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Nonstoichiometry and luminescent properties of ZnSe crystals grown from the melt at high pressures



CRYSTAL GROWTH

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ABSTRACT

50 mm diameter ZnSe crystals have been grown from the melt by a vertical Bridgman technique at 100 atm argon pressure in a graphite crucible. 3D impurities concentration and nonstoichiometry mappings of the grown crystals have been defined by ICP-MS and a direct physic-chemical method, correspondingly. Photoluminescence mapping of the analyzed crystal has been done. It was found out that along the crystal height the nonstoichiometry changed from Se excess over stoichiometrical composition in the cone (bottom) part to Zn excess in the tail (upper) part passing through the stoichiometrical composition in the cylindrical part of the crystal. Metal impurities concentrated in the upper part of the crystal. The gas-forming impurities (H, C, O, N, F) had stochastic distribution but Cl impurity concentrated in the crystal peripheral part (near the crucible walls). It was found out that the as-grown crystal had a single wide PL peal with maximum of 583 nm. A proposal about complex structure luminescent center based on Cl dopant an overstoichiometric Se has been made.

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1. Introduction

ZnSe single crystals are of great interest as perspective materials due to their technological importance for optoelectronic applications such as blue-light semiconductor lasers, light-emitting diodes [1,2] and multi-energy X-ray sensors [3]. To date, growth methods from vapor have been applied to grow high-quality crystals. However, growth method from melt has attracted attention because it is more suitable to obtain large bulk crystals for relatively short growth duration.

A^{II}B^{VI} single crystals have a number of unique properties which significantly depend on nano-scale defect type and concentration. Native point defects generating as a result of deviation from stoichiometric composition influence on luminescence, conductivity, and other structure sensitive properties similar to dopants. Electrical and optical properties of ZnSe crystals are affected by deviations from stoichiometry [4] which can varied within the homogeneity limits of ZnSe (Fig. 1). But the reliable information about ZnSe nonstoichiometry above 1300 K is missing. This information is very important to adjust the

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http://dx.doi.org/10.1016/j.jcrysgro.2016.04.026 0022-0248/© 2016 Elsevier B.V. All rights reserved. crystal growth process and it could be obtained from growth experiments.

The goal of the present research was to determine the correlation between nonstoichiometry, dopant defects and luminescent properties of ZnSe crystals grown by highly productive vertical Bridgman technique under inert gas high pressure.

2. Experiment techniques

ZnSe crystals were grown in the Bridgman configuration from "stoichiometric" melt in a graphite crucible under high static argon pressure 100 atm using the growth setup presented in Fig. 2 (left). The axial thermal gradient was 60 K/cm in the crucible cone part and 20 K/cm in the crucible upper cylindrical part. The average crystallization rate varied from 3 to 2 mm/h when grown conical and cylindrical parts of the crystal. The crystal was cooling with 100 K/h rate.

The HP-ZnSe as-grown crystals had several blocks. Some of them had a size about 1/3 crystal diameter and 2/3 crystal length. The blocks' dislocation density was $(1-5) \times 10^5$ cm⁻² with FWHM 0.1–0.3°. The HP-grown crystals were cut into $18.82 \times 2.30 \times 0.60$ mm elements which were assembled in a scintillating linear matrix. The block boundaries as well as single



Fig. 1. ZnSe homogeneity region with the proposed 3C-2H polymorphous transformation scheme [5]: the blue line is liquidus; the dash lines are solidus' which limit the homogeneity: 1 - [5], 2 - [7], 3 - calculated from free carrier concentrations [8], 4 - [9]. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)



Fig. 2. The large-grained crystalline ZnSe ingot (right) grown form «stoichiometrical» melt under high static Ar pressure 100 atm at 2–3 mm/h growth rate and 100 K/h cooling rate in the growth setup (left): 1-water chilled cover; 2-high pressure stainless steel camera; 3-graphite heater; 4-thermal insulation; 5-ZnSe melt; 6-graphite or glass carbon crucible; 7-ZnSe crystal; 8-support; 9-current leads; 10-translational rod; 11-pressure-vacuum system inlet pipe.

microvoids did not diminish the scintillating properties. The basic requirement is homogeneity of properties along a crystalline element. The difference between elements could be easily corrected by an electronic device processing.

ZnSe samples shaped as plates were cut from the grown ingot along the growth direction (Fig. 2 right). Then the every plate was cut in several pieces for crystal mappings of impurities, nonstoichiometry and luminescence properties. The pieces were etched for 2 min in a freshly prepared solution of Br₂ in CH₃OH (5 vol%) at 285–298 K. After the etching ZnSe samples were annealed at about 573 K for 30 min in a vacuum $< 10^{-3}$ Pa to remove coating excess component from samples' surfaces.



Fig. 3. Impurity concentration in the initial charge and the central part of HP-ZnSe crystal ingot measured by ICP-MS (a) and SIMS (b).

The preparation purity was measured by ICP-MS in KED mode (NexION 300D, Perkin Elmer Inc.) and SIMS (MiniSIMS, Millbrook Ltd.) analyses.

The CVD-ZnSe powder (the initial charge) used in this experiment was as pure as 99.9996 wt% according to ICP-MS analysis and 99.9991 wt% according to SIMS analysis (Fig. 3).

As-grown crystal was less pure (99.9992 wt%) comparing to the charge material (99.9996 wt%) due to the ICP-MS determination. The similar result was obtained by SIMS analysis taking into consideration gas-forming impurities (C, O, N, Cl, F). According to ICP-MS Al, Cu, Te were the main impurities in the HP-grown crystal. Cu impurity inherited from the initial charge. Origins of Al and Te impurities will be described in the Section 3.

The nonstoichiometric compositions of samples were determined using the "extraction" (direct physic-chemical) method [7,10]. We used the extraction conditions which provided a residual nonstoichiometric composition of the sample to be one order lower in comparison with the determined value of nonstoichiometry – (relative quantity of extracted excess component). In this case we could assert that at $T_{\text{extraction}} = 750 \text{ K}$ and P_{Se2} (or P_{Zn}) corresponding to congruent sublimation conditions the residual nonstoichiometry was estimated to be $\sim 1 \times 10^{-7}$ mol excess Se (or Zn) per mole ZnSe (1×10^{-5} mol%). This is the limit of nonstoichiometry determination in ZnSe preparations.

Photoluminescent (PL) spectra were measured at 300 K by a spectrofluorimeter Fluorolog – 3 FL3-22 (Horiba Jobin Yvon) at continuous excitation λ_{ext} =370 nm generated by Xe lamp and filtered by a double grating monochromator. The tested samples were 7 × 5 × 2 mm³ polished pieces of ZnSe crystals fixed on a carbon film. The PL spectra were processed by OriginPro 8 Software (OriginLab Corp.).

3. Results and discussion

3D mapping of the impurities in the HP-grown ZnSe crystal (Fig. 4) showed that light molecular weight impurities (presented by Al) were concentrated in the upper part of the ingot. Copper



Fig. 4. Distribution of Al, Cu, and Te inside the ZnSe grown form the melt at P_{Ar} = 100 atm.

being a representative of middle molecular weight impurities demonstrated nearly instant distribution with a slight tendency to concentrate in the bottom part of the ingot. Tellurium impurity representing high molecular weight impurities (towards ZnSe) had a clear tendency: Te concentration grew in 5 times from the bottom to the top of the ingot. In the case of Al and Te impurities the equilibrium distribution coefficient is k < 1 while for Cu impurity k > 1 [11]. But the exact values of individual as well as multiple distribution coefficients for the range of impurities' concentrations under investigation are missing in the literature.

For X-ray scintillators we need high pure ZnSe crystals doped by Te. So, it was interesting to find out the influence of Te doping on distributions of nonstoichiometry and residual impurities' concentrations inside the ZnSe crystal volume. We analyzed the undoped ZnSe crystal grown in the crucible which had been previously used for the growth of ZnSe:Te crystal. The initial charge, the crucible, and the crystal growth parameters were the same in both processes. The results of analysis of ZnSe:Te crystal will be published in the nearest future.

In the preparation of the charge it is necessary to reduce to fragments large pieces of CVD-ZnSe. Outwardly simple task in practice is much more complex, because ZnSe material is firm enough. In order not to contaminate the charge by metal impurities during the fragmentation we used the sapphire cylinder weighing about 1 kg as a hammer. Sapphire is a hard and brittle material with a high density. However, sometimes small pieces could cleave from sapphire edges and go into the charge. If these sapphire debris had contacted with the graphite crucible walls at melt overheating before the crystallization, then, apparently, there might occur partial reduction of sapphire (Al_2O_3) and Al contamination of the melt. Al impurity did not significantly influence on the scintillating properties of the elements.

The gas-forming impurities (H, C, O, N, F, Cl) had stochastic distribution (see green values in Fig. 6). For the most parts of the crystal the H, C, O, N, F concentrations were less than 3×10^{-4} wt% and these impurities did not make worse scintillating properties.

Cl impurity concentrated in the crystal peripheral part (near the crucible walls). It was found out that Cl concentration was responsible for PL intensity of the grown crystal.

Analysis of nonstoichiometry distribution (Fig. 5) showed that the most part of the crystal had Se excess over stoichiometry. We observed several accidental releases with Zn excess but, in general, Zn excess was observed in the upper part of the crystal. A small part of the crystal cylinder had a stoichiometrical or close to stoichiometry composition. It should be noted that the maximal determined concentrations of both Se and Zn excess in the crystal were 2.6×10^{-5} and 4.6×10^{-6} mol excess Se(Zn)/mole ZnSe, correspondingly. Mind the specific feature of the «extraction» technique when the determined excess concentration does not depend on the defect state of native point defects generated by an excess component dissolving in a crystal lattice we can assume that the obtained values characterized limits of components solubility in ZnSe at temperatures close to the maximum melting temperature of 1799 K. It means that the proposed scheme of ZnSe homogeneity range (Fig. 1) should become narrower up to 1-2 orders of composition at high temperatures.

Analysis of photoluminescent properties of different crystal parts (Fig. 6) showed that all pieces had the same luminescent band with maximum of 583 nm (2.12 eV) attributed to Se excess over stoichiometry in ZnSe [6]. But we failed to establish the correlation between PL intensity and nonstoichiometry as well as total donor or acceptor concentrations in the analyzed samples. The only correlation which we succeeded to find out was a clear dependence of the PL intensity vs Cl concentration (Fig. 7). But according to the literature data [12,13] Cl, F-related centers produced a PL band with maximum in the 630–666 nm range (1.97–1.88 eV).



Fig. 5. Nonstoichiometry distribution inside ZnSe crystal determined by the «extraction» technique [9].

Chalcogen nonstoichiometry in A^{II}B^{VI} compounds associated with generation of vacancies in metal sublattice. In the case of ZnSe it could be complex associations of vacancies like $(V_{Zn})_{Zn}^{\times}$ [9]. An addition of equimolar concentration of Cl dopant in ZnSe which fitted into Se node could generate a similar associated defect with corresponding energy level of Se excess component according to the reaction

 $m\mathrm{Cl}_{2}^{\nu} + n \mathrm{Se}_{2}^{\nu} \rightarrow \mathrm{Se}_{\mathrm{se}}^{\times} + (V_{\mathrm{Zn}})_{2(n+m)}^{\times} + 2\mathrm{Cl}_{\mathrm{se}}^{\bullet} + 2e'$

This assumption could explain the dependence of the PL intensity *vs* Cl dopant concentration in a presence of Se excess in ZnSe crystal.

4. Conclusions

A detail analysis of impurity and nonstoichiometry distribution in ZnSe crystal grown from the melt by a vertical Bridgman technique at 100 atm argon pressure in a graphite crucible showed that at 2–3 mm/h growth rate we can obtain ZnSe crystals with a sufficient purity level better 99.999 wt%. The main impurity concentrations depend on the initial charge purity.



Fig. 6. PL spectra of ZnSe samples cut from different parts of the HP-ZnSe single crystal at 300 K (λ_{ext} =370 nm) with indication of impurities concentration (wt%) of metal detected by ICP-MS, gas-forming impurities determined by SIMS and nonstoichiometry (mol%) measured by the «extraction» technique [9]. Allocation of a PL spectrum corresponds with the colored pieces in Fig. 4. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)



Fig. 7. Photoluminescence intensity vs Cl concentration in ZnSe crystals.

As-grown crystal photoluminescence basically depends on a dopant level. The active luminescent centers with energy level 2.12 eV are complex defects based on V_{Zn} generated by both Se excess over stoichiometry and Cl dopant.

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