pb_2MoO_5 crystal as well as studying electronic structure and EPR [5,6]. In particular, slow dielectric relaxation was observed in as-grown crystal [4]. It was shown that after heating up to 600-700 K, ε anomaly disappeared. Temperature-frequency dependencies of ε demonstrated behavior quite different from usual Debye-like relaxation. Namely, with increasing frequency of measuring field, $\varepsilon(T)$ peaks decreased in amplitude but almost did not shift by temperature. Such behavior gave evidence that in the temperature range of ε anomaly, the dipole defects contributing to dielectric relaxation were not stable and their thermal decomposition became noticeable.

Slow dielectric relaxation, observed in [4], could be associated with certain dipole complexes involving ionic and electronic defects. In order to examine the nature of the dipole defects, in this paper we study permittivity ε and conductivity σ of the Pb_2MoO_5 crystals subjected previously to UV irradiation.

Experimental results

The Pb_2MoO_5 single crystals were grown from the melts by Czochralski method, the information on the technology can be found in [7]. The samples for ε and σ measurements were prepared as the plane-parallel plates with the main surfaces (010) coated with Pt electrodes. Permittivity ε and conductivity σ were measured in AC field (f=1 kHz) by bridge method. Temperature of the samples was varied in the interval 290–700 K. Before each measuring cycle the short-circuited samples were annealed for 30 min at 700 K in order to eliminate ε relaxation observed in [4]. After annealing the samples were cooled to room temperature and through the end faces irradiated

with UV light of mercury ball lamp during the certain time which was varied up to 60 min. Then ε and σ were measured on heating run, performed with the rate 8 K/min. After that the samples were kept at 700 K (30 min), cooled to room temperature, irradiated for chosen time and the measuring cycle was repeated.

Fig.1 shows the dependencies $\varepsilon(T)$ and $\sigma(1/T)$ for Pb_2MoO_5 sample irradiated at room temperature. One can see that irradiation causes appearance of $\varepsilon(T)$ maximum which magnitude increases for longer times of exposure (Fig.1a). Fig.1b shows the temperature dependences of conductivity σ plotted in Arrhenius scale. The broad maximums, observed for irradiated crystals around 530 K, are caused by dielectric losses accompanying ε relaxation (Fig.1a). At higher temperatures the dependences $\sigma(1/T)$ are nearly linearized and almost independent on the time and the doze of UV irradiation.
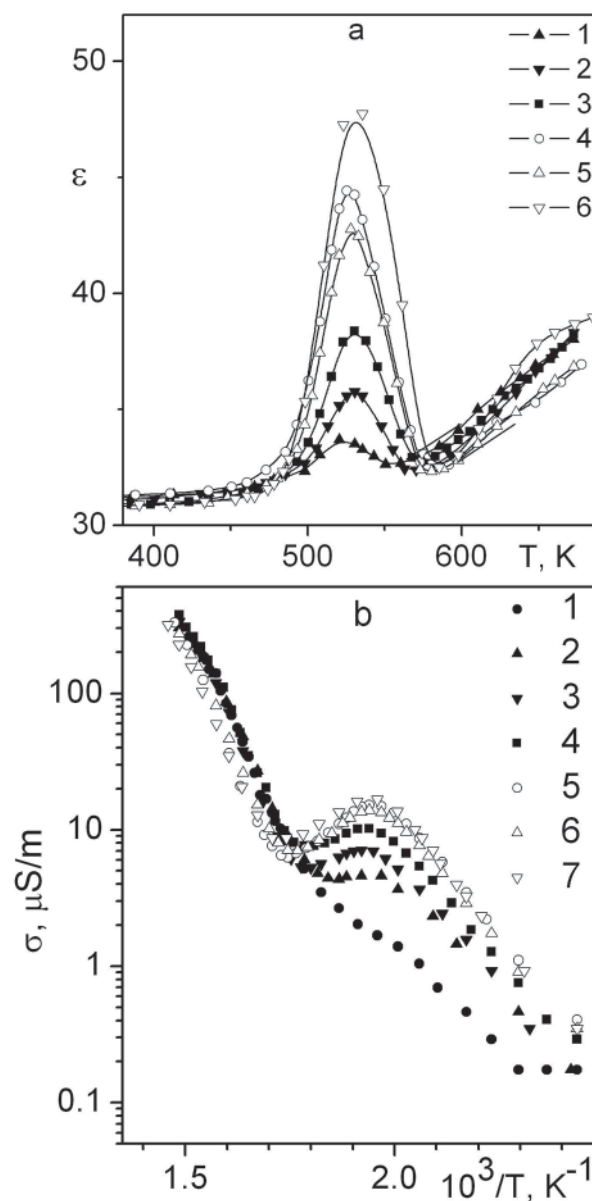

Fig. 1. Volnyanskaya I.P. et al

The detected dielectric anomalies (Fig.1a) indicate that UV irradiation induces defects with electric dipole moment in the Pb_2MoO_5 structure. Maximums of ε and σ disappear after annealing at 700 K, which preceded each measuring cycle. Thus, the dipole defects are thermally destroyed after annealing and can be recovered by subsequent irradiation at room temperature. Dielectric losses, accompanying reorientations of the defects dipoles, give rise to maximums in $\sigma(1/T)$ dependences (Fig.1b). At higher temperatures σ behavior is practically independent on UV irradiation exposure time since conduction currents become the main process. Nevertheless, some slight decrease of σ for the samples irradiated for longer exposure times can be mentioned.

Discussion

The crystal structure of Pb_2MoO_5 belongs to C_{2h}^3 space symmetry group [8, 9]. The unit cell includes four formula units Z=4 and has the parameters a=14.206 Å, b=5.759 Å, c=7.284 Å with the monoclinic angle β=114.29° in the setting b∥[010]∥C_2. Molybdenum with four oxygen atoms O1, O2, O2', O3 form MoO_4 tetrahedra. Lead atoms occupy two inequivalent sites Pb_1 and Pb_2. The Pb_2MoO_5 unit cell contains additional oxygen atom O4, which is surrounded by tetrahedron of four lead atoms. O4 atoms occupy specific positions and form the rows along symmetry axis C_2∥b.

Discussing the nature of the dipole defects, induced by UV irradiation, one can make certain assumptions based on the recent results presented in [10]. The photoinduced defects were studied by EPR and photoluminescence methods in $PbMoO_4$ crystal which is another representative of PbO-MoO_3 system. Besides that, it is useful to account information on various types of photoinduced defects arising in lead tungstate $PbWO_4$ crystal [11-13]. As it was noted in [10], EPR spectra of the light induced defects in $PbMoO_4$ and $PbWO_4$ were similar and characterized by very close spin-Hamiltonian parameters. Thus, the models of the photoinduced defects, proposed for $PbWO_4$ [11-13], with certain remarks can be used for $PbMoO_4$. In particular, it was shown [10], that irradiation of $PbMoO_4$ (λ=420 nm) at low temperatures (35 K) induced photoelectrons trapped by regular Mo ions: $e^- + (MoO_4)^{2-} \rightarrow (MoO_4)^{3-}$. Such polaron centers are relatively shallow (the depth was estimated as E_t=0.05 eV below the conduction band bottom) and exist up to 40-50 K. At higher temperatures the $(MoO_4)^{3-}$ centers are thermally destroyed that was manifested by disappearance of the EPR spectrum and thermally stimulated luminescence glow. Some part of released photoelectrons recombine with holes and the rest are captured by deeper traps. The latter are formed by oxygen vacancy V_O and neighboring lead ion capturing an electron: $V_O - Pb^+$. These F^+ centers are thermally stable up to 180-190 K (E_t=0.55 eV) and decompose on further heating. The most stable photoinduced centers can exist up

to room temperature and even above (E_t=0.9 eV). Accurate studying the EPR spectra anisotropy showed that such centers are formed by W(Mo) – O tetrahedrons distorted by V_O and stabilized by the unidentified defect in neighboring Pb site: $(W(Mo)O_3)^- - A_{Pb}$.

Accounting the results in [10-13], one can suppose that the dipole defects, induced by UV light and giving rise to the maximums of ε and σ (Fig.1a, b), can be attributed to photoelectrons captured by molybdenum atoms within tetrahedrons distorted by oxygen vacancy $(MoO_3)^-$. Quite possibly, such complexes can be stabilized by additional defect in the next coordination spheres similarly to the defects observed by EPR in $PbWO_4$. Excess negative charge of molybdenum capturing photoelectron, and excess positive charge introduced by V_O, produce electric dipole moments of the distorted $(MoO_3)^-$ tetrahedra. Due to thermal activation V_O can hop through the vertexes of the $(MoO_3)^-$ complex. Such hopping results in reorientation of the $(MoO_3)^-$ group electric dipole moment and contributes to permittivity and conductivity anomalies shown in Fig.1a, b. It should be noted that apart from molybdenums, lead atoms represent probable traps for photoelectrons. In such case one can expect appearance of F^+ centers consisting of photoelectron trapped by lead with neighboring oxygen vacancy: $Pb^+ - V_O$. For these centers dipole moment can reorient through motion of the photoelectron between structurally equivalent lead sites.

Fig.1b shows that magnitude of σ maximums around 530 K increases for longer times of exposure. That reflects growth of dielectric losses and confirms that photoelectrons participate in formation of the photoinduced dipole centers. Above 600 K $\sigma(1/T)$ dependences are nearly independent on the time of UV light irradiation. One can conclude that the photoelectrons do not contribute to charge transfer because they are bound in dipole complexes (presumably $(MoO_3)^-$ centers), recombine with holes or get captured by more deep traps.

The assumptions given above can be confirmed by the following experiments. Fig.1 shows that the magnitudes of ε and σ maximums depend on the time of UV irradiation. The latter determines the dose of UV irradiation and the number of excited photoelectrons. Besides that, the magnitude of ε and σ anomalies should depend on the content of another oppositely charged defects which form the photoinduced dipole centers. Hence annealing the Pb_2MoO_5 crystals at different temperatures and in various atmospheres (air, argon, vacuum) should verify the assumed role of oxygen vacancies in formation of the photoinduced dipole centers. Of course, the most direct information can be obtained by using EPR spectroscopy. Study of EPR spectra anisotropy can give most direct information on the local structure of the photoinduced dipole centers in Pb_2MoO_5 crystal. Such experiment is now in progress.

Conclusions

Dielectric permittivity and electrical conductivity were studied in Pb_2MoO_5 single crystals irradiated with UV light at room temperature. It is shown that UV irradiation causes appearance of $\varepsilon(T)$ and $\sigma(T)$ anomalies around 530 K (AC field frequency f=1 kHz). This fact demonstrates that the photoelectrons induced by irradiation, participate in formation of the dipole centers contributing to ε and σ maximums. Isothermal treating at 700 K results in thermal disassociation of the dipole defects. The local structure of the photoinduced dipole defects is discussed on the basis of the available data. It is proposed that dielectric relaxation in Pb_2MoO_5 crystals irradiated with UV light is determined by $(MoO_3)^-$ complexes.

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