

Liquid encapsulation zone-refining of PbS

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A technique for removing impurities and controlling the metal/chalcogen composition in PbS is reported. It enables large device-grade single crystals to be grown from the vapour phase within the solidus range.

1. Introduction

Lead chalcogenide lasers have been successfully applied to gas spectroscopy and pollution monitoring [1]. For the wavelength range of 4 to 8 μm , double heterostructure devices have been developed consisting of a $\text{PbS}_{1-x}\text{Se}_x$ active layer and a PbS confinement layer [2, 3]. The perfection of the epitaxial layers and thus the performance of these devices depends largely on the quality of the PbS substrate crystal, i.e. the absence of low-angle grain boundaries, inclusions or precipitates, and the lowest possible dislocation density. In principle, several sublimation growth techniques are capable of supplying the required crystalline perfection [4, 5], but their results are strongly governed by the purity of the source material and the controllability of its stoichiometry or deviation thereof. These prerequisites can be fulfilled by a dynamic vacuum sublimation process, which, apart from an effective purification, allows the adjustment of a desired cation/anion composition very accurately [6, 7].

In the present paper we report on an alternative method of zone-refining the PbS source material. It has already proved to be useful for PbTe [8]. Particular care must be taken to prevent the re-diffusion of volatile impurities and vaporized chalcogen from the accumulation zones into the purified ingot. The necessary separation of the solid and the vapour phase can be achieved by the liquid encapsulation zone-refining (LEZOR [9]) technique.

2. LEZOR apparatus

To ensure a fast and effective process, a multi-zone design has been chosen which is shown in Fig. 1a. The furnace contains three melt-zones, resistance-heated by U-shaped molybdenum disilicate elements with thermal insulation provided by alumina shells.

The elements are connected in series and driven by PID controlled thyristors. Narrow melt-zones are accomplished by air-flushed cooling tubes neighbouring each heater. Viewing ports, evacuated quartz tubes of 14 mm diameter, allow an inspection of the liquid zones during the process. The furnace is alternately moved on tracks by two variable-gear motors. The ampoule diameter is 2 cm, its length 30 cm and the distance between the melt-zones is 10 cm. The lateral displacement of the furnace (11 cm) includes small overlaps of the liquid zones.

The temperature profile of the empty furnace is shown in Fig. 1b. Our design provides very narrow hot zones separated by temperature valleys of about 100°C. This profile will be flattened somewhat when the ampoule and material are inserted, but the melt-zone width could still be kept as narrow as 1.5 cm, corresponding to a ratio of melt-zone width to ingot length of 20.

3. Refining procedure

After synthesizing the approximately stoichiometric PbS from the elements in a vertical furnace for 4 h at 1160°C, a roughly crushed charge of

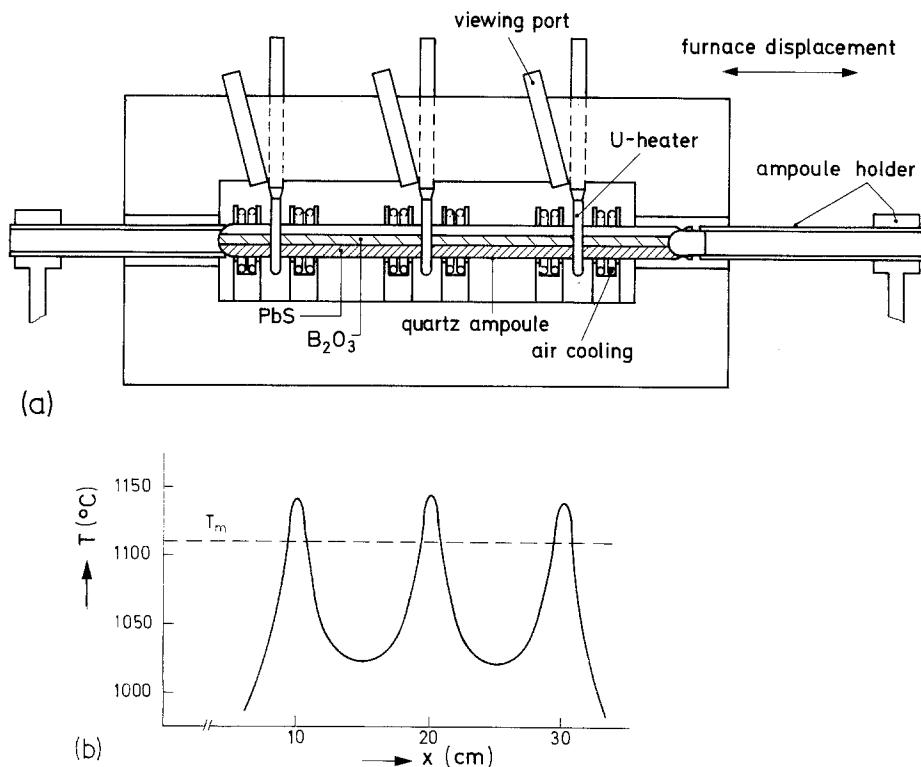


Figure 1 (a) Liquid encapsulation zone-refining apparatus (b) furnace temperature profile.

about 200 g is filled into the zone-refining ampoule. This ampoule is evacuated to 10^{-6} Torr, back-filled with 200 Torr argon and sealed. The charge is then smelted into a massive ingot, covering the whole ampoule length, in a horizontal furnace. The ampoule is opened and, after placing a rod of B_2O_3 above the ingot, evacuating and refilling it with 200 Torr argon, it is resealed. The B_2O_3 is previously baked under vacuum in a quartz boat of the same diameter and length and inlaid with a platinum foil. The ampoule thus prepared is inserted into the zone-refining apparatus and slowly heated to ensure that the PbS is totally covered by the molten B_2O_3 encapsulant before substantial PbS vapour transport to the top of the ampoule can reduce its optical transparency. To date, up to 45 melt-zone passes have been performed with a speed of 2.5 cm h^{-1} . After the last run, the furnace is cooled down to 600°C and the hot ampoule is removed and inserted into a protection tube connected to a vacuum pump. It cracks during the solidification of the B_2O_3 . Usually the centre of the PbS ingot is largely single-crystalline, whereas about 2 cm on both ends are polycrystalline. These ends are cleaved

off and discarded. Most of the B_2O_3 is removed from the ingot mechanically in an atmosphere of dry nitrogen. The remainder can be separated by transporting the PbS from one end of a short closed ampoule to the other at 700°C in a temperature gradient of approximately 1°C cm^{-1} . This process proved to be more effective and less sensitive to recontamination than washing in deionized water.

4. Mass spectrometry analysis

Six samples of $3 \text{ mm} \times 3 \text{ mm} \times 12 \text{ mm}$ were prepared from several ingots, one from each end and four from equally spaced central parts, and inserted as electrodes into a spark mass spectrometer (AEI, type MS 702). With 40 kV pulses of $100 \mu\text{sec}$ at a frequency of 100 Hz and by gradually reducing the current with an ion beam chopper, seven exposures on ion-sensitive photo plates were recorded from each sample and evaluated by a micro-densitometer (Joyce Loebel MK III). Usually the singly charged ions could be used for element analysis. However, for Cl strong S halos demanded the evaluation of the signals from doubly charged ions which were weaker by a factor of 5 to 7.

TABLE I Relative concentrations of several impurities after 18 melt-zone passes. A labels the first-to-freeze, F the last-to-freeze of the samples cleaved equidistantly from the zone-refined ingot.

Imp	A	B	C	D	E	F
Mg	14	14	7	4	12	4
Al	> 100	100	37	15	40	80
Si	> 220	220	100	50	40	90
Ti	150	75	40	25	20	20
Cr	200	25	15	10	55	45
Mn	7	3	1	1	5	3
Fe	14	14	4	4	16	73
Cu	20	20	12	10	12	43
As	40	4	1.5	1.3	3	0.7
Rb	23	n.d.	n.d.	n.d.	n.d.	n.d.
Ag	10	3	3	1.5	3.5	5
Sn	14	3	1.5	0.5	0.5	2
Ba	n.d.	0.5	n.d.	n.d.	0.5	0.5
F	*	*	n.d.	n.d.	n.d.	n.d.
P	*	n.d.	*	n.d.	*	n.d.
Cl	*	n.d.	n.d.	n.d.	*	n.d.

Key; * = qualitatively detected, n.d. = not detectable

Taking into consideration all the major isotopes, the relation between peak heights and exposure time was calculated. Its linear range yielded the uncorrected relative concentrations. These enabled a comparison of the different samples of one ingot to be made. In order to compare the concentrations of different ions, they must be multiplied by the relative sensitivity factors (RSF) which comprise line widths, ionization probabilities and mass-dependent sensitivity of the photo plate. They have not yet been determined for a PbS matrix but may be assumed to lie within 0.5 and 10 [10].

Table I presents the results for an ingot after 18 melt-zone passes which are not markedly different after 45 zone passes. Sample A denotes the first-to-freeze and sample F the last-to-freeze part of the ingot. The data are relative, i.e. a comparison between ions is restricted by the unknown RSFs. The negative ions could only be detected qualitatively. The results reveal an effective segregation of most of the ions. Although the concentrations usually increase towards both ends of the ingot, the first-to-freeze part exhibits higher accumulation values except for Fe and Cu. Thus with these two exceptions the segregation coefficients k of the investigated impurities in PbS exceed 1.

5. Crystal growth

The zone-refined source material is ground to a particle size of 1 to 3 mm, and 20 g portions are

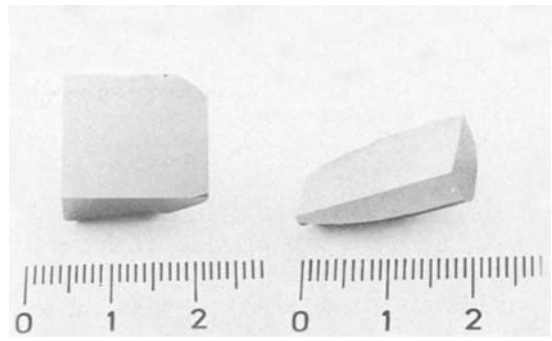


Figure 2 PbS single crystals, sublimation grown from zone-refined source material.

placed into growth ampoules (diameter 2.5 cm, length 12 cm). The sublimation growth occurs in a horizontal furnace with a carefully adjusted temperature profile ($<0.05^\circ\text{C cm}^{-1}$ parallel, 1°C cm^{-1} perpendicular to the ampoule axis). The growth period is 6 to 7 days.

Typical crystals grown without additional chalcogen or dopant are shown in Fig. 2. They exhibit well pronounced (100) facets with areas up to 2.5 cm^2 . The crystals are free of metal inclusions which formerly have restricted their applicability in devices. Their dislocation densities are of the order 10^5 cm^{-2} if the ampoule is air quenched by removing it from the hot furnace, but decreases to about 10^3 cm^{-2} if a slow linear cooling of 30°C h^{-1} is chosen. However, this improved metallurgical perfection is accompanied by an extraordinary softness which complicates the further handling of the crystals.

The bulk of the crystals is n-type with typically $n = 4 \times 10^{18}\text{ cm}^{-3}$ irrespective of the cooling procedure. If, however, the furnace is slowly cooled, an unavoidable annealing of the surface in the S_2 atmosphere of the growth ampoule takes place, causing a p-type layer approximately $50\text{ }\mu\text{m}$ thick to be formed. These phenomena indicate that the growth process indeed takes place within the homogeneity range and close to the stoichiometric composition.

Experiments were performed in order to adjust the type and concentrations of the carriers to desired values within the homogeneity range by adding small amounts of chalcogen to the source material. This had formerly been achieved successfully with PbSe [6] and $\text{Pb}_{1-x}\text{Sn}_x\text{Se}$ [7] crystals. With PbS, too, low carrier concentration n-type and p-type as-grown crystals could be attained, although for the latter the high S_2 vapour

pressure (10 mb at 830° C for stoichiometric composition) introduces serious disadvantages. First it renders a close prediction of the effective carrier concentration difficult since the major part of added chalcogen is necessary to provide the vapour pressure in the ampoule: the carrier concentrations aimed for and actually obtained may diverge by a factor of 2 or 3. Secondly, it suppresses the fast, unperturbed growth of p-type crystals. Smaller crystals and reduced metallurgical bulk homogeneity are the consequences.

Some initial experiments have also been undertaken with foreign impurity doping, to overcome the above difficulties and to achieve a desirable hardening of the crystals. As a donor Bi [11], as acceptors Tl and As [12] were added to the growth ampoule. Their solubility in PbS crystals is high, although only small fractions are electrically active. A maximum electron concentration of $n = 6 \times 10^{19} \text{ cm}^{-3}$ was found (even in slowly cooled crystals by adding 8×10^{-3} at. fractions of Bi. It should be noted that Tl was indeed capable of reducing the electron concentration (down to $n = 5 \times 10^{17} \text{ cm}^{-3}$). However, p-type crystals could not be obtained unless small amounts of extra chalcogen or As were added as well, to provide the necessary Pb vacancies. This would re-introduce the above difficulties, albeit to a lesser extent. Hence, to produce large p-type PbS crystals, a two-zone annealing [13] of n-type crystals grown by the present method appears to be preferable.

6. Conclusion

Very high purity and an exactly controllable metal/chalcogen ratio of the source material are the major prerequisites for the sublimation growth of large device-grade lead chalcogenide single crystals, particularly for PbS with its high equilibrium sulfur vapour pressure. We have shown that liquid encapsulation zone-refining is a

technique capable of fulfilling these requirements. Its effectiveness has been demonstrated by mass spectrometric analysis of many representative impurities. Furthermore, it yields a source material with a composition reproducibly fixed by the maximum melting point. Within narrow limits this composition and hence the carrier concentration of the as-grown crystals can be affected by adding small amounts of Pb or S into the growth ampoule.

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