THE INFLUENCE OF PbO EXCESS IN THE CHARGE ON THE OPTICAL TRANSMISSION OF Pb_2MoO_5 CRYSTALS

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The single crystals of acousto-optic Pb_2MoO_5 were grown by the Czochralski technique from a charge of stoichiometric composition and with an excess of lead oxide. Optical transmission spectra of these crystals were measured in the visible wavelength range. The effect of the heat treatment in air and in vacuum was considered. Changes in the valence state of a part of Mo^{6+} ions to Mo^{5+} and possible microinclusions of foreign phases are supposed to be responsible for the decrease in the optical transmission of crystals obtained from the charge with PbO excess.

Keywords: double lead molybdate Pb_2MoO_5, optical transmission spectra.

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1. Introduction

Crystals of double lead molybdate attract attention due to their acousto-optical properties [1]. The lattice of Pb_2MoO_5 belongs to monoclinic system with a space symmetry group C_{2h}^3–C2/m [2]. 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 (β=114.0°), where *b* axis is directed along C_2 symmetry axis. The crystals are optically biaxial, have a strong anisotropy of the acousto-optical parameters; they can be used to create new specific acousto-optic devices [3]. The main obstacle to the use of this material is the lack of a developed technology for growing high-quality crystals.

According to the phase diagram [4], Pb_2MoO_5 melts congruently at 950°C. This makes it possible to use the Czochralski technique, i.e. pulling the crystal on the seed from the melt. Pb_2MoO_5 single crystals were first obtained by this method in 1970 [2, 5]. However, the quality of crystals grown from a stoichiometric charge obtained by solid-phase synthesis was unsatisfactory. X-ray phase analysis and electron microscopy showed the presence of microinclusions of foreign phases in the crystals, in particular, Pb_5MoO_8, $PbO_{1.57}$ and amorphous lead oxide [6]. In addition, the obtained crystals had a yellow color, which indicates the presence of impurity or intrinsic defects. A typical defect for lead-containing oxide materials is lead vacancies in the crystal lattice due to the evaporation of PbO. Among the methods preventing the formation of such defects is the use of initial mixture with a deviation from the stoichiometric ratio of components towards an excess of lead oxide. In this paper, we consider the effect of an excess of PbO in the charge on the optical transmission of Pb_2MoO_5 crystals.

2. Samples and experimental details

Single crystals of Pb_2MoO_5 were grown from the melt in air by the conventional Czochralski technique using Pt crucible. The charge was prepared according to [7] by two-stage solid phase synthesis of PbO and MoO_3 oxides (purity rating 99.99%) taken in stoichiometric ratio and with 0.2 wt% PbO excess. Crystals were grown along [010] direction. Typical growth conditions are the following: 950°C initial temperature; 30 rpm rotation rate; 2 mm/h pulling rate; 30°C/h cooling rate.

The obtained Pb_2MoO_5 crystals were up to 20 mm in diameter and up to 40 mm in length. They were free from macroscopic inclusions (gas bubbles, cracks) and had a light yellowish color. High-temperature treatment of the crystals was carried out in air and in vacuum at 600-700°C for 2 h.

The measurements of the optical spectra were carried out on the polished plane-parallel samples cut perpendicularly to the [010] crystallographic direction. To study the photochromic properties of Pb_2MoO_5 crystals grown from the charge with PbO excess we irradiated the samples of the crystals with the light of 250-W high-pressure Hg lamp. The optical spectra were measured using a "Specord-UV-VIS" spectrophotometer at 295 K.

3. Results and discussion

Data on the optical spectra of Pb_2MoO_5 crystals are extremely scarce. The luminescence of Pb_2MoO_5 caused by VUV synchrotron radiation excitations was considered in [8]. In particularly, it was shown that Pb_2MoO_5 is an indirectgap material. The calculated value of the indirect band gap is 2.64 eV, while the minimal value of direct gap is 2.85 eV. The optical transmission of Pb_2MoO_5 crystals obtained from the charge of stoichiometric composition was studied in [9]. It was found that the processes associated with a change in optical transmission under the action of heat treatment of the crystals in air and in vacuum at 600–700°C and UV irradiation differ significantly in $PbMoO_4$ and Pb_2MoO_5 crystals. And although there are a number of works devoted to the study of $PbMoO_4$ crystals grown from a mixture with deviations from stoichiometry [10–13], similar studies on Pb_2MoO_5 are unknown to us.

Fig.1. shows the optical transmission spectra of Pb_2MoO_5 crystals grown from the charge of stoichiometric composition (curve 1) and the charge with excess of lead (curve 2).

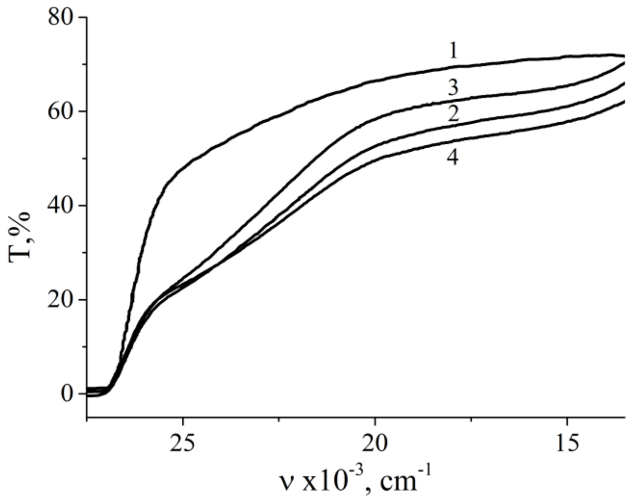

Fig. 1. The optical transmission Pb_2MoO_5 crystals: 1- crystals grown from stoichiometric charge. The sample thickness is 5.3 mm; 2-4 - crystals grown from the charge with 0.2 wt% PbO excess. The sample thickness is 8 mm; 3 – after heat treatment in air; 4 – after heat treatment in vacuum.

It can be seen from Fig.1 that the optical transmission of the crystal decreases in a wide range of wavelengths. The difference between spectra 1 and 2 is shown in Fig.2 (curve 5). Two wide maxima at 23000-25000 cm^{-1} and 15000-18000 cm^{-1} are clearly visible on the difference curve. However, their origin is not obvious. An excess of lead in the charge can lead to the filling of lead vacancies in the crystal lattice and, consequently, hinder the $Pb^{2+} \rightarrow Pb^{3+}$ transition, which, according to [13–16], is the reason for the absorption of light in the region of 23000 cm^{-1} in $PbMoO_4$ crystals. The very possibility of the existence of such a center in the Pb_2MoO_5 structure, which is different from the scheelite structure, needs to be discussed. The appearance of anti-site point defects (the presence of Pb ions in Mo sites – Mo_{Pb}), similar to the supposed situation in $PbMoO_4$ according to [17], seems unlikely to us. More likely, lead excess causes a decrease in the valence state of some of the Mo^{6+} ions to Mo^{5+}, which causes light absorption associated with internal transitions in the Mo^{5+} ions [14–16]. This correlates with the data [13] that an excess of lead in the $PbMoO_4$ charge led to the $Mo^{6+} \rightarrow Mo^{5+}$ transition and even the appearance of molybdenum vacancies to maintain electrical neutrality. Microscopic inclusions of foreign phases can also cause a decrease in the optical transmission of Pb_2MoO_5. The crystals did not contain visually observable inclusions; however, detailed microscopic and X-ray studies of Pb_2MoO_5 crystals grown from a charge with 0.2 wt% PbO excess are needed to clarify the situation.

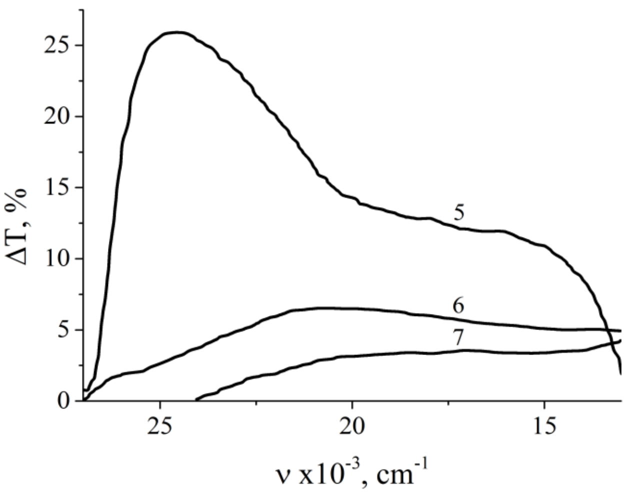

Fig. 2. The curves of the difference of corresponding spectra of the optical transmission: 5= 1-2(Fig. 1); 6=3-2(Fig. 1); 7=2-4 (Fig. 1).

Fig. 1 also shows the optical transmission spectra of Pb_2MoO_5 crystals grown from the charge with excess of lead after heat treatment in air and in vacuum (curves 3 and 4). The difference curves of the corresponding spectra are shown in Fig. 2 (curves 6 and 7). Treating in vacuum leads to a decrease in the transmission of crystals; treating in air, on the contrary, increases the optical transmission in a wide range of wavelengths. The changes themselves are not significant in magnitude. In general, these results correlate with the data obtained for Pb_2MoO_5 crystals grown from a stoichiometric charge [9]. Irradiation with UV light from a mercury lamp did not lead to noticeable changes in the transmission of crystals both before and after heat treatment.

5. Conclusions

In a wide wavelength range the optical transmission of Pb_2MoO_5 crystals grown from the melts from a charge with 0.2 wt% PbO excess decreased as compared with the crystals grown from stoichiometric charge. The most probable reasons of additional light absorption include the transition of some of the ions $Mo^{6+} \rightarrow Mo^{5+}$ and the content of microinclusions of parasitic phases. Heat treatment of the samples in vacuum at 600-700°C for 2 h decreased the transmission of the crystals; heat treatment of the samples in air under similar conditions increased the optical transmission in the visible range of wavelengths. Photoinduced changes in the optical transmission after UV irradiation of the crystals were not observed.

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