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DIELECTRIC PROPERTIES OF THE Pb₂MoO₅ CRYSTALS IRRADIATED WITH UV LIGHT

The dielectric properties of the Pb₂MoO₅ crystals, exposed to UV light radiation (290 K), were studied. It was shown that UV irradiation led to appearance of permittivity maximum near 530 K (AC field frequency $f=1$ kHz). Heating up to 700 K resulted in thermal dissociation of the dipole complexes, induced by UV light irradiation and contributing to ϵ peak. The magnitude of the ϵ maximum increased with increasing time of UV light exposure and saturated for $t>90$ min. It is supposed that the observed anomaly of ϵ is determined by dielectric response of (MoO₃)⁻ complexes. These centers arise when photoelectrons are trapped by molybdenum ions with oxygen vacancy V_O in the nearest surroundings.

Keywords: double lead molybdate crystal, dielectric permittivity, light induced defect.

1. Introduction

In the double PbO-MoO₃ system, there are a few compounds, two of which melt congruently: PbMoO₄ and Pb₂MoO₅ [1]. These compounds attract attention due to high acousto-optical parameters and are promising for application in optoelectronics. Double lead molybdate Pb₂MoO₅ is of particular interest since it is optically biaxial crystal usable in specific acousto-optic devices [2, 3]. The lattice of Pb₂MoO₅ belongs to monoclinic system with a space symmetry group C_{2h}³-C₂/m [4]. The unit cell contains four formula units Z=4, the lattice parameters are $a=14.225$ Å, $b=5.789$ Å, $c=7.336$ Å ($\beta=114.0^\circ$), where b axis is directed along C₂ symmetry axis. Pb₂MoO₅ structure is characterized by a cleavage plane with indices $(\bar{2}01)$.

Up to now, there were the papers devoted to Pb₂MoO₅ crystal growing [4-6], study of its optical [3], acoustic [7], and dielectric properties [8]. Investigation of permittivity in as-grown Pb₂MoO₅ crystals [8] revealed the peak of $\epsilon(T)$ around 530–540 K ($f=1$ kHz). This anomaly of ϵ could be measured only on the first heating run and disappeared after heating up to ~700 K. It was concluded that nominally pure Pb₂MoO₅ crystals contained intrinsic (proper) dipole defects that thermally dissociated upon heating to the interval 600–700 K. In this paper, we investigate the effect of UV radiation on the dielectric properties of Pb₂MoO₅ single crystals.

2. Experimental details

The single crystals of Pb₂MoO₅ were grown by Czochralskii method in accord with the procedure described in [5]. The samples for measurements of ϵ were prepared as the plane-parallel plates $5\times 5\times 1$ mm³ perpendicular to the main axes [010]. Taking into account the data reported in [8], before the measurements all the samples were heated in the short-circuited state up to 700 K, and after that were cooled to room temperature. As a result, the dipole centers, found in [8], were thermally destroyed and for the treated samples the anomaly of $\epsilon(T)$ at 540 K was absent.

Pt electrodes were deposited on the samples main planes by cathode sputtering method. At room temperature Pb_2MoO_5 samples were irradiated through the butt ends with UV light of DRSH mercury ball lamp. Exposure time t was chosen from zero to 60 minutes. After irradiation, the temperature dependences $\varepsilon(T)$ were measured by bridge method at frequency $f=1$ kHz in the temperature range 290–700 K.

3. The results and discussion

In order to choose the appropriate temperature regime for ε measuring, the following experiment was carried out. The sample was irradiated for 30 min according to the procedure described above. Then, $\varepsilon(T)$ dependence was measured on heating up to 700 K with linear rate 8 K/min. After that the sample was cooled to room temperature and, as it was mentioned above, for subsequent temperature cycling the maximum of $\varepsilon(T)$ was absent. At room temperature the sample was irradiated for 30 min. The dependence $\varepsilon(T)$ was measured on heating run again, but in stepwise regime, for each measurement the temperature was stabilized for 5 min, so that the average heating rate was about 2.3 K/min. The data given in Fig. 1 show that $\varepsilon(T)$ behavior depends strongly on the temperature regime and magnitude of the ε peak decreases noticeably for lower heating rate. Hence, dissociation of the dipole complexes becomes noticeable already in the temperature range, where ε anomaly is registered. Accounting this fact, all subsequent measurements were carried out on heating with the same rate 8 K/min.

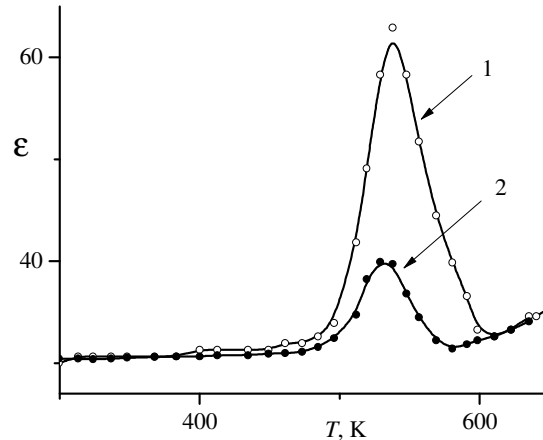


Fig. 1 $\varepsilon(T)$ dependences for irradiated Pb_2MoO_5 crystal measured on heating: 1 - with rate 8 K/min; 2 - in stepwise regime with an average rate 2.3 K/min.

Fig. 2 shows the $\varepsilon(T)$ curves measured on heating the Pb_2MoO_5 samples which were pre-irradiated at room temperature during time t . It can be seen that irradiation leads to appearance of $\varepsilon(T)$ peak, the magnitude of which grows significantly with increasing time of exposure. The ε peak is practically undistinguishable for $t=5$ min, but it is already reliably detected for $t=10$ min. Similarly to the results presented in [8], maximum of permittivity was observed only on the first heating run and was absent on subsequent cooling. Temperature growth of $\varepsilon(T)$ observed above 600 K, is usual feature for real dielectric structures. This effect can be connected with contribution of mobile defects,

which concentrate near blocking electrodes and effectively increase capacity of the sample.

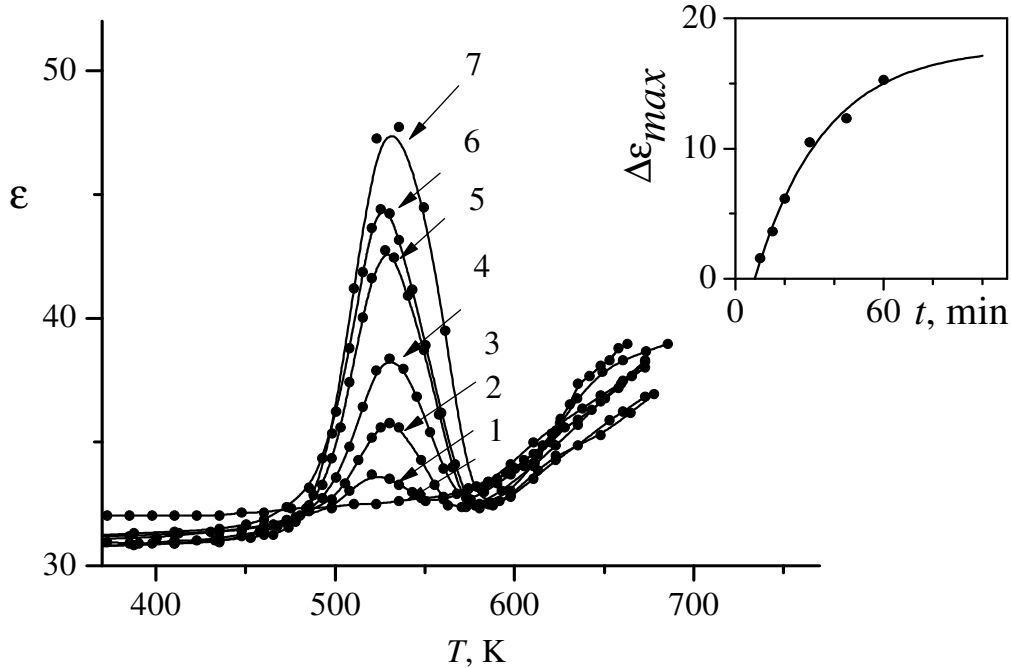


Fig. 2 $\epsilon(T)$ dependences for Pb_2MoO_5 crystal irradiated with UV light for the following exposure times t : 1 – 5, 2 – 10, 3 – 15, 4 – 20, 5 – 30, 6 – 45, 7 – 60 min.

The inset shows the dependence of the permittivity peak magnitude $\Delta\epsilon_{max}$ on t .

The magnitude of the permittivity maximum $\Delta\epsilon_{max}$ vs the time of irradiation t is shown in the inset to Fig. 2. The plotted values of $\Delta\epsilon_{max}$ were corrected for the background permittivity, which was contributed by another mechanisms not related to the dipole defects induced by UV light. One can see that up to the exposure times near 30 min, an approximately linear increase of $\Delta\epsilon_{max}$ value is observed. For more long exposure times $\Delta\epsilon_{max}(t)$ dependence deviates from linear behavior and is noticeably weakened. The results, shown in Fig. 2, indicate that UV irradiation of Pb_2MoO_5 crystals generates the defects possessing electric dipole moment. The number of the induced dipole defects increases for longer exposure times t and higher irradiation doses (inset to Fig. 2). Heating the irradiated Pb_2MoO_5 samples to the temperature range 600–700 K, leads to thermal dissociation of the dipole complexes and disappearance of ϵ anomaly.

Considering the nature of the defects induced by UV light, one can note that the F-centers demonstrate the features similar to those observed in the experiment. It is known that F- center represents an anionic vacancy that captures an unpaired electron. According to [9], in the Pb_2MoO_5 unit cell, the molybdenum atoms and the four oxygen atoms O1, O2, O2' and O3 form MoO_4 tetrahedra (Fig. 3). Oxygen atoms O4, which are not included into the MoO_4 groups, form specific columns along b axis and are tetrahedrally coordinated by four Pb atoms. Lead atoms are located in two structurally nonequivalent sites Pb1 and Pb2. Obviously that for such structure, F- center can be created by oxygen vacancy V_O which captures an electron. If V_O is located near Mo, then thermally activated V_O hopping between the vertexes of the distorted (MoO_3) tetrahedron can be expected.

Such hopping is accompanied by re-orientation of the electric dipole moment of $(\text{MoO}_3)^-$ complexes that contributes to ϵ anomaly detected in the experiment (Fig. 2).

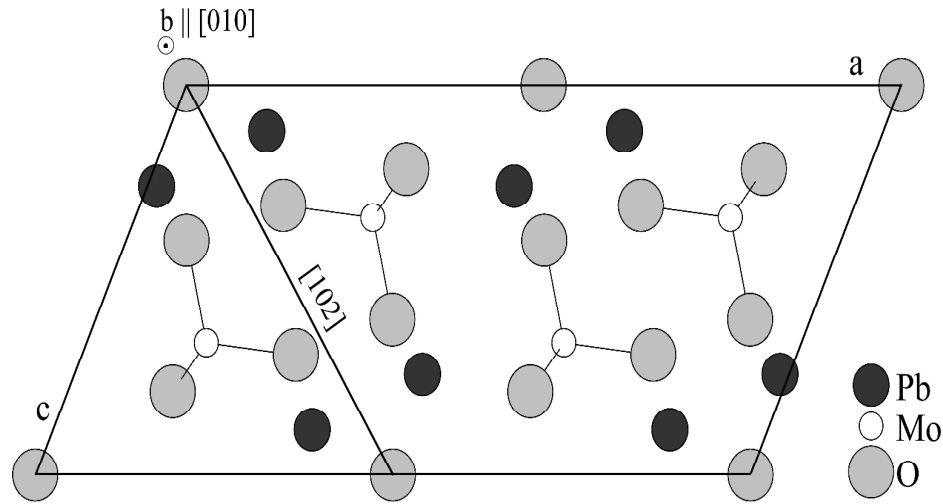


Fig. 3 The unit cell of Pb_2MoO_5 crystal, projected on (010) plane. In accord with the data in [9].

Indeed, EPR study of another representative of the family, PbMoO_4 crystal [10], has shown that irradiation with UV light at helium temperatures produces photoelectrons localized on regular Mo ions in accord with the scheme: $e^- + (\text{MoO}_4)^{2-} \rightarrow (\text{MoO}_4)^{3-}$. The depth of such traps is about $E_t=0.05$ eV below the bottom of the conduction band. The $(\text{MoO}_4)^{3-}$ polaron centers are stable up to 40 K and at higher temperatures are thermally destroyed [10]. Subsequent recombination of photoelectrons with holes or capturing photoelectrons by deeper traps is accompanied by thermally stimulated luminescence glow [10]. Obviously, that presence of a neighboring defect can increase thermal stability of these centers. Such situation can be expected for Mo-O tetrahedron with absent oxygen in one of the vertexes. Mo-O tetrahedron distorted by V_O can be much more deep trap for photoelectron as compared with un-perturbed $(\text{MoO}_4)^{2-}$ tetrahedron. Consequently, the complexes $(\text{MoO}_3)^-$ can be stable up to much higher temperatures.

It is clear, that permittivity peak magnitude $\Delta\epsilon_{max}$ is proportional to the concentration of dipole defects. The number of these defects, presumably $(\text{MoO}_3)^-$ groups, should depend both on the dose of UV irradiation which determines the number of released photoelectrons, and also on the concentration of vacancies V_O . One can assume that dependence of the dipole defects content n on exposure time t can be described by the simple equation $dn(t)/dt=[N - n(t)]/\tau$, where N represents the concentration of V_O , τ is the time parameter. In that case one can expect that the dependence of permittivity peak magnitude $\Delta\epsilon_{max}(t)$ (inset to Fig.2) saturates for exposure times $t>3\tau=90$ min. This happens when almost all $(\text{MoO}_3)^-$ complexes (i.e. Mo-O tetrahedra distorted by V_O) have already captured photoelectrons and further increase of the exposure time does not increase the dipole centers concentration. Consequently, after saturation the magnitude of the anomaly $\Delta\epsilon_{max}$ is determined by V_O content. The latter can be regulated by heat treatment of the crystal in different atmospheres. The results of studying the electrical properties of Pb_2MoO_5 crystal, annealed in air, argon and vacuum, will be reported elsewhere in the nearest future.

And finally one can note that the most complete information on the local structure of the photoinduced dipole defects can be obtained by studying EPR in Pb_2MoO_5 crystal irradiated at room temperature. This experiment is now in progress.

4. Conclusions

It is shown that irradiation of Pb_2MoO_5 single crystals with UV light leads to appearance of the permittivity maximum near 530 K ($f=1$ kHz). Dipole defects contributing to the anomaly of ϵ are thermally destroyed upon heating to 700 K. On the basis of the available data, it is proposed that the detected dielectric response is due to complexes $(\text{MoO}_3)^{\cdot-}$. Such complexes are formed by Mo, which are located within Mo-O tetrahedra with an oxygen vacancy in the vertex. $(\text{MoO}_3)^{\cdot-}$ complexes capturing photoelectrons are thermally stable up to the temperature region where ϵ anomaly is observed. It is expected that $(\text{MoO}_3)^{\cdot-}$ centers can cause photochromism, which worsens optical quality of double lead molybdate crystals. Undesirable effect of electrically and optically active $(\text{MoO}_3)^{\cdot-}$ complexes can be eliminated by heterovalent doping with transition groups ions [11].

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