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Research on phase transition and crystal growth of lead iodide

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ABSTRACT

Based on Pb-I phase diagram, phase transition of PbI_2 immiscible melt ($L_2 + L_3$) was analyzed. It indicates that PbI_2 crystal growth is accompanied with precipitation of excessive Pb. Hereby, with an improved growth ampoule, an intact and translucent PbI_2 crystal was growth by vertical Bridgman technique. X-ray diffraction (XRD) analysis shows that the structure of the grown crystal is 2H with hexagonal space group ($P\bar{3}m1$). Energy dispersive X-ray (EDX) microanalysis shows the precipitated material is 100% Pb. The experimental results accord with the phase transition analysis and indicate a convenient way to grow single crystals from immiscible melt.

1. Introduction

PbI_2 single crystal is one of the important room temperature radiation detector materials [1]. The high atomic number ($Z_{Pb} = 82$, $Z_I = 53$) promises its ability to stop X-ray. The large band gap (2.30 eV) and theoretic resistivity at room temperature ($10^{12}\ \Omega$ cm) lead to higher energy resolution and detection efficiency [2–4]. Nevertheless, PbI_2 detector has not been applied widely in the fields of nuclear physics, radiology, non-destructive testing and so on, which is resulted from the growth difficulty of this crystal. The properties of crystals grown by physical vapor deposition technique or sol–gel method cannot meet for the fabrication of detectors [5,6].

Usually, PbI_2 crystal can be grown from melt for it does not undergo phase transition below its melting point (679 K). But, there are still many unsolved problems in crystal growth by vertical Bridgman technique and zone melting technique [7,8], which is probably due to absence of investigation on the phase transition of Pb-I system. In this paper, we expounded phase transition of PbI_2 immiscible melt ($L_2 + L_3$) during crystallization based on Pb-I phase diagram proposed previously by us [9]. And an improved growth ampoule was employed to grown PbI_2 single crystal using vertical Bridgman technique. To verify the phase transition theoretic analysis results of Pb-I system, the grown crystal ingot and the precipitated material were respectively investigated by XRD and EDX.

2. Phase transition

In Pb-I phase diagram (Fig. 1), one temperature falling path was chosen to be $0 \rightarrow 1 \rightarrow 2 \rightarrow 3$, which covers $L_2 + L_3$. The four numbers denote temperature of the melt at T_0, T_1, T_2, and T_3 respectively. The PbI_2 immiscible melt rich in Pb crystallizes along with this path.

As $T > T_0$, the melt does not show immiscible behavior. When $T = T_0$, the melt presents to be immiscible, depicted as $L \rightarrow L_2 + L_3$. From T_0 to T_1, the composition of L_2 and L_3 change along with liquid lines. L_2 sinks under L_3 because of L_2 is rich lead due to a larger density.

As $T = T_1$ (melting point of PbI_2, 679 K), PbI_2 crystal is separated from L_3 till exhaustion, denoted as $L_3 \rightarrow L_2 + PbI_2$. From T_1 to T_2, PbI_2 crystal is separated from L_2 melt, and the composition of L_2 changes along with 'eb' line.

As $T = T_2$ (eutectic point of Pb-I system, 641 K), the composition of L_2 melt moves from point 'b' to 'a', with three phase coexistence of PbI_2, L_2 and L_1. It can be expressed as $L_2 \rightarrow L_1 + PbI_2$. Iodine ingredient reduces gradually in PbI_2 grains and lead ingredient increases in L_2. From T_2 to T_3, PbI_2 separation from L_1 proceeds and the composition of L_1 goes along with 'ad' line.

As $T = T_3$ (melting point of Pb, 600 K), L_1 is liquid lead namely Pb (L). From T_3 to room temperature, Pb (S) separates out in Pb (L) until

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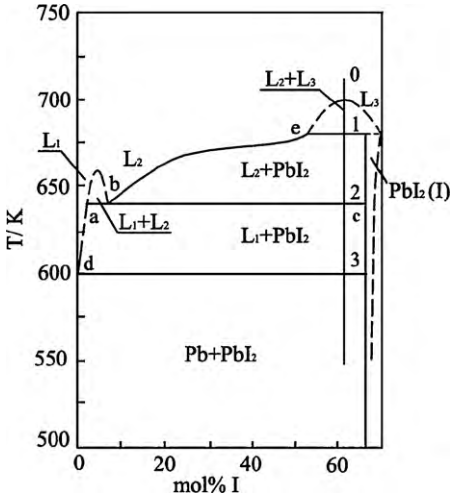

Fig. 1. The chosen path in Pb-I phase diagram.

all excessive Pb curdles and precipitates under PbI_2, this process is expressed as Pb(L) → Pb(S).

So, when the immiscible PbI_2 melt with excessive Pb is cooled to room temperature, it can crystallize to be single-phase PbI_2, and the excessive Pb can precipitate under the crystal. For crystal growth, we can improve the seeding pocket of growth ampoule to ensure crystal grains competition and growth. The traditional ampoule as shown in Fig. 2(a) cannot guarantee development of single crystal. The improved ampoule, as shown in Fig. 2(b), was fabricated to attach a hollow bulb under the seeding pocket. The bulb's size was suitable for holding the precipitated excessive Pb. And the conical part between the seeding pocket and the bulb can ensure crystal grains compete and grow to be single crystal.

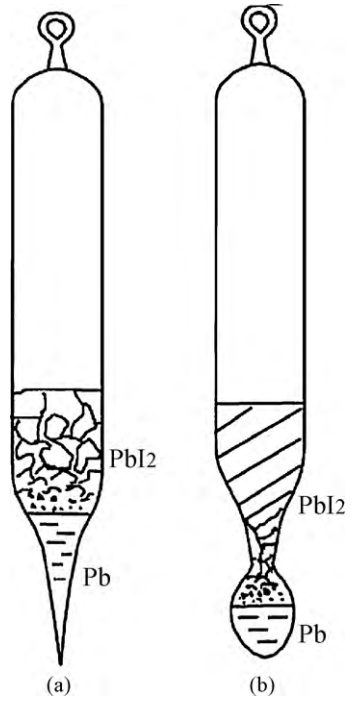

Fig. 2. Sketch diagram of two different growth ampoule and crystallization progress.

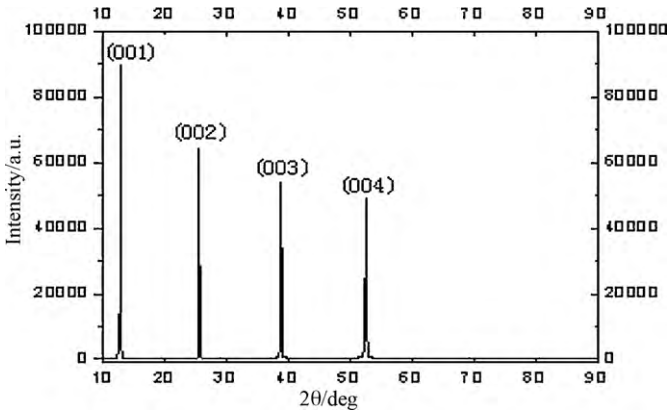

Fig. 3. The XRD spectrum of the PbI_2 crystal, λ(Cu Kα) = 0.154178 nm.

3. Experiment and results

3.1. Growth process

Starting material (99.999%) of lead and iodine was weighed with excessive Pb, and then loaded into the improved quartz ampoule, evacuated for 3 h and sealed under 1.5×10^{-3} Pa. After this, the ampoule was put into a horizontal tubular furnace. PbI_2 polycrystalline material was synthesized by vapor transporting method (VTM) to avoid explosion of ampoule. Using the same quartz ampoule, PbI_2 single crystal was grown by vertical Bridgman technique in a two zone tubular furnace. Temperatures of the upper and the lower were controlled at 450 °C and 200 °C separately by the FP93. Temperature gradient of the solid liquid interface is about 25 °C/cm. Descending velocity of the ampoule is 10 mm/day. After growth, the ampoule was cooled to room temperature naturally. The grown crystal ingot is nacarat, translucent and intact. Some of crystal sample and the precipitated material in the bulb were taken out for further investigation.

3.2. Characterization results

The grown crystal was cut along its natural cleavage face, which is smooth and shining. XRD spectrum of the cleavage face was obtained by DX-2000, as shown in Fig. 3. Compared with PDF cards, four diffraction peaks of high intensity were founded to be {0 0 1} faces of PbI_2. Furthermore, rocking curve of the (0 0 1) cleaving face of the crystal was obtained also, as shown in Fig. 4. The rocking peak is situated at $\theta = 6.231°$, and its full width at half maximum

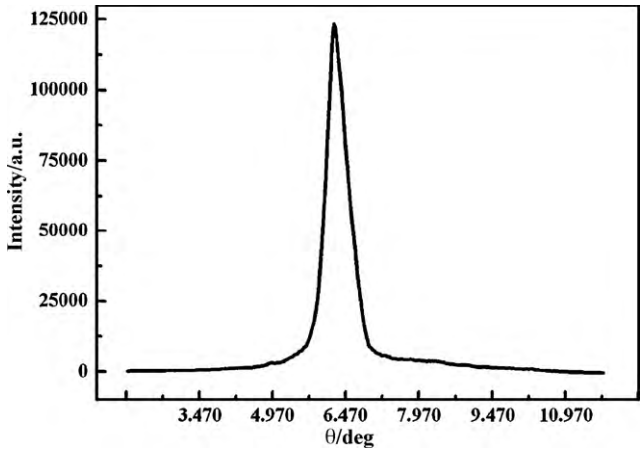

Fig. 4. The XRD rocking curve of (0 0 1) cleaving face of the PbI_2 crystal.

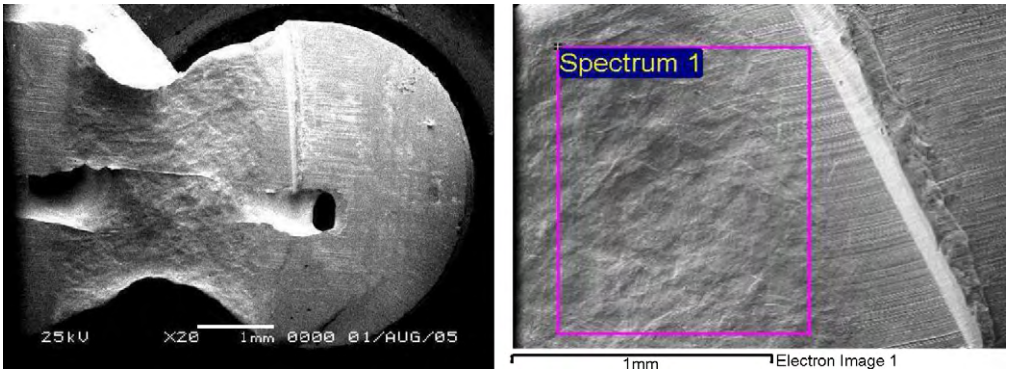

Fig. 5. The SEM topography of the incision section plane of the deposit lead.

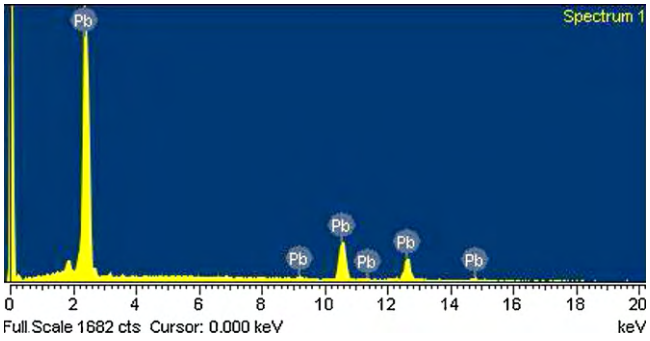

Fig. 6. The EDX spectrum of the deposited lead.

(FWHM) is 37.2′, which is accurate and symmetric relatively. All these indicate that the crystal grown by our craft is of preferable crystallization quality. XRD analysis was also done on the powder sample of the crystal. It is found that the structure of the crystal grown by this craft is 2H with hexagonal space group ($P\bar{3}m1$), and the lattice constants accord with PDF values. Test on plenty of other powder samples brought similar results, just with some differences in intensity of peaks at same diffraction angles. The precipitated material in the bulb is black with metallic luster, and shows good metal flexibility when it was incised. Using the Hitachi S-450 scanning electronic microscope (SEM), we observed the incision section plane. The topography is shown in Fig. 5, in which there is one shrink hole formed during solidification. The EDX result (Fig. 6) indicates the deposited material in the bulb is pure Pb, which is in accordant with the phase transition analysis.

4. Conclusions

We analyzed phase transition of the $L_2 + L_3$ immiscible melt during crystallization according to Pb-I phase diagram. It indicates PbI_2 crystal growth is accompanied with precipitation of excessive Pb, and the excessive Pb can precipitate under single-phase PbI_2. With an improved growth ampoule, PbI_2 single crystal was grown by vertical Bridgman technique. The XRD results indicate the grown crystal is 2H structure, and The EDX result indicates the precipitated material in the bulb is lead. The growth experiment and the investigation on the samples are consistent with the phase transition analysis, which indicate a convenient way to grow single crystals from immiscible melt.

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