Variations of the initial charge composition and physical properties of the single crystals of PbO – MoO_3 system

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Introduction

Lead molybdate ($PbMoO_4$) and double lead molybdate (Pb_2MoO_5) are perspective materials for acousto-optical devices. These applications require good optical quality and high radiation resistance. However, the crystals grown from the melt in air by the conventional Czochralskii technique, as a rule, have specific color and demonstrate photochromism after irradiation with UV light. Such undesirable phenomena can be associated with nanometer sized phase inclusions, coordination complexes based on intrinsic defects and/or impurities. Comprehensive study of the typical defects is of high importance to obtain PbO – MoO_3 single crystals more suitable for practical applications. It is known that $PbMoO_4$ exhibits vacancy disorder due to violation of stoichiometry and oxygen exchange with surrounding atmosphere. One can expect that an increase in the volatile component in the composition of the charge helps to prevent the formation of cation vacancies. Regarding Pb_2MoO_5, there is no any information on this issue.

In this work we want to discuss the data of the study of $PbMoO_4$ and Pb_2MoO_5 single crystals grown by Czochralskii method using of the initial charge composition with deviations from the stoichiometric ratio of components.

Experimental details

The single crystals of $PbMoO_4$ and Pb_2MoO_5 were grown in air from the melt by Czochralskii technique. The charge was prepared by two-stage solid phase synthesis from the lead and molybdenum oxides of "high purity" grade. The reagents were taken both in a stoichiometric ratio and with deviations towards an excess of MoO_3 up to 1.5 mol% (for $PbMoO_4$) and with 0.2 wt% PbO excess (for Pb_2MoO_5). The obtained $PbMoO_4$ crystals had a diameter of up to 35 mm and a length of about 50–60 mm; Pb_2MoO_5 crystals were up to 20 mm in diameter and up to 40 mm in length. Both types of the crystals were free from macroscopic inclusions (gas bubbles, cracks) and had a light yellowish color. High-temperature treatment of the $PbMoO_4$ crystals in air was carried out in a muffle furnace at 1200 K. The annealing time in the experiments varied from 2 to 90 hours. Treatment of Pb_2MoO_5 crystals was carried out in air and in vacuum at 600-700°C for 2 h.

Results and discussion

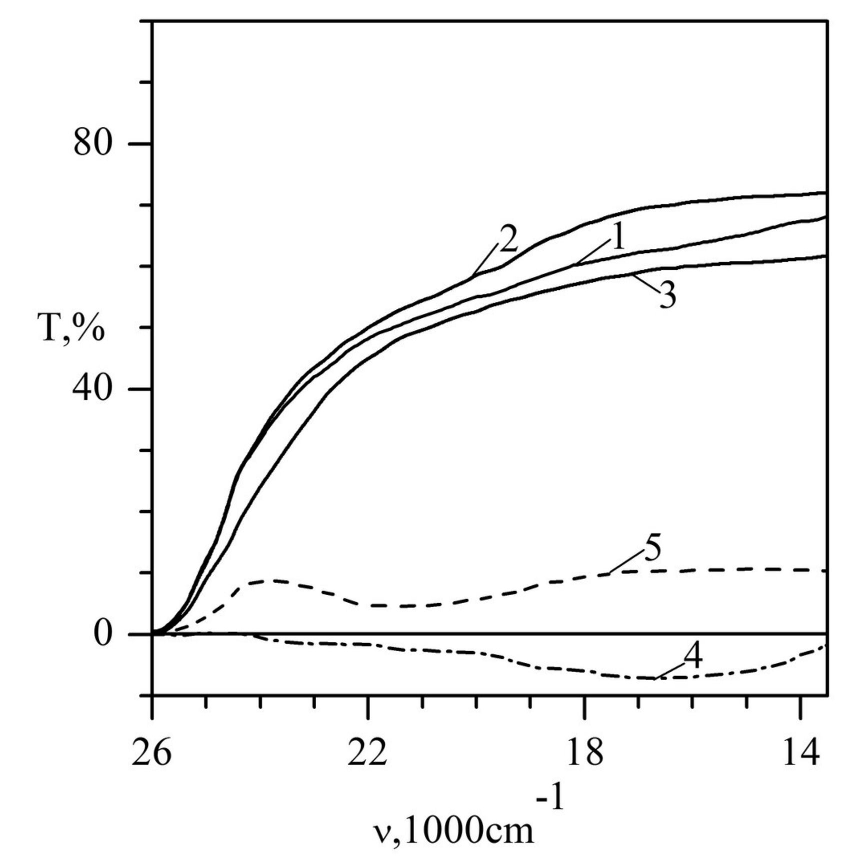

Fig. 1. The effect of the charge nonstoichiometry on the optical transmission of $PbMoO_4$ crystals: 1 – stoichiometric charge; 2 – charge; with 0,5 mol % MoO_3 excess; 3 – charge; with 1,5 mol% MoO_3 excess. The results of the spectra subtraction are shown by the curves 4, 5: 4=1 – 2; 5=2 – 3. The thickness of the samples was 10.5 mm.

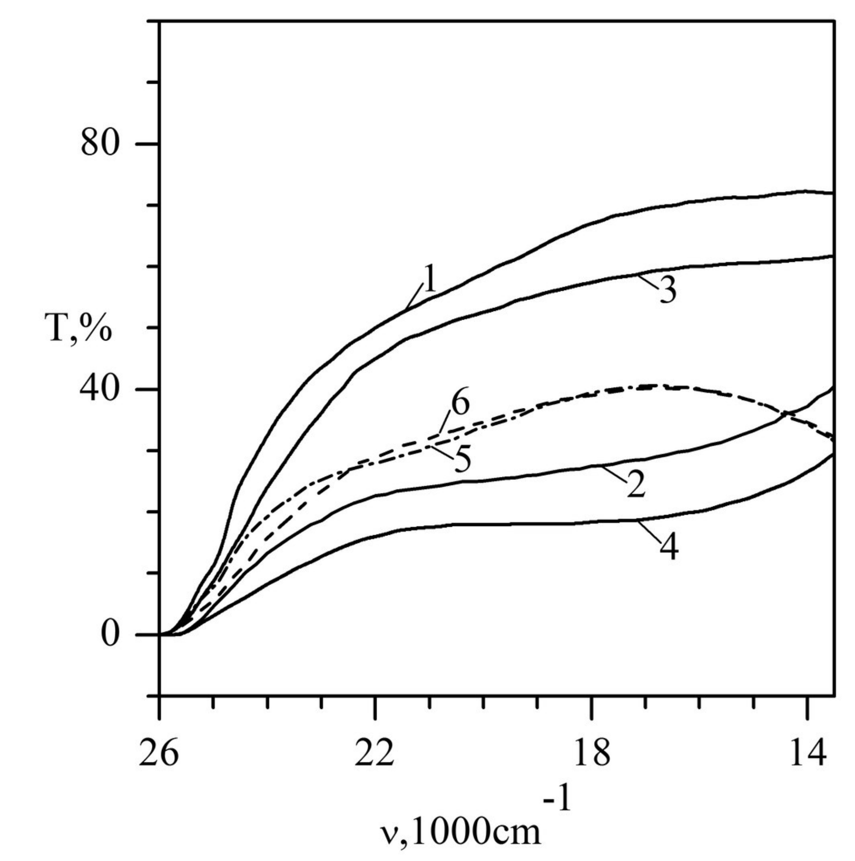

Fig. 2. The influence of UV irradiation on the optical transmission of $PbMoO_4$ crystals grown from the stoichiometric charge (curves 1, 2) and the charge; with 0,5 mol% MoO_3 excess (curves 3, 4): 1, 2 – before and 3, 4 – after UV exposition. The curves 5, 6 demonstrate the spectral difference: 5=1 – 2; 6=3 – 4. The thickness of the samples was 10.5 mm.

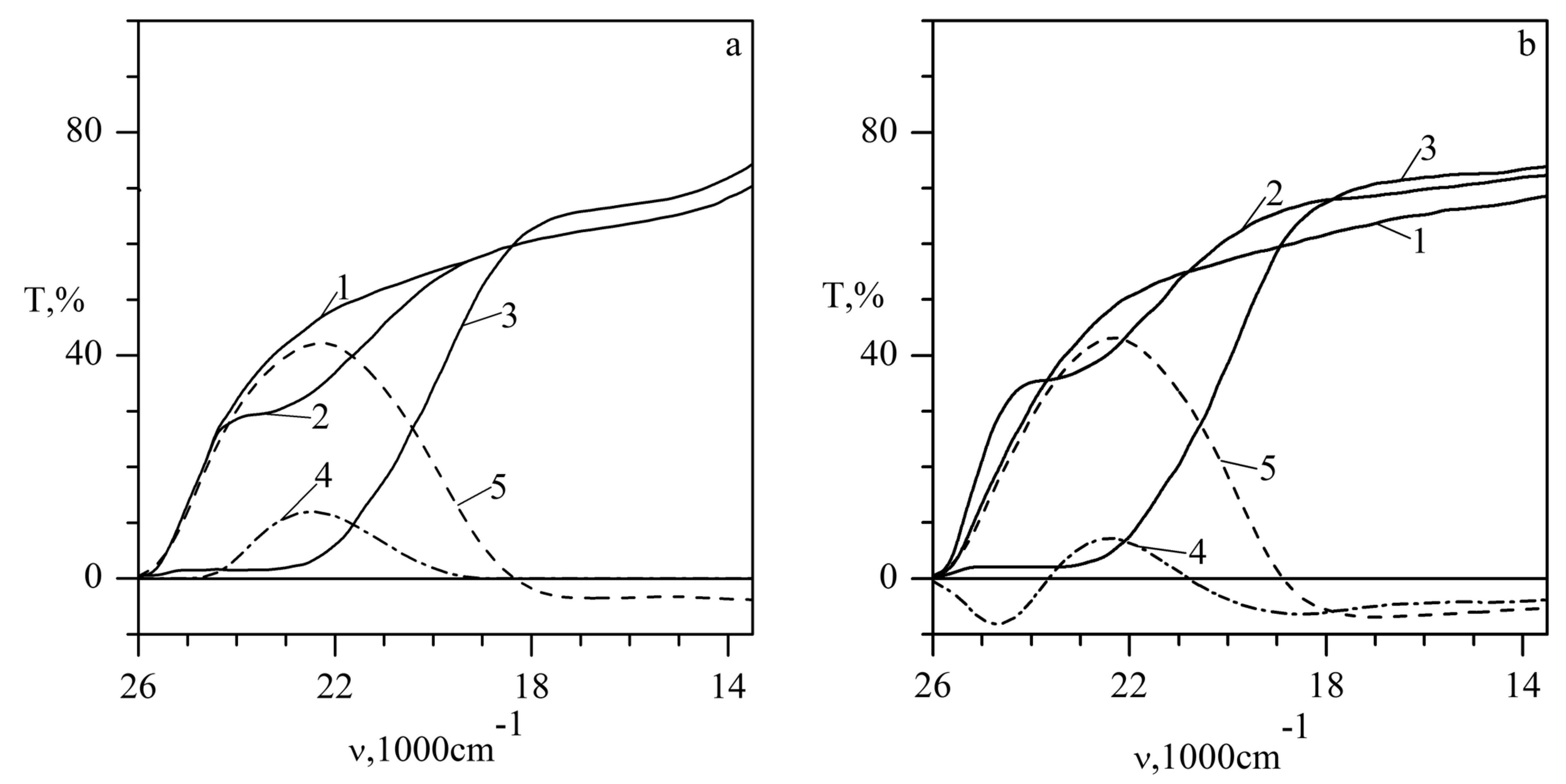

Fig. 3. The effect of isothermal treatment in air (T=1200K) on optical transmission of the $PbMoO_4$ crystals grown from the stoichiometric charge (a) and the charge; with 0,3 mol% MoO_3 excess (b): 1 – initial state; 2 – after heat treatment for 7 hours; 3 – after heat treatment for 87 hours. The spectral differences are shown by the curves 4, 5: 4=1–2; 5=1–3. The thickness of the samples was 10.8 mm.

Lead molybdate possess the scheelite-type crystal structure of the tetragonal system (space group I 4_1/a). The lattice of Pb_2MoO_5 is monoclinic (space group C 2/m). Both crystals contain the characteristic molecular anionic groups $(MoO4)^{2-}$ with almost the same Mo – O distance. The similarity and differences in the structure of crystals determine the features in their optical and electrical properties.

Earlier, different reactions of $PbMoO_4$ and Pb_2MoO_5 crystals to such external influences as UV irradiation and high-temperature annealing in different atmospheres were found [1,2]. The influence of charge composition deviations from stoichiometry on structural defects in the crystal lattice of $PbMoO_4$ and Pb_2MoO_5 is considered in this work. Changes in the optical spectra for crystals grown from various compositions are shown in the figures.

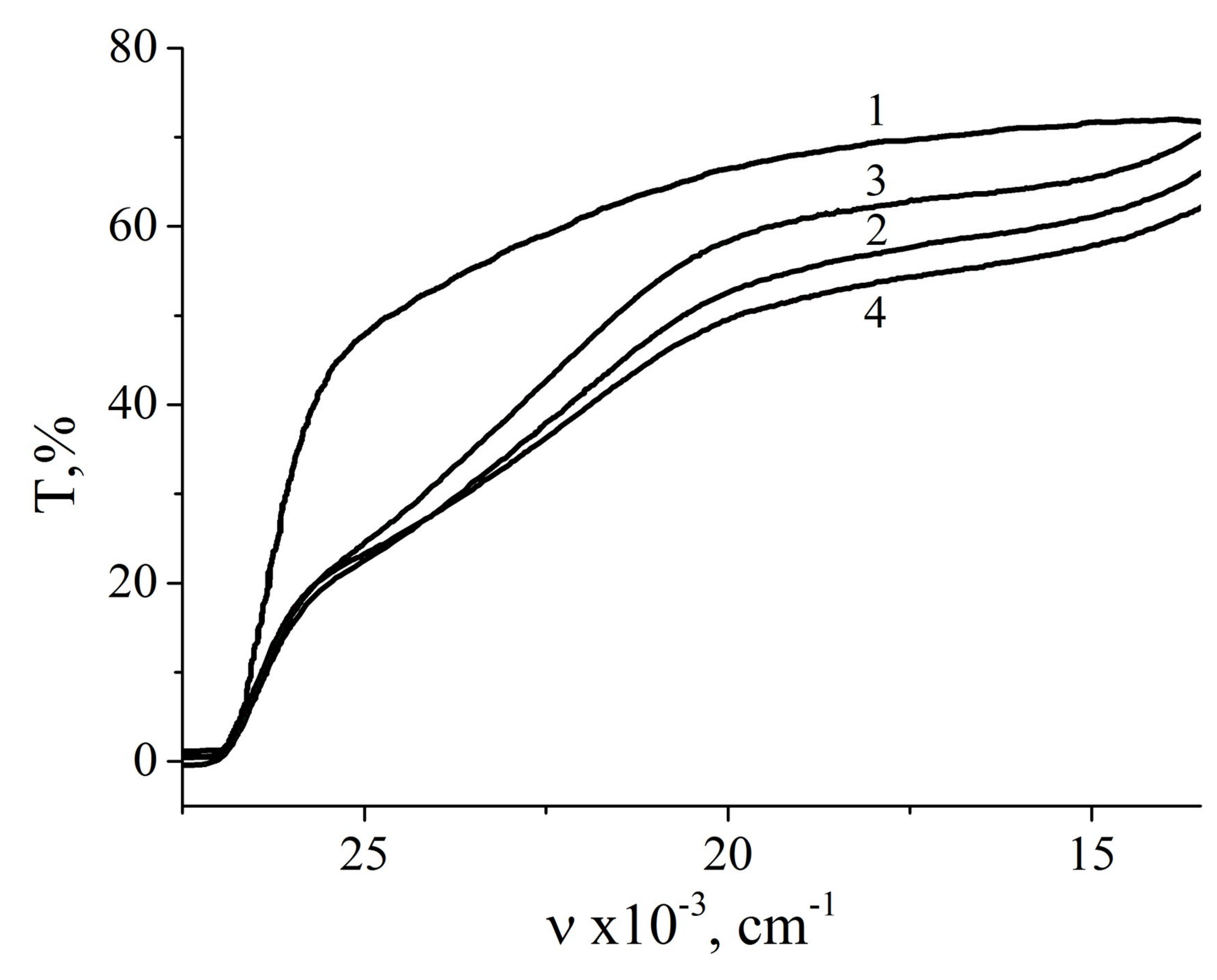

Fig. 4. The optical transmission Pb_2MoO_5 crystals: 1- crystals grown from stoichiometric charge. The sample thickness is 5.3 mm; 2-4 - crystals grown from the charge with 0.2 wt% PbO excess. The sample thickness is 8 mm; 3 – after heat treatment in air; 4 – after heat treatment in vacuum

References

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