UV IRRADIATION EFFECT ON THE ELECTRICAL PROPERTIES OF Pb$_2$MoO$_5$ SINGLE CRYSTAL

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Electrical properties of 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 V$_O$ in one of the vertexes. The dipole moments of (MoO$_3$)$^-$ groups reorient at V$_O$ hopping through the tetrahedron vertexes. Annealing at 700 K thermally decomposes (MoO$_3$)$^-$ complexes. For T>600 K behavior of σ(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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1. Introduction

Pb$_2$MoO$_5$ 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$_2$MoO$_5$, 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$_2$MoO$_5$ 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, ε(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$_2$MoO$_5$ crystals subjected previously to UV irradiation.

2. Experimental results

The Pb$_2$MoO$_5$ single crystals were grown from the melts by Czochralsky 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 irradiated with UV light of mercury ball lamp through the end faces during a 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 ε(T) and σ(1/T) for Pb_2MoO_5 sample irradiated at room temperature.
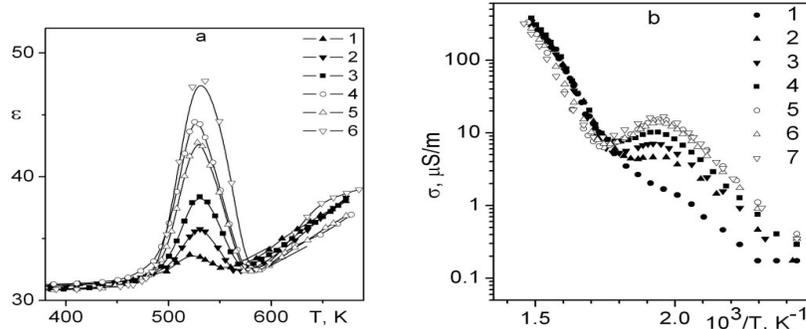
Fig. 1. Dependencies of permittivity ε(T) (a) and conductivity σ(1/T) (b) for Pb_2MoO_5 crystal irradiated with UV light during the following times:
1 – 5, 2 – 10, 3 – 15, 4 – 20, 5 – 30, 6 – 45, 7 – 60 min. Measuring field frequency f=1 kHz.

One can see that irradiation causes appearance of ε(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 σ(1/T) are nearly linearized and almost independent on the time and the doze of UV irradiation. 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 defect dipoles, give rise to maximums in σ(1/T) dependences (Fig. 1b). At higher temperatures σ behavior is practically independent of 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.

3. Results and 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', and O3 form MoO_4 tetrahedra. Lead atoms occupy two inequivalent sites Pb1 and Pb2. The Pb_2MoO_5 unit cell contains an additional oxygen atom O4, which is surrounded by a tetrahedron of four lead atoms. O4 atoms occupy specific positions and form the rows along the 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], can be used for $PbMoO_4$ with certain remarks. In particular, it was shown [10], that irradiation of $PbMoO_4$ ($\lambda=420$ 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 the 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 study of 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 along the vertices 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 molybdenum, lead atoms represent probable traps for photoelectrons. In such case one can expect the appearance of F^+ centers consisting of photoelectron trapped by lead with neighboring oxygen vacancy: Pb^+-V_O. For these centers the dipole moment can reorient through motion of the photoelectron between structurally equivalent lead sites. Fig. 1b shows that the magnitude of σ maximums around 530 K increases for longer times of exposure. That reflects the growth of dielectric losses and confirms that photoelectrons participate in the formation of photoinduced dipole centers. Above 600 K $\sigma(1/T)$ dependences are nearly independent of the time of UV light irradiation. One can conclude that photoelectrons do not contribute to the charge transfer because they are bound in dipole complexes (presumably $(MoO_3)^-$ centers), recombine with holes or get captured by deeper 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 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

the 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.

4. 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 photoelectrons induced by irradiation participate in the formation of dipole centers contributing to ε and σ maximums. Isothermal treating at 700 K results in the 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 supposed that dielectric relaxation in Pb_2MoO_5 crystals irradiated with UV light is determined by $(MoO_3)^-$ complexes.

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