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## Heat treatments of ZnSe starting materials for physical vapor transport

Ching-Hua Su<sup>a,\*</sup>, W. Palosz<sup>a,1</sup>, S. Feth<sup>a,2</sup>, S.L. Lehoczky<sup>a</sup>

<sup>a</sup>Space Sciences Laboratory, NASA Marshall Space Flight Center, Huntsville, AL 35812, USA

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## Heat treatments of ZnSe starting materials for physical vapor transport

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### Abstract

The effect of different heat treatments on stoichiometry and residual gas pressure in ZnSe physical vapor transport system was investigated. The dependence of the amount and composition of the residual gas on various heat treatment procedures is reported. Heat treatment of ZnSe starting materials by baking under the condition of dynamic vacuum to adjust its stoichiometry was performed and the effectiveness of the treatment was confirmed by the measurements of the partial pressure of  $\text{Se}_2$ ,  $P_{\text{Se}_2}$ , in equilibrium with the heat treated samples. Optimum heat treatment procedures on the ZnSe starting material for the physical vapor transport process are discussed and verified experimentally. © 1998 Elsevier Science B.V. All rights reserved.

### 1. Introduction

The predominant vapor species in equilibrium with the II–VI compounds in the temperature range of the physical vapor transport (PVT) process are the atomic species of the Group II elements, such as Zn, Cd and Hg, and the diatomic molecules of the Group VI elements, i.e.,  $\text{S}_2$ ,  $\text{Se}_2$  and  $\text{Te}_2$  [1–8]. The diffusive mass flux in a PVT process is determined by four parameters [4,9–11]: the temperature at the source and at the crystal, the ratio of the partial pressure of the two transport species, and the pressure and composition of the

inert gas in the system. The first two parameters can be easily adjusted by controlling the thermal profile inside the crystal growth furnace. At elevated temperatures the mass flux is a relatively weak function of the temperature at the source [10] and this flux increases as the temperature difference between the source and the crystal,  $\Delta T$ , increases but levels off as  $\Delta T$  approaches 30 to 40°C [4,10,11]. The partial pressures of the species II and VI<sub>2</sub> in equilibrium with the compounds, at a fixed temperature, can vary over orders of magnitude as the composition of the compound within the narrow homogeneity range changes from Group II saturation to Group VI saturation [1–3,5,8]. As a result, the transport rate of the vapor species can also vary from a maximum transport rate corresponding to the condition of congruent sublimation (i.e., the compositions of the solid phase and

\* Corresponding author. Fax: +1 205 544 8762.

<sup>1</sup> Universities Space Research Association.

<sup>2</sup> Raytheon STX Corp.



the equilibrium vapor phase are the same, or  $\alpha \equiv P_{\text{II}}/P_{\text{VI}} = 2.0$ ) to transport rates which may be orders of magnitude lower when the solid composition deviates significantly from that of congruent sublimation. Generally, in the PVT growth temperature range, the congruent sublimation condition exists inside the homogeneity range for most of the II–VI binary compounds [1,2,5,8]. However, a sufficiently precise and reproducible control of the starting compound stoichiometry by weighing the constituent elements is practically impossible due to the very narrow homogeneity range. For instance, the values of  $(X_{\text{Te}} - \frac{1}{2})$  for the Te-rich solidus of  $\text{Cd}_{1-x}\text{Te}_x$  are in the range of  $1 \times 10^{-5}$ – $1 \times 10^{-4}$  at temperatures between 680 and 1050 °C [12–14]. Nevertheless, with appropriate heat treatments the partial pressures over the starting compound material can be reasonably reproduced to approach  $\alpha = 2.0$ , i.e. the congruent sublimation condition [14].

On the other hand, in a real PVT process, volatile impurities such as  $\text{H}_2$ ,  $\text{H}_2\text{O}$ ,  $\text{CO}$ ,  $\text{CO}_2$ ,  $\text{N}_2$ , and  $\text{O}_2$  may be present as a result of the outgassing of the silica ampoule and/or from the source material [15–19] and form a significant amount of residual gas. Since these residual species remain in the vapor phase, they decrease the diffusivity of the transport species and reduce mass flux in the PVT system.

The effects of the latter two parameters, i.e. vapor-phase stoichiometry and residual gas pressure, on the mass flux is clearly illustrated in Fig. 1. The figure shows the calculated results on the mass flux of ZnSe, using a one-dimensional diffusion model [4,11] as a function of residual pressure at different values of  $\alpha(L)$ , i.e. the pressure ratio at the source. The calculation indicates (i) that at the ideal condition of zero residual gas pressure the mass flux decreases by a factor of 6 when  $\alpha(L)$  increases from 2.5 to 8 and (ii) that the residual gas starts to noticeably reduce the mass flux when its total pressure approaches the excess constituent pressure  $|P_{\text{Zn}} - 2P_{\text{Se}}|$ . Beyond this region, the residual gas becomes the mass flux limiting factor in the system. Therefore, to enhance the mass flux in such a system one needs to (i) adjust the stoichiometry of the starting material to approach that of congruent sublimation and (ii) reduce the residual gas pres-

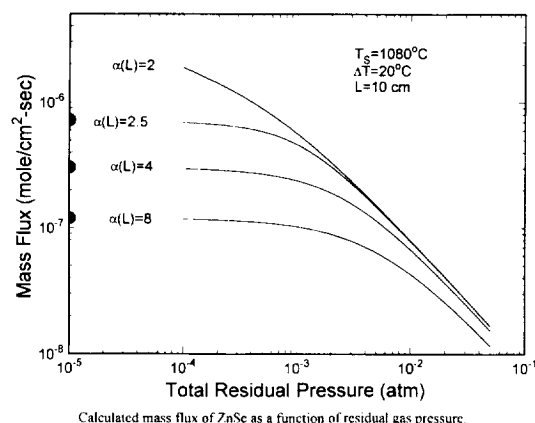


Fig. 1. Theoretically calculated mass flux of ZnSe as a function of the residual gas pressure for different partial pressure ratios at the source,  $\alpha(L)$ , with the source temperature at 1080 °C,  $\Delta T = 20^\circ\text{C}$  and transport length  $L = 10$  cm. The composition of the inert gas used in the calculation was 35%  $\text{CO}_2$ , 50%  $\text{CO}$  and 15%  $\text{H}_2$ . The solid dots on the left axis are the respective mass flux values assuming zero inert gas pressure.

sure. One of the methods to improve the stoichiometry of the starting material is to bake out the compound at the processing temperature under dynamic vacuum [14]. Besides purifying the material by preferentially subliming moisture and other volatile impurities, the process changes the stoichiometry of the starting material towards that of congruent sublimation. However, the method may result in a significant loss of the starting material, thus the temperature and duration of the baking process should be optimized. Such optimization requires a direct determination of vapor-phase stoichiometry, i.e. the partial pressures of the vapor species coexisting with the solid sample. One of the available techniques for such measurements is the optical absorption method developed by Brebrick and co-workers for partial pressure measurements over a number of II–VI and IV–VI compounds [1,4,5,8,11,13,20–30]. In this paper, using this optical absorption method we investigate the effectiveness of this heat treatment by measuring the partial pressures of  $\text{Se}_2$ ,  $P_{\text{Se}_2}$ , in equilibrium with a series of ZnSe samples that have been heat-treated by baking under the dynamic vacuum condition.

An effective adjustment of the solid composition requires that the diffusion length, the square root of the product of the diffusion coefficient of the relevant species in the material and time,  $(Dt)^{1/2}$ , is of the order of the particle size. Therefore, to minimize the bake-out duration, thus the loss of the material, the particle size of the starting material should be as small as possible. However, a small particle-sized powder has a large surface area and, consequently, a higher degree of surface oxidation. Since the oxygen content affects the pressure and composition of the vapor phase, the removal of the oxides from the material is necessary. One of the vapor phase processes used to remove oxides is to anneal the sample in a hydrogen atmosphere at elevated temperatures [31]. By measuring the total pressures and compositions of the residual gas inside the ampoules with the starting materials that have been heat treated and processed under various conditions, the effectiveness of different heat treatment procedures on reducing the residual gas pressure was also investigated.

## 2. Experimental procedure

### 2.1. Residual gas

#### 2.1.1. Sample preparation and treatments

All the processed ampoules were made from 15 mm ID and 18 mm OD fused silica tubing of low  $H_2O$  content (GE-214 or ST-10 brand). The ampoules were cleaned and outgassed under vacuum at 1040 to 1080 °C for 16–24 h. The starting material was either 59 purity ZnSe powder from Cleveland Crystals, Inc. or high-purity grade ZnSe chunks from Eagle-Picher, Inc. Except where indicated, the materials were ground with mortar and pestle into particles of diameter less than 0.7 mm in size. Before loading into the ampoules, some of the ZnSe starting materials were preprocessed in cleaned and outgassed ampoules by one of the following processes: (i) the ground sample was first annealed in 0.5–0.7 atm  $H_2$  pressure, baked and then distilled under dynamic vacuum at elevated temperatures (ampoule ZST-6 and ZSTO-3) or (ii) the ground ZnSe was baked and distilled under dynamic vacuum (ZST-7 and ZST-10).

The preprocessed ampoules were opened and the materials retrieved and ground. A few grams of these preprocessed materials were loaded into each ampoule and evacuated. In one case, eight chunks of ZnSe from the vendor were loaded directly into the ZST-13 ampoule and in another case, (ZSTO-3), the preprocessed sample was ground inside a glove box under Ar atmosphere to reduce oxidation of the powder by air. Before sealing under vacuum in the mid- $10^{-7}$  atm range some of the loaded ampoules were heat-treated by baking under dynamic vacuum at elevated temperatures with or without a preceding annealing under 0.5 atm of  $H_2$ . The sealed ampoules were then placed inside a furnace and processed at temperatures between 1070 and 1130 °C for 60–210 h. Table 1 gives the detailed preparation and heat treatment procedures.

#### 2.1.2. Residual gas measurements

The pressure and composition of the residual gas were measured using the technique described in Ref. [19]. Briefly, the processed ampoule was placed in a vacuum chamber connected to a pressure gauge and a high-vacuum system. After outgassing the chamber and the ampoule at room temperature under high vacuum, the valve between the chamber and the vacuum system was closed. The ampoule was slid inside the chamber and opened. The pressure change in the chamber was recorded. The original pressure in the sealed ampoule was calculated based on the chamber-to-ampoule volume ratio. Determination of the gas composition was made by fractional condensation of the gas components in the cold finger cooled to a predetermined temperature with appropriate cold bath mixtures. For temperatures below 77 K, the tip of the cold finger was placed in a stream of liquid helium droplets and the changes in the pressure as a function of temperature were recorded. Based on Refs. [15–17], it was assumed that the residual gas may consist of  $H_2$ ,  $H_2O$ , CO,  $CO_2$ ,  $N_2$ , and  $O_2$  molecules. Independent measurements and a detailed analysis of the pressure–temperature condensation curves under our typical experimental conditions indicated that the amounts of molecular oxygen and nitrogen in the ampoules could be ignored.

Table 1

Source preprocess and sample treatment procedures for residual gas pressure measurements. Vendor I – Cleveland crystals, 59 purity; vendor II – Eagle-Picher high purity grade

Run #	Source batch				Sample			Process time (h)
	Vendor	Mass (g)	Hydrogen treatment	Vacuum treatment	Mass (g)	Hydrogen treatment	Vacuum treatment	
ZST-6	I	26.0	0.66 atm at 1070°C for 45 min	1080°C for 8 min then distilled	2.1	None	None	162
ZST-7	I	19.7	None	1050°C for 8 min then distilled	3.0	None	None	140
ZST-9	II	7.9	None	None	7.9	None	1055°C for 10 min	210
ZST-10	II	21.7	None	1080°C for 18 min then distilled	2.7	None	500°C for 10 min	77
ZSTO-3	II	26.7	0.71 atm at 800°C for 5 min twice	1080°C for 17 min then distilled	3.0	None <sup>a</sup>	None	120
Empty	–	–	–	–	–	–	–	168
ZST-13	II	3.5	None	None	3.5 (8 chunks)	None	1140°C for 10 min	72
ZST-15	II	5.25	None	None	5.25	0.54 atm at 910°C for 20 min	1010°C for 8 min	60

<sup>a</sup>Ground and loaded into the ampoule in Ar atmosphere.

## 2.2. Partial pressure

### 2.2.1. Sample preparation and heat treatment

The optical cells were made from GE-214 15 mm OD 18 mm ID fused silica tubing and furnished with 20 mm diameter optical windows and a 19 mm optical path length. The ampoules were cleaned and then outgassed under vacuum at 1080°C for 10 h. The high-purity grade ZnSe samples supplied by Eagle-Picher, Inc. were ground, loaded and evacuated. Before sealing the samples were baked under dynamic vacuum with or without a preceding annealing under 0.5 atm of H<sub>2</sub>. After the partial pressure measurements (see below) the optical cells were opened and the amount of each sample was weighed. Table 3 lists the detailed sample preparation and heat treatment as well as material loss during the heat treatment.

### 2.2.2. Partial pressure measurements

An OLIS-14H near-IR/visible/UV spectrophotometer and a custom-made high-temperature furnace with two 12.5 × 150 mm rectangular windows were assembled to perform the partial pressure measurements. The basic principles for the measurements and the experimental procedure are given in Refs. [1,4,5,8,11,13,20–30]. In brief, the sample beam of a double-beam monochromator passes through the optical windows on the top of the cell and its intensity is compared with that of the other, reference, beam while the sample (at the bottom of the cell) was maintained at a series of temperature lower than that of the optical windows. The optical absorbance was measured between 190 and 800 nm and the partial pressure of Se<sub>2</sub> was determined from the absorbance of the Se<sub>2</sub> vibronic peaks at 340.5, 350.8, 361.3, and 379.2 nm

using the Beer's law constants established in the calibration runs of pure Se [1]. The partial pressures of Zn were calculated using the Gibbs energy of formation [1]

$$RT \ln(P_{\text{Zn}} P_{\text{Se}_2}^{1/2}) = -361\,807 + 191.485T \quad (\text{J/mole}). \quad (1)$$

### 2.3. Crystal growth experiments

To verify the effectiveness of the heat treatment procedures on the mass transport rate, crystal growth experiments using source materials provided by another vendor were performed. Two unseeded growth experiments were performed and the starting material was 69 purity ZnSe supplied by Furukawa Co. Ltd. Two conical shaped ampoules were cleaned and outgassed at 1150 °C for 16 h. One ampoule was loaded with 12 g of ZnSe in chunks (~0.35 g per chunk) and the sample was baked at 280 °C for 13 min under vacuum to remove residual moisture before sealing. The other growth ampoule was loaded with 16 g of ground ZnSe and heat-treated first by annealing under 0.5 atm H<sub>2</sub> at 1015 °C for 30 min, followed by baking at 1045 °C for 20 min under dynamic vacuum before sealing. For the PVT growth experiments a horizontal three-zone translational furnace was used [32–35]. The growth conditions were identical for both experiments. The source was held at

1140 °C and the furnace translation rate was 4.9 mm/day.

## 3. Results and discussion

### 3.1. Residual gas pressure and compositions

The residual gas pressure and composition (at room temperature) for each ampoule and that of a reference, unloaded, ampoule processed under similar conditions are given in Table 2. The residual gas pressures can be categorized into two groups. The pressures for the first group (ampoules ZST-6, 7, 9, 10 and ZSTO-3) range from 1.1 to  $4.1 \times 10^{-3}$  atm. The source materials for these ampoules were either directly from the vendor (ZST-9) or from batches of ZnSe that were preprocessed without (ZST-7, 10) or with H<sub>2</sub> annealing (ZST-6, ZSTO-3) followed by baking and distillation under vacuum. The ground, preprocessed materials were sealed without (ZST-6, 7 and ZSTO-3) or with a prior baking under vacuum (ZST-9 and 10). The residual gas pressures for the second group (ZST-13 and -15) were up to 15 times lower than that of the first group. In the ampoule ZST-13, eight unground chunks of the original material from Eagle Picher were loaded directly and the residual gas pressure was close to that of the empty reference ampoule. As for the ZST-15 ampoule the as-supplied chunks were ground and then treated by H<sub>2</sub> annealing as

Table 2  
Residual gas pressures and compositions in the processed ZnSe ampoules

Run #	Pressure ( $10^{-3}$ atm)			Composition (vol%)			
	Total	H <sub>2</sub> + H <sub>2</sub> O	H <sub>2</sub> O + CO + 2CO <sub>2</sub>	H <sub>2</sub> O	CO <sub>2</sub>	CO	H <sub>2</sub>
ZST-6	4.13	0.33	5.0	< 1	30	62	8
ZST-7	1.09	0.23	1.3	< 1	43	35	21
ZST-9	1.66	0.17	2.2	< 1	42	48	10
ZST-10	1.95	0.16	2.3	< 1	28	64	8
ZSTO-3	4.96	0.06	4.8	< 2	< 1	96	< 2
Empty <sup>a</sup>	0.23	0.10	0.23	40	< 1	60	< 1
ZST-13	0.32	-	0.5	< 1	53	47	< 1
ZST-15	0.76	0.46	0.4	< 1	13	25	61

<sup>a</sup>Ref. [19].

well as baking under vacuum prior to sealing. The residual gas pressure in the ampoule was about three times higher than that in the empty ampoule, but most of the gas consisted of hydrogen. Apparently, the hydrogen was trapped in the material during the hydrogen treatment and was not removed completely during the subsequent bake-out process. Except for this case (ZST-15), the residual gas consists mainly of CO, CO<sub>2</sub> and small quantities of H<sub>2</sub> which are comparable to that of the empty ampoule. The original hydrogen pressure in the ampoule must have been higher than that found in the H<sub>2</sub>-annealed ampoules since at elevated temperature the gas can diffuse through fused silica at considerable rates [36]. A moderate amount of H<sub>2</sub> in a PVT system has a relatively small effect on mass flux due to the high diffusivity of H<sub>2</sub> in the vapor and its relatively fast diffusion through the silica ampoule wall. The major factor in limiting the diffusive rates of the transport species in our system is the presence of the carbon oxides. The high content of oxides in the ampoules loaded with ZnSe is apparently due to the presence of solid oxides and/or graphite in the original source materials. The total amount of oxygen in the first group is about one order of magnitude higher than that in the empty ampoule (Table 2). The oxygen amount is significantly reduced in the second group where the source materials either had a limited surface area or were hydrogen treated prior to sealing. Evidently, oxidation of the source surface from exposure to air plays a major role in contributing to the amount of residual gas in the ZnSe ampoules annealed at elevated temperatures. Even a short,

about 1 min, exposure to air (ZSTO-3) may lead to some oxidation of the material. Removal of most of the oxides can be achieved by H<sub>2</sub> annealing without any subsequent exposure of the material to air.

### 3.2. Partial pressure measurements

The measured partial pressure of Se<sub>2</sub>,  $P_{\text{Se}_2}$ , for the optical cells ZnSe(O)-1, -2, -3 and -4 are plotted against  $1000/T$  (K) in Fig. 2 between 1035 and 1145 °C. The pressure ratio,  $\alpha \equiv P_{\text{Zn}}/P_{\text{Se}_2}$ , at the highest experimental temperature for each cell was calculated and labelled as given in Table 3. The

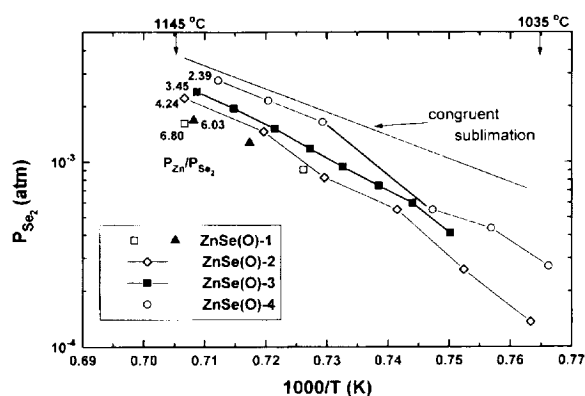


Fig. 2. The measured partial pressures of Se<sub>2</sub>,  $P_{\text{Se}_2}$ , for the optical cells ZnSe(O)-1, -2, -3 and -4, in equilibrium with ZnSe solid at different temperatures. The pressure ratio,  $\alpha$ , at the highest experimental temperature of each cell was labelled. The calculated  $P_{\text{Se}_2}$  for the congruent sublimation condition is also given.

Table 3

Sample heat treatment procedures for the partial pressure measurements. Source sample: ground Eagle-Picher high-purity grade ZnSe

Optical cell	Sample weight (g)	Hydrogen treatment	Vacuum treatment	Sample loss (g)
ZnSe(O)-1	6.78	None	Baked at 600 °C for 10 min	< 0.1
ZnSe(O)-2	12.28	0.56 atm at 1000 °C for 30 min	Baked at 1000 °C for 12 min	0.64
ZnSe(O)-3	11.64 <sup>a</sup>	0.56 atm at 1000 °C for 30 min	Baked at 1035 °C for 20 min	1.71
ZnSe(O)-4	12.11	0.53 atm at 1000 °C for 30 min	Baked at 1050 °C for 43 min	5.41

<sup>a</sup>Sample recovered from ZnSe(O)-2.

$P_{\text{Se}_2}$  for the condition of congruent sublimation was also calculated using Eq. (1). The measured partial pressure in the ZnSe(O)-1 cell, which was heat-treated by baking at 600°C under vacuum for

10 min to sublime the moisture and other volatile impurities in the ground sample, shows that the typical stoichiometry for the Eagle-Picher starting ZnSe material was moderately Zn-rich; with the

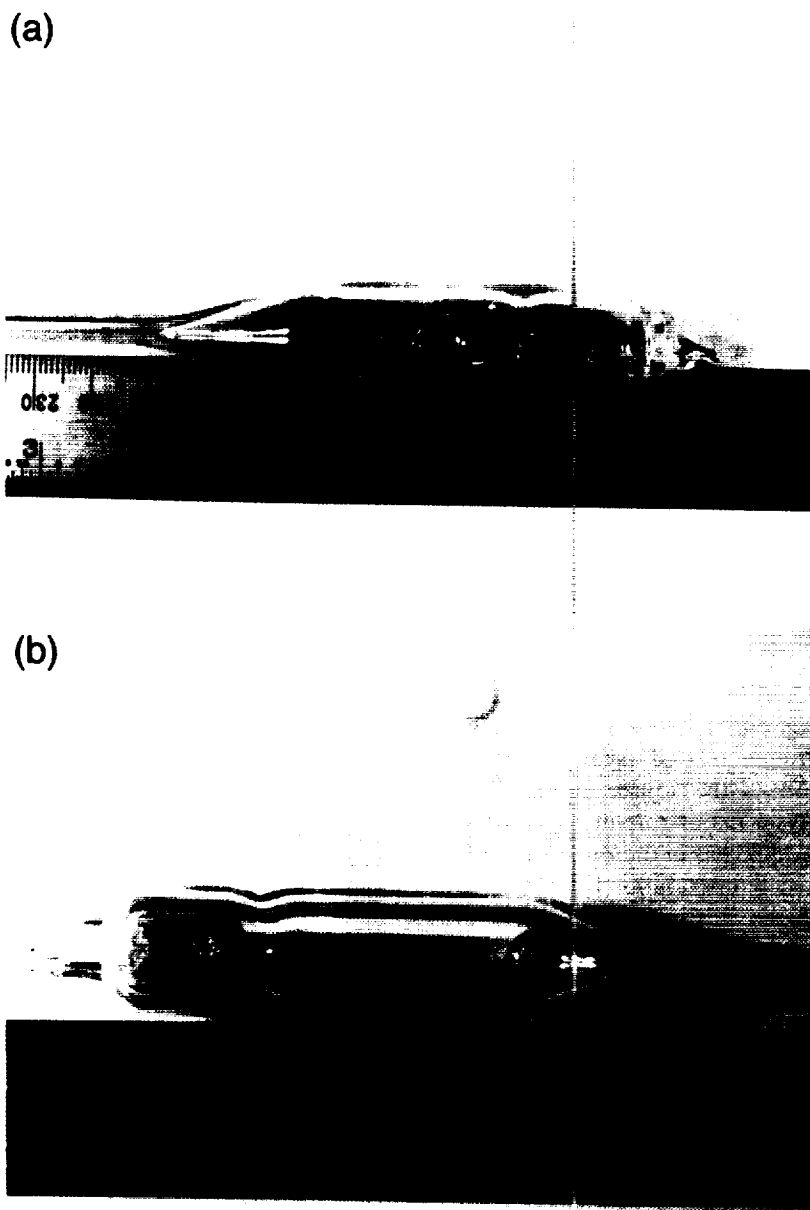


Fig. 3. The ampoules after the crystal growth process. (a) Chunk source material, baked at 280 °C under dynamic vacuum for 13 min. (b) Powdered source, annealed under  $\text{H}_2$  atmosphere at 1015 °C for 30 min then baked at 1045 °C for 20 min.

pressure ratio,  $\alpha = 6.0\text{--}6.8$  at  $1145^\circ\text{C}$ . A heat treatment by baking at  $1000^\circ\text{C}$  for 12 min improved this ratio to 4.24 as measured on the ZnSe(O)-2 cell. Another baking at  $1035^\circ\text{C}$  for 20 min on the sample retrieved from ZnSe(O)-2 cell further improved the stoichiometry to  $\alpha = 3.45$  at  $1145^\circ\text{C}$  as indicated from the results of ZnSe(O)-3. With a treatment of baking under vacuum at  $1050^\circ\text{C}$  for 43 min on the ground ZnSe sample, as shown by ZnSe(O)-4, the stoichiometry reached a value corresponding to  $\alpha = 2.39$ . The error associated with the measured  $P_{\text{Se}_2}$  is estimated to be 15%. The error for the Gibbs energy of formation given in Eq. (1) was estimated to be 2.5% [1]. The combined estimated error in  $\alpha$  is about 29% and the measured value of 2.39 is within the estimated uncertainty range for the congruent sublimation condition. For ZnSe(O)-2 and -3 the sample loss during the heat treatment of baking under dynamic vacuum was reasonable; 5% for ZnSe(O)-2 and 15% for ZnSe(O)-3. The loss of 45% of the starting material for ZnSe(O)-4 during the heat treatment was considered to be high.

### 3.3. Crystal growth

From the results of the previous sections, to maximize the mass flux in the PVT process, a reduction in the amount of both residual as well as the excess constituent species in the ampoule is necessary. The following procedure was considered to be optimum for the heat treatment of ZnSe starting materials and was adopted for our crystal growth experiments: 0.5 atm  $\text{H}_2$  over pressure annealing at  $1000^\circ\text{C}$  for at least 20 min followed by baking under dynamic vacuum at  $1045^\circ\text{C}$  for 20 min. Fig. 3 shows two growth ampoules after 6 days of the growth process. The first ampoule, which was loaded with chunk starting material, as shown in Fig. 3a, had a very limited transport rate. Only specks and spots of ZnSe deposited on the cooler conical part of the ampoule and the chunks of the source material were essentially unaffected. The chunky source material in the ampoule has a limited surface area and, thus, should result in a low amount of residual gas. However, the large grains of the source and the low heat treatment temperature apparently did not allow for a proper adjustment of the composition towards that of the

congruent sublimation condition. Fig. 3b shows that in the second ampoule, which was heat-treated using the optimized procedure, a 2.8 cm long ZnSe crystal has been grown in the conical part of the ampoule with a convex crystal–vapor interface and a well-defined source surface.

## 4. Conclusions

We have shown that both the residual gas pressure and the partial pressures of the transport species in the ZnSe PVT system depend strongly on the heat treatment procedures of the starting materials. When exposed to air the ZnSe starting materials oxidize but the oxides can be removed by annealing the material under  $\text{H}_2$  atmosphere. The adjustment of the source composition towards that of congruent sublimation can be accomplished by baking the material at elevated temperatures under dynamic vacuum. Using the optimized heat treatment procedures on the source materials, good mass transport/growth rate can be achieved with limited loss of the source material during the heat treatment.

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