COMPOSITION VARIATIONS AND UV IRRADIATION EFFECT ON CHARGE TRANSFER IN $PbMoO_4$ SINGLE CRYSTALS

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The effect of nonstoichiometry of the composition, PbO polymorphism, and preliminary irradiation with ultraviolet light on electrical conductivity of alternating current (AC) was studied in $PbMoO_4$ crystals. The crystals were grown by Czochralski method in a direction deviated by 30° from *a*-axis in (001) plain. The charge was prepared from MoO_3 and PbO, lead oxide was used of α- or β- structural modifications. The reagents were taken both in a stoichiometric ratio and with an excess of 0.5 mol % of MoO_3. It was shown that the magnitude of the dark and irradiation-induced AC conductivity was affected both by the type of polymorphic form of PbO and by the excess amount of MoO_3. The influence of the $PbMoO_4$ crystal structural disorder on charge transfer processes are discussed within the framework of the model of hopping conduction in disordered media.

Keywords: lead molybdate $PbMoO_4$, disordered media, hopping conductivity.

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1. Introduction

$PbMoO_4$ crystals are widely used in modern engineering. As a rule, they are grown by pulling from the melt on a seed. The grown crystals contain a few types of structural defects. Among them, there are point defects such as intrinsic ones and uncontrolled impurities. Extended and cluster defects, including photoinduced ones were also observed [1, 2]. In fact, the crystal lattice of $PbMoO_4$ can be considered as a partially disordered medium. A change in the degree of structural disorder has a strong effect on the electrical properties of crystals and, in particular, on electrical conductivity.

The purpose of this work is to study changes in the AC conductivity of $PbMoO_4$ crystals under the influence of factors such as deviation from the charge stoichiometry towards an increase in molybdenum oxide, the use of various crystalline modifications of lead oxide, and preliminary UV irradiation of the samples.

2. Samples preparation and experimental details

The single crystals of $PbMoO_4$ were grown from the melt by conventional Czochralski technique in air by using platinum crucibles. The charge was prepared by solid phase synthesis at 925–975 K for 2 hours from MoO_3 and PbO of α - or β - modifications of "high purity" grade. The reagents were taken both in a stoichiometric ratio and with excess of 0.5 mol % of MoO_3. To improve the optical quality [3], the crystals were grown in the direction deviated by 30° from *a*-axis in (001) plane. The obtained crystals were free from gas bubbles, cracks and had a weak yellowish color.

The samples for measurements were prepared as plane-parallel plates with dimensions 5×5×1 mm^3. The main planes of the samples were cut perpendicular to the growth axis. Before measurements the samples were heat treated at 700 K for 1 hour and cooled to room temperature in order to eliminate the possible influence of the sample pre-history on the electric properties. After thermal treatment the samples were irradiated through main faces using light-emitting diode with radiation wavelength λ = 365–370 nm for 30 – 60 minutes. Then platinum electrodes were deposited by cathode sputtering. Conductivity was measured in AC field by the bridge method at fixed frequency (f = 1 kHz) in the temperature interval 290–700 K.

3. Results and discussion

$PbMoO_4$ crystals are high-resistance semiconductors. According to optical measurements, the value of the energy gap E_g of $PbMoO_4$ has been estimated as 3.4 eV [4]. The electrical conductivity of the nominally pure and doped $PbMoO_4$ crystals was studied in [5-9]. It was assumed that, in the temperature range below 700 K, electron (hole) conduction occurred due to intrinsic lattice defects. At higher temperatures, intrinsic or ionic conduction is possible. In the latter case, the conduction is carried out by oxygen vacancies.

The mechanism of charge transfer in $PbMoO_4$ crystals grown from the stoichiometric mixture was studied in the temperature range < 700 K in [7]. It was found that mobile charge carriers had an extremely low concentration and low drift mobility, which increased exponentially with temperature. AC conductance increased with frequency and temperature. Conclusion about the hopping mechanism of conduction was drawn.

In the $PbMoO_4$ crystal grown from a mixture with excess of MoO_3, a significant increase in conductivity is observed over the entire temperature range studied (Fig. 1). Earlier, we studied the effect of deviation from the stoichiometric composition of the charge towards an increase in the amount of molybdenum oxide on the optical properties of $PbMoO_4$ crystals [10].

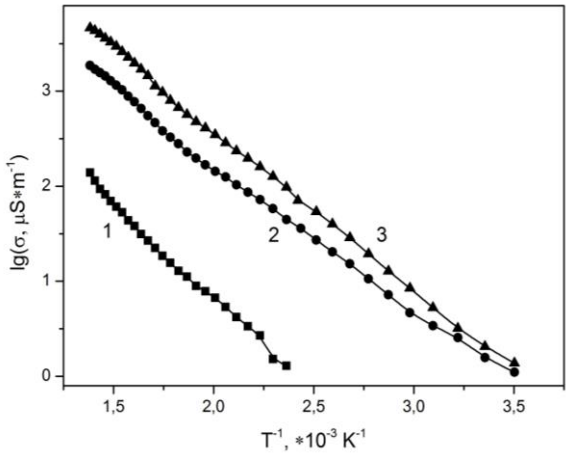

Fig. 1. The temperature dependence of AC conductivity (f = 1 kHz) of $PbMoO_4$ crystals grown using: 1-2 – β-modification of PbO (1 – charge of stoichiometric composition, 2 – charge with 0.5 mol% MoO_3 excess); 3 – α-modification of PbO with the stoichiometric composition of the charge.

It was found that only small additions (up to 0.5 mol %) of MoO_3 in the charge improved the optical transmission of the crystals in the visible region of the spectrum. Further increase in excess MoO_3 (>0.5 mol %) decreased the optical transmission of the crystals due to the formation of lead and oxygen vacancies and a change in the charge state of lead from Pb^{2+} to Pb^{3+} and molybdenum from Mo^{6+} to Mo^{5+}. It is obvious that the increase in conductivity is associated with the appearance of structural defects caused by the deviation from the stoichiometric composition.

Fig. 2a shows the effect of the excess of molybdenum oxide on the conductivity induced by preliminary UV irradiation of samples of $PbMoO_4$ crystals grown from the β-modification of lead oxide. The phenomenon under consideration should not be confused with photoconductivity. Photoconductivity in $PbMoO_4$ crystals was observed in [11-12], which confirmed the electronic character of conductivity. It was pointed out that it

increased upon irradiation with light with a wavelength near the intrinsic absorption edge. However, in the case considered, the crystals were preliminarily irradiated several days in advance. It allowed to disregard the contribution of photoconductivity and, moreover, indicated sufficient thermal stability of the photoinduced defects.

In an irradiated crystal with excess of MoO_3, a maximum of σ is observed in the region of 390 K. After heating the sample up to 700 K, the maximum disappears and reappears after repeated irradiation. Apparently, an increase in the disorder of the crystal lattice causes a redistribution of the density of localized states in the bandgap in accordance with the band model developed for disordered solids [13].

The use of the α-modification of PbO for the charge preparation leads to an increase in the conductivity of the crystals by almost two orders of magnitude (Fig. 1). After UV irradiation of the sample the significant increase in conductivity is observed with the maximum at 390 K. The introduction of an excess of MoO_3 into the mixture does not increase the dark conductivity. But preliminary UV irradiation greatly increases the conductivity values of such crystals at the maximum (Fig. 2б).

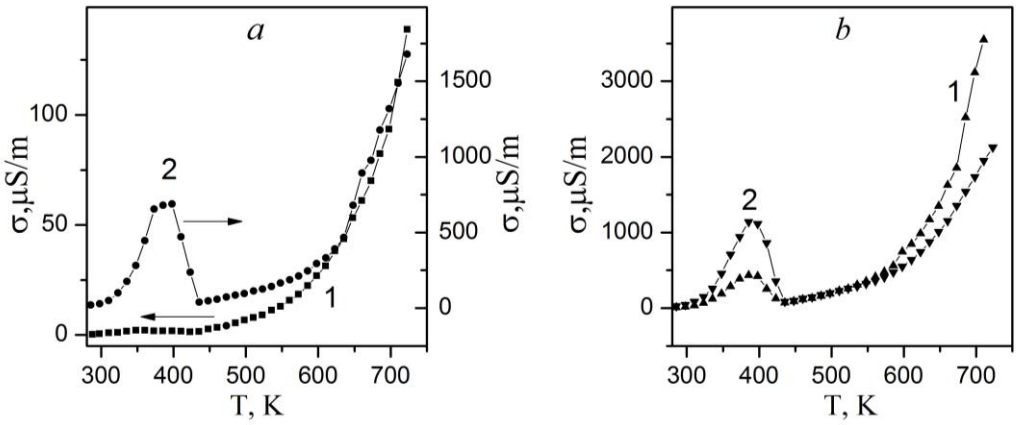

Fig. 2. The temperature dependence of AC conductivity (*f* = 1 kHz) of pre-illuminated with UV light $PbMoO_4$ crystals: a – the crystals grown using β-modification of PbO (1 – the charge of stoichiometric composition, 2 – the charge with 0.5 mol % MoO_3 excess); b – the crystals grown from the charge using α-modification of PbO (1 – the charge of stoichiometric composition, 2 – the charge with 0.5 mol % MoO_3 excess).

The α-modification of PbO is thermodynamically stable at low temperatures up to the phase transition temperature (762 K), at which the transformation into the β-modification of PbO takes place. The β-modification is metastable, however, upon slow cooling to room temperature, it can exist for a long time and turns into α-modification under external influences. During the transition, the structures undergo compression and tension in different directions. Lead ions, as heavier ones, practically do not shift, while oxygen ions shift significantly [14]. It is quite possible that the $\alpha \rightarrow \beta$ phase transition process of PbO is superimposed on the lead molybdate synthesis process and even enhances disorder into the $PbMoO_4$ crystal structure.

4. Conclusions

It has been shown that the introduction of an excess of molybdenum oxide in the amount of 0.5 mol % into the mixture for growing $PbMoO_4$ crystals increases AC electrical conductivity (*f* = 1 kHz) in a wide temperature range. Preliminary illumination of the samples with UV light leads to the appearance of a maximum in the temperature dependence of the conductivity. Using the different polymorphic forms of PbO as the

initial reagent also strongly affects the conductivity. The use of the α-modification of PbO increases the overall conductivity and significantly increases the conductivity value at the maximum caused by pre-illumination of the sample. Within the framework of the hopping conductivity model, it is assumed that the observed changes in conductivity behavior are associated with a redistribution of the density of localized states in the bandgap of $PbMoO_4$ crystals, caused by the appearance of the structural and the photoinduced defects in the crystal lattice.

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