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SOLID-PHASE SYNTHESIS AND X-RAY ANALYSIS OF THE CHARGE FOR GROWING ACOUSTO-OPTIC Pb_2MoO_5 CRYSTALS

Growing single crystals of double lead molybdate Pb_2MoO_5 is usually accompanied by the appearance of additional phases of PbO–MoO_3 system. To improve quality of the grown crystals, it is necessary to provide single phase composition of the charge used. In the paper the regimes of the charge solid-phase synthesis are varied and the phase composition of the obtained charge is studied for the first time. The initial charge stoichiometry, number of stages of synthesis procedure, heating rate, temperature, and time of synthesis are varied in the experiment. X-ray phase analysis is performed for a number of the charge samples obtained under different technological conditions of solid-phase synthesis. It is shown that the appropriate choice of the synthesis regimes make it possible to reduce significantly the content of PbO–MoO_3 impurity phases in the charge. The obtained results should make for increasing quality of Pb_2MoO_5 single crystals which are promising for use in acousto-optic devices.

Keywords: solid-phase synthesis, X-ray phase analysis, double lead molybdate Pb_2MoO_5.

Вирощування монокристалів подвійного молибдату свинцю Pb_2MoO_5 зазвичай супроводжується появою додаткових фаз системи PbO–MoO_3. Для підвищення якості вирощуваних монокристалів необхідно забезпечити однофазний склад шихти. У статті вперше варіювалися режими твердофазного синтезу та досліджувався фазовий склад отриманої шихти. В експерименті використовувалися різні стехіометрії вихідної шихти, швидкості нагріву, кількості стадій, температури та часи синтезу. Для зразків шихти, отриманих за різних технологічних умов твердофазного синтезу, проведено рентгенофазовий аналіз. Показано, що використання відповідних технологічних режимів синтезу дозволяє значно знизити вміст домішкових фаз PbO–MoO_3 в шихті. Отримані результати сприятимуть підвищенню якості монокристалів Pb_2MoO_5, які є перспективними для використання в акустооптичних приладах.

Ключові слова: твердофазний синтез, рентгенофазовий аналіз, подвійний молібдат свинцю Pb_2MoO_5.

Выращивание монокристаллов двойного молибдата свинца Pb_2MoO_5 обычно сопровождается появлением дополнительных фаз системы PbO–MoO_3. Для повышения качества выращиваемых монокристаллов необходимо обеспечить однофазный состав шихты. В статье впервые варьировались режимы твердофазного синтеза и исследовался фазовый состав полученной шихты. В эксперименте использовались различные стехиометрии исходной шихты, скорости нагрева, количества стадий, температуры и времена синтеза. Для образцов шихты, полученных при различных условиях твердофазного синтеза, проведен рентгенофазовый анализ. Показано, что использование соответствующих технологических режимов синтеза позволяет значительно снизить содержание примесных фаз PbO–MoO_3 в шихте. Полученные результаты будут способствовать повышению качества монокристаллов Pb_2MoO_5, которые перспективны для использования в акустооптических приборах.

Ключевые слова: твердофазный синтез, рентгенофазовый анализ, двойной молибдат свинца Pb_2MoO_5.

1. Introduction

Interaction of optical and acoustic waves in the crystals of active dielectrics is the basis for operating of acousto-optic devices, which are widely used in modern electronics [1-4]. Lead molybdate $PbMoO_4$ is one of the most popular acousto-optic material. Besides that, another representative of this family, double lead molybdate Pb_2MoO_5 is considered as promising crystal for use in acoustooptics due to low monoclinic symmetry and high anisotropy [5]. According to the phase diagram, these two compounds of PbO–MoO_3 system melt congruently: $PbMoO_4$ at 1070^0C and Pb_2MoO_5 at 950^0C [6]. The growing technology of lead molybdate $PbMoO_4$ single crystals has been worked out in details. At the same time, growing double lead molybdate Pb_2MoO_5 crystals of high enough quality remains unsolved problem owing to some technological difficulties. The structure of Pb_2MoO_5 crystals belongs to 2/m point symmetry group of monoclinic system [7]. The parameters of Pb_2MoO_5 unit cell, determined by X-ray diffraction, are a=14.225Å, b=5.789 Å and c=7.336 Å [7] with monoclinic angle $\beta=114^o$ between a and c axes. The crystal structure is characterized by a cleavage plane $(\bar{2}01)$. According to [8], the Pb_2MoO_5 single crystals grown from the melt by Czhochralski method contain additional impurity microphases Pb_5MoO_8, $PbO_{1,57}$ and amorphous Pb-oxides.

The purpose of this paper is to develop technology of solid-phase synthesis of the initial charge used for growing Pb_2MoO_5 single crystals with optical quality, high enough for using in acousto-optic devices. To control the phase homogeneity of the synthesized charge, the stoichiometry of the starting reagents and temperature regimes of solid-phase synthesis were varied. The phase composition of the synthesized charge was controlled by X-ray phase analysis.

2. Experimental results

The initial charge was prepared as follows. PbO and MoO_3 chemical reagents in a molar ratio 2:1 and with total weight of about 100 g were taken. To reduce microphase inclusions in the charge, various regimes of solid-phase synthesis were selected. In the experiment the following synthesis parameters were varied: the rate of linear heating the initial mixed reagents to the temperature of synthesis; temperature and time of synthesis.

The synthesis procedure was carried out in one or two stages, between which additional homogenization of the charge was carried out or was not performed. Experimental samples of the charges prepared under different processing conditions, were titled with consecutive numbering from PM2-1 to PM2-13. Note, that PM2-1 sample was prepared by milling Pb_2MoO_5 single crystal of high optical quality with no visible pores and inclusions, and further was used to measure the etalon X-Ray diffraction pattern.

At the first stage of research, for all samples the X-ray powder diffraction patterns were obtained by using DRON 2.0 facility operating with monochromatic Cu Kα radiation. Then, the experimental plots were scanned and digitized with using software Get Data Graph Digitizer.

The phase composition of the etalon charge sample PM2-1 was checked by comparing with the powder diffraction data presented in the Joint Committee on Powder Diffraction Standards (JCPDS) PDF 24-579. The positions of all major reflexes of PM2-1 sample coincide with the tabular data that shows that the etalon sample corresponds to pure Pb_2MoO_5 phase and has no additional impurity phases of other PbO–MoO_3 compounds.

3. Discussion

The comparison of the diffraction patterns of PM2-2,...PM2-13 samples with the patterns of etalon PM2-1 sample showed how deviations from stoichiometry and various regimes of solid- phase synthesis influenced the phase composition of the charges prepared. It was found that carrying out additional second stage of synthesis with certain temperature and time regimes sufficiently improved degree of the charge homogeneity and decreased the content of undesirable impurity phases. For example, Figure 1 shows the diffraction pattern of the etalon PM2-1 sample and diffractograms of PM2-5, PM2-6 samples. One can see that in comparison with etalon PM2-1, for PM2-5 sample a new reflex at $2\theta=27^0$ 24' appears. In the PM2-6 sample this reflex is absent. The reflex at $2\theta=27^0$ 24' corresponds to the interplanar distance d=3.255 Å. In accordance with the data available, intense reflection from the family of planes with indices (0 3 2) and interplanar distance d=3,265 Å is observed in the X-Ray diffraction pattern of Pb_5MoO_8 structure (PDF 37-1086). Therefore, it can be assumed that the new reflex at $2\theta=27^0$ 24' in the diffraction pattern of the sample PM2-5, reflects existence of Pb_5MoO_8 microphase in the charge. In the diffraction pattern of the sample PM2-6, which was prepared by additional heat treating the sample PM2-5, the discussed reflex ($2\theta=27^0$ 24') is practically absent as for etalon PM2-1 sample (Fig. 1).

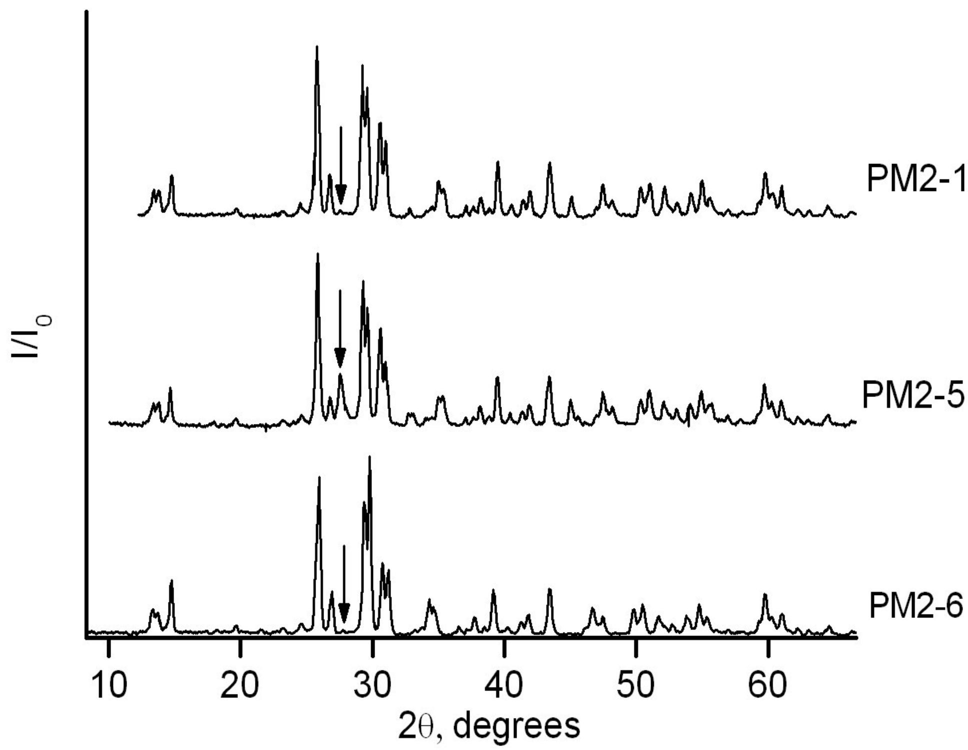

Fig.1. Diffraction patterns of Pb_2MoO_5 charge samples prepared under different conditions of solid state synthesis. The arrows show the reflex ($2\theta=27^0$ 24'), indicating existence of Pb_5MoO_8 microphase as discussed in the text.

4. Conclusions

Optical homogeneity and applicability of Pb_2MoO_5 single crystals for acousto-optical devices strongly depends on the single-phase content of initial charge used for crystal growing. In the paper we study the effects of stoichiometric ratio of the starting chemical reagents, number of synthesis stages, temperature, and time of solid-phase synthesis on the phase composition of the prepared charge. As a result, the solid-phase synthesis regimes were determined, which made it possible to prepare single-phase charge, available for growing high-quality Pb_2MoO_5 single crystals by Czochralski method.

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