

EFFECT OF LATTICE DISORDER ON CHARGE TRANSFER IN LEAD MOLYBDATE CRYSTALS

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Electrical properties of PbMoO₄ crystals, grown from the stoichiometric charge and non-stoichiometric charge with an excess of MoO₃, are studied and compared in this work. The crystals are grown by Czochralski method in the direction at an angle of 30° to [100] axis in (001) plane. The single crystals are free from gas bubbles, cracks and have a weak yellowish color. It is found that the addition of MoO₃ excess (0.5 mol.%) to the stoichiometric charge notably increases the crystal lattice disorder. It is assumed that the appearance of lead ion vacancies plays the main role in the structural disordering. An increase of conductivity in DC and AC field, changes of current-voltage characteristics and AC-conductivity spectra are interpreted based on the model of hopping conductivity in disordered systems.

Keywords: lead molybdate PbMoO₄, disordered crystalline media, hopping conductivity.

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1. Introduction

Lead molybdate crystal (PbMoO₄) is widely known as a multifunctional inorganic material. The effectiveness of this crystal depends on its optical quality and radiation resistance. To obtain large crystals, the Czochralski method is usually used. However, crystals grown from a melt often have a yellowish color and are predisposed to cracking. Exposure to irradiation leads to the appearance of photoinduced phenomena, such as photochromic and photodielectric effects [1]. X-ray diffraction, luminescence, and EPR studies have shown that the crystal lattice of such crystals contains point and extended defects, various clusters, including photoinduced ones, based on anionic MoO₄ groups that have captured photoelectrons [2, 3]. In fact, PbMoO₄ single crystal is a partially disordered medium. The deviation from the stoichiometric composition of the crystal is one of the factors causing disorder in the crystal lattice. To compensate the increased evaporation of MoO₃, many technologists add an excess of MoO₃ to the charge, used for crystal growth, in an amount of about 1 wt.% [4]. However, it is still unclear how exactly this technological factor influences the formation of the defects in the PbMoO₄ crystal lattice. It is well known that electrical properties of crystals are very sensitive to the presence of structural defects. The purpose of this work is to make clear the nature of the influence of excess molybdenum oxide in the charge on the conduction in PbMoO₄ crystals.

2. Sample preparation and experimental details

The single crystals of PbMoO₄ were grown from the melt by Czochralski technique in air by using platinum crucibles. The charge was prepared from MoO₃ and PbO of "high purity" grade by solid phase synthesis. The reagents were taken in two proportions: in a stoichiometric ratio and with excess of 0,5 mol.% of MoO₃. The crystals were grown in the direction deviated at 30° from [100] in (001) plane. The grown crystals were free from gas bubbles, cracks and had a weak yellowish color. The main planes of the samples with dimensions 8×6×1.5 mm³ were cut perpendicular to the growth axis. Platinum electrodes were deposited by cathode sputtering. Current-voltage relations were measured using standard equipment at 300 K, AC conductivity was studied using Keysight E4980AL LCR meter at different frequencies ($f = 0.1\text{--}350$ kHz) in the temperature interval 300–700 K.

3. Results and discussion

PbMoO₄ crystal can be classified as a high-resistivity semiconductor. According to optical measurements, the energy gap E_g of PbMoO₄ is estimated as 3.4 eV [5]. The conductivity of PbMoO₄ crystals was studied in [6-8]. It was assumed that in the temperature range below 700 K, conductivity is electronic.

Charge transfer mechanism in the region of electronic conductivity was discussed in [8]. It was shown that at room temperature PbMoO₄ is characterized by low values of conductivity σ and mobility μ of charge carriers. The exponential growth of σ and μ with temperature and the power-law nature of the frequency dependences of AC conductivity were observed. These features are characteristic of hopping conductivity which is carried out in disordered media through thermally activated jumps of electrons/holes over localized states.

We have found that the introduction of MoO₃ excess into the charge for crystal growth significantly changes the electrical properties of PbMoO₄ crystals. Conductivity increases considerably both in DC and AC field (Figs.1-3) The character of the I - V relations changes (Fig. 1).

I - V relations ($I \sim U^m$) of the crystals grown from the charge of stoichiometric composition have characteristic linear ($m=1$) and quadratic ($m=2$) regions, which at higher voltage change into regions with higher slope. It is typical for space-charge limited currents (SCLC) in dielectrics with monoenergetic traps. The conductivity σ and effective drift mobility μ_{ef} of charge carriers calculated from I - V characteristics at $T=300$ K are $\sim 10^{-12}$ S·m⁻¹ and $2 \cdot 10^{-8}$ m²·V⁻¹·s⁻¹, respectively. These values of transfer parameters are very low and are close to those obtained in [8]. However, the I - V relations of crystals grown using the charge with excess of MoO₃ have extended cubic ($m=3$) regions. According to the band model developed for disordered systems, localized states in the band gap in this case have exponential distribution [9]. This indicates systemic disturbances in the crystal lattice.

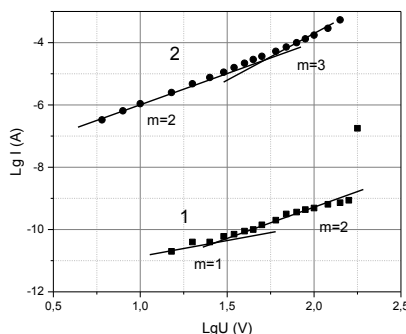


Fig. 1. I - V relations of PbMoO₄ crystals measured at 300 K: 1 - crystals grown from the charge of stoichiometric composition; 2 - crystals grown from the charge with 0.5 mol.% MoO₃ excess.

Previously, we studied the effect of excess molybdenum oxide in the charge on the optical properties of PbMoO₄ crystals [1]. It has been shown that changes in the optical transmittance occur due to the formation of lead and oxygen vacancies and a change in the charge state of lead from Pb²⁺ to Pb³⁺ and molybdenum from Mo⁶⁺ to Mo⁵⁺.

Figs. 2, 3 show temperature and frequency dependences of AC conductivity for the crystals grown from the charge of stoichiometric composition and the charge with excess of MoO₃. In general, the frequency dependences of σ correlate with the data in [8]. In both

cases, an increase in σ with temperature and frequency is observed. This confirms the hopping mechanism of charge transfer.

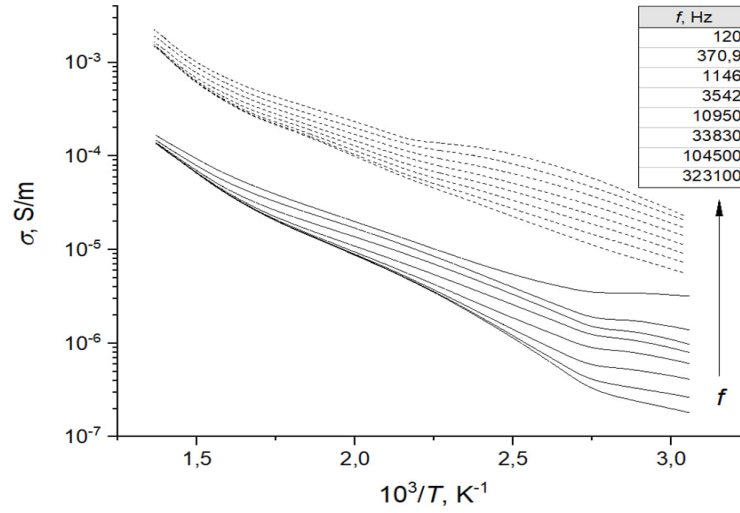


Fig. 2. Temperature dependences of AC conductivity of the PbMoO_4 crystals grown from the charge of stoichiometric composition (the solid lines below) and from the charge with 0.5 mol.% MoO_3 excess (the dashed lines above).

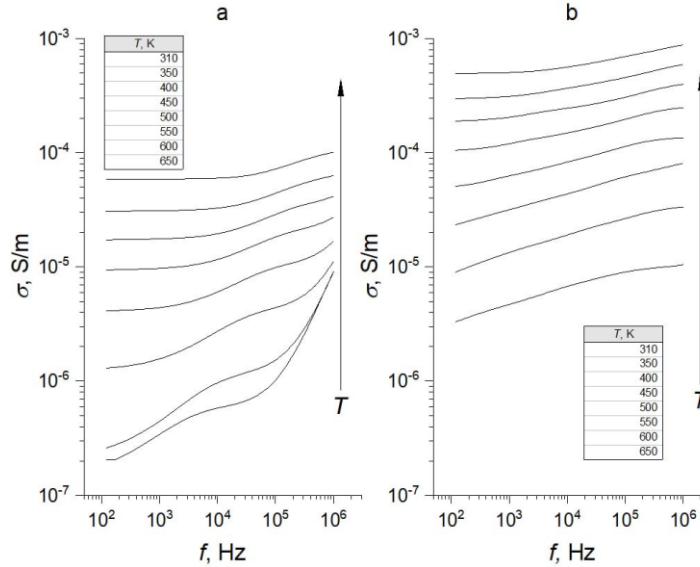


Fig. 3. Frequency dependences of AC conductivity of PbMoO_4 : a - the crystals grown from the charge of stoichiometric composition; b - the crystals grown from the charge with 0.5 mol.% MoO_3 excess.

The temperature dependences of AC conductivity of the crystals grown from the charge of stoichiometric composition are typical for complex oxides with electronic hopping conductivity. It is assumed that carrier movement is carried out by thermally activated jumps within clusters of various lengths. In the low-frequency region, the cluster sizes are comparable with the sample sizes. As the frequency increases, the cluster sizes decrease and conductivity increases. At low temperatures, σ weakly depends on T , which argues in favor of the model of pair hopping near the quasi-Fermi level. On heating, the thermally activated growth of σ becomes dominant. It means that conduction occurs by carriers hopping across fairly extended clusters, which may represent some associates of intrinsic defects. The

absence of regions with a weak temperature dependence in AC conductivity of crystals grown from the charge with 0.5 mol.% MoO₃ excess indicates that the model of hopping within pair centers cannot be applied in this case and conductivity is realized by carriers hopping across extended clusters of finite size.

5. Conclusions

Growing PbMoO₄ crystals from a charge with excess of molybdenum oxide in the amount of 0.5 mol.% leads to a significant change in their electrical properties. Conductivity increases for both direct and alternating current. The appearance of I – V characteristics changes. For crystals grown from the charge of stoichiometric composition, I – V relations correspond to the case of SCLC for dielectrics with monoenergetic traps. The introduction of an excess amount of MoO₃ leads to the emergence of exponential tails in the density of localized states in the band gap, which indicates systemic imperfections in the crystal lattice. The temperature and frequency dependences of AC conductivity confirm the hopping transfer mechanism in both cases. However, in the crystals grown from a charge with an excess of MoO₃, in the temperature range studied, there are no paired hops of charge carriers and conduction is carried out by activated hops along clusters of a finite size. This points out an increasing influence of lattice disorder on charge transfer processes.

Acknowledgments

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