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LETTER

Bridgman growth of lead molybdate crystals

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Lead molybdate ($PbMoO_4$, PMO) crystal is well known as an acousto-optic material with excellent properties such as higher acoustic-optic figure of merit and lower acoustic loss [1]. The crystal has been attracted much interest for its application in acousto-optic modulators, deflectors and filters. The phase diagram of PbO–MoO_3 system [2] shows that PMO crystal can be melted congruently with the composition of 50 mol% PbO at 1,065 °C. Much effort has been made to grow large-size crystals with high quality for acoustic-optic devices. In the previous works, most investigations are focused on the conventional Czochralski process, in which the crystals were pulled from the melts with congruent composition [3–7]. Almost all commercially available PMO crystals are grown by Czochralski process. The main difficulties for Czochralski growth of the crystals are (1) continuous composition change of melts during the growth because of serious volatilization of PbO and MoO_3 and (2) cracking in as-grown crystals due to the anisotropy of thermal expansion. Considering that PMO crystal is a congruently melted compound with a moderate temperature, an alternative method, Bridgman method is a promising technique to overcome the difficulties in Czochralski growth. Recently, the modified vertical Bridgman process was used to grow PMO crystals in our laboratory. In this letter, we present what is to our knowledge the first report on the vertical Bridgman growth of PMO crystals.

The feed material for PMO crystal growth was synthesized from the high purity PbO (99.99%) and MoO_3 (99.99%) according to the chemical stoichiometry. The starting agents were sintered at 200 °C for 3 h to remove the moisture. The agents were mixed for 3–4 h in a nylon ball mill and filled in a platinum crucible. The mixture was sintered at the temperature of 900–950 °C for 5 h and then at 1,100 °C for 0.5 h so that the compound PMO was synthesized and homogenized by the solid phase reaction. Through the sintering and homogenization procedures, the PMO polycrystalline material had been well synthesized. The feed material obtained was identified to be PMO phase by X-ray powder diffraction and DTA analysis. The dense polycrystalline charge without moisture allowed more efficient filling of the crucibles in the following process. As a comparison, the feed material was alternatively synthesized from the high purity $Pb(NO_3)_2$ (99.9%) and $(NH_4)_2MoO_4$ (99.9%) by the precipitating reaction in aqueous solution. The two agents with the molar ratio 1:1 were dissolved to be saturated solutions and a precipitation occurred as the two solutions mixed together by stirring. The feed material with accurate stoichiometry was obtained after the precipitation was filtered and dried.

PMO crystal was grown by a resistively heated vertical Bridgman furnace shown in Fig. 1. The furnace temperature was adjusted by a WJK-100A fine temperature controller with an accuracy of ±0.5 °C during the experiments. According to the axial temperature distribution, the furnace chamber can be divided into three zones, i.e. the high-temperature zone, the gradient zone and the low-temperature zone. The high-temperature zone was usually controlled at 1,140–1,200 °C, which was about 75–135 °C higher than the melting point of crystal. The horizontal temperature distribution was kept as uniform as possible. The platinum crucible used in crystal growth was 25–40 mm in diameter and 200–250 mm in length with a seed well of 10 mm in diameter at the conical bottom to hold the seed crystal. In order to obtain the seed crystal, the initial tries of the growth

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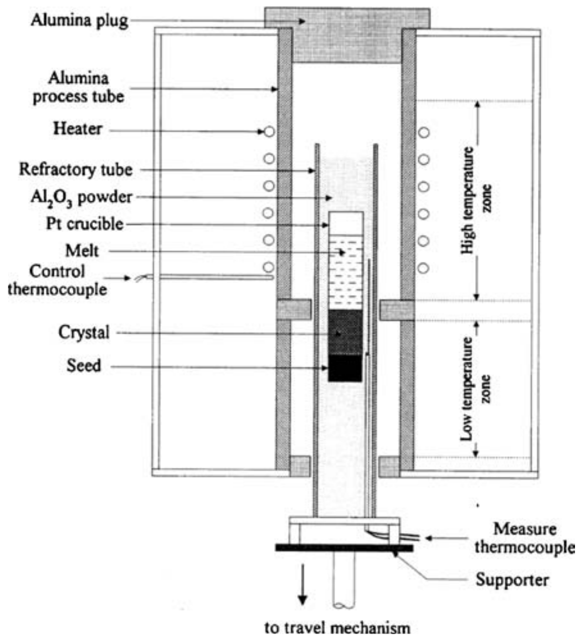

Fig. 1 Scheme of vertical Bridgman furnace

were done by spontaneous nucleation from the seed wells. Transparent single crystals with size of $\Phi 10 \times 40$–$60\ mm^2$ were chosen as the seeds after the crystals were oriented, cut and ground. The seeds were put in the seed wells, and then the feed materials were filled in the cylinder of crucibles. The assembled crucible was sealed in order to prevent the volatilization of the melt during crystal growth. The crucible was installed in a refractory tube filled with Al_2O_3 powder to isolate it from external temperature fluctuations. In order to detect the axial temperatures along the crucible, the crucible was fitted with two Pt–Pt/Rh 10% thermocouples.

After the crucible had been placed in the furnace, it was heated to the controlled temperature at the rate of 100 °C/h. Seeding process was performed by adjusting the crucible to such a position that only the seed top was melted. The feed material and the seed top were kept at the melting state for 6–8 h so that a stable solid–liquid (s–l) interface can be established on the top region of the seed. The temperature gradient across s–l interface was around 20–40 °C/cm. Growth process was driven by lowering the crucible at a rate of 0.6–1.2 mm/h. After the growth had finished, the furnace was cooled to room temperature at a rate of 20–50 °C/h. The crucible was stripped after taking out of the refractory tube and as-grown crystal was obtained. In order to eliminate the residual stress inside the crystals, they were annealed further in a resistant furnace. The crystals were heated to 800–900 °C at the rate of 50 °C/h, held at that temperature for 20 h and finally cooled to room temperature at the rate of 30 °C/h.

The composition of melts should be kept stable in order to grow high quality crystals. However, in the Czochralski growth process, the melts volatilize significantly under normal atmosphere. The DTA/TG analysis of the crystal shows a weight loss more than 10 wt% occurs above the melting point. Because of different volatility of PbO and MoO_3, the composition of PMO melts changes continuously in the growth process. It is usually difficult to compensate the weight loss precisely to avoid the composition deviation of the melts. In our Bridgman process, the volatilization could be avoided effectively by sealing the crucibles. No evident weight losses occurred and the composition of the melts could be kept in constant during the growth. Compared to the Czochralski growth, the temperature gradient across the s–l interface was usually smaller and the crystal was annealed in the low-temperature zone simultaneously in our Bridgman growth. Additionally, the grown crystal was annealed further to eliminate the residual stress inside the crystals. These technical measurements are helpful to decrease the cracking of the crystals. The previous literatures had dealt with the bubbles in the crystals due to the forced convection in the Czochralski process [5, 6]. In our Bridgman process, the bubbles could be avoided since the fluidity of melts was very stable. The experiments showed that the optimum growth direction was parallel to $\langle 100 \rangle$, along which the cracking was alleviated. In view of above points, the Bridgman technique is a favorable process to overcome the difficulties in the conventional Czochralski method.

By means of the optimum conditions listed in Table 1, PMO single crystals have been grown successfully by the described process. All the melt was converted into crystals without any remains in the crucibles. As-grown crystals take the shape of the crucibles, so the crystals with different shapes such as cylinder or block can be grown arbitrarily. Figure 2 shows an as-grown crystal, which is colorless and transparent along $\langle 100 \rangle$ orientation with the

Table 1 The growth parameters for PMO crystals by vertical Bridgman method

Crucible material	Platinum
Crucible size	$\phi 25$–40×200–$250/\phi 10 \times 50$–70
Seed size	$\phi 10 \times 40$–60
Growth direction	$\langle 100 \rangle$
Composition of feed material	Stoichiometric
Batch weight	300–800 g
Furnace temperature	1,140–1,200 °C
Soaking time	6–8 h
Seeding temperature	1,065–1,075 °C
Temperature gradient across l–s interface	20–40 °C/cm
Lowering rate	0.6–1.2 mm/h
Cooling rate	20–50 °C/h
Annealing temperature/time	800–900 °C/20 h

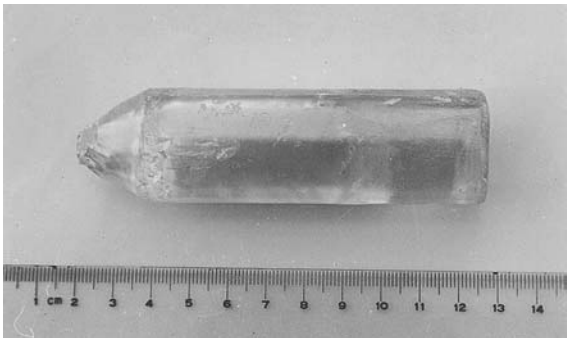

Fig. 2 $PbMoO_4$ crystal grown by modified Bridgman method

size of 30 mm in diameter by 100 mm in length. The crystal was examined to be free from scattering centers by a He–Ne laser. The grown crystal was analyzed with an X-ray diffractometer, using monochromatic CuK_α radiation with a working voltage of 40 kV and current of 100 mA. X-ray diffraction pattern is showed in Fig. 3. The grown crystal was confirmed to be $PbMoO_4$ without other phases.

To measure the optical transmittance of crystals, the samples with 40 mm in thickness were fabricated from the crystal grown. The transmission spectra were measured with a SUIMADZU UV-2501(PC)S spectrometer in the range of 300–800 nm at room temperature. Figure 4 presents the transmission spectrum of crystal, in which the absorption edge is located around 380 nm and the transmittance above 500 nm is about 70%. For the samples obtained from different part of the crystals, almost no difference in the transmission is recognized. However, for the crystal grown with the material synthesized from the solution, its optical transmittance is somewhat higher. The result indicates that this kind of material is more desirable for growing high quality PMO crystals because of its exact stoichiometry.

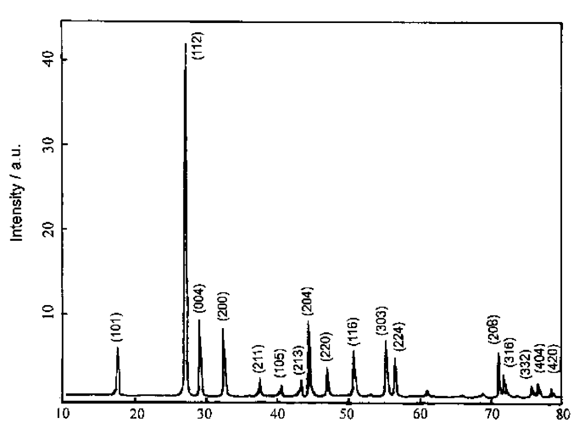

Fig. 3 X-ray diffraction pattern of $PbMoO_4$ single crystal

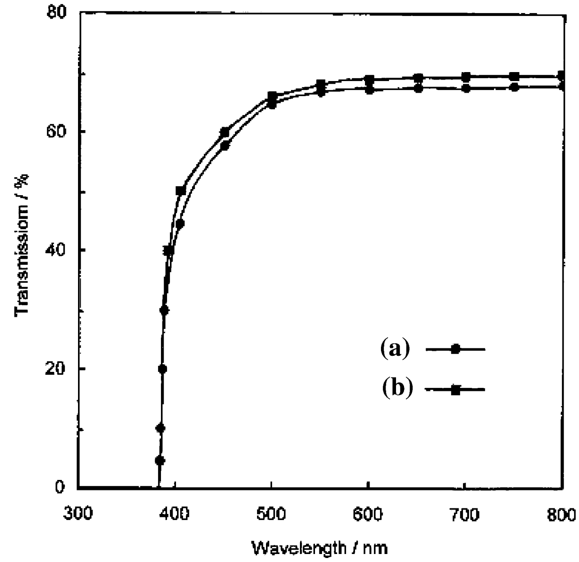

Fig. 4 Transmission spectrum of $PbMoO_4$ crystals grown with the feed material synthesized by (**a**) solid state reaction or (**b**) solution reaction

Now the authors are trying to grow 2 inches diameter PMO crystals by the modified Bridgman method with multi-crucibles. In our process, as many as six crystal boules can be grown in one furnace simultaneously. Moreover, using block shaped crucible, we can also grow the crystals with block shape, which is more convenient for device fabrication with higher material utilization ratio. Owing to the advantages mentioned above, the present Bridgman process is promising for mass production of PMO crystals with lower cost.

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