



Obtaining a ZnSe furnace charge from aqueous solution

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The influence of synthesis conditions on the process of obtaining a charge of zinc selenide from alkaline solutions via the interaction of zinc with selenium and zinc oxide with selenium in the presence of a reducing agent is reported. It is shown that the interaction of zinc and selenium in alkaline solution and the ZnSe output increases with increasing concentration of alkali and synthesis time and reaches a maximum of about 85 wt% in 15 molar NaOH after 2 hours, resulting in the formation of 0.1–0.3 μm spherical particles. The use of hydrazine hydrate can increase ZnSe output up to 97 wt %. The powder is formed in spherical agglomerates with an average size of 0.5 μm . The main impurity phases are oxide, carbonate and zinc hydroxide, which are removed during vacuum heat treatment at 800–900 °C for 1 hour.

Keywords: optical components, particles, powder for growing crystals, sensors, solar energy converters

1. Introduction

Compounds of the A^{II}B^{VI} group are widely used as UV detectors, gamma and X-ray sensors (ZnSe, CdTe), solar energy converters (CdS/CdTe), infrared sensors (CdSe/ZnS), and optical components (HgTe, ZnSe, CdTe).^{1–6} The increased interest in this class of compounds can be

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¹ P. Michler, M. Vehse, J. Gutowski, M. Behringer, D. Hommel, M.F. Pereira and K. Henneberger. Influence of Coulomb correlations on gain and stimulated emission in (Zn,Cd)Se/Zn(S,Se)/(Zn,Mg)(S,Se) quantum-well lasers. *Phys. Rev. B* **58** (1998) 2055–2063.

explained by the combination of many interesting physical properties, which allows the use of the crystals in a variety of devices for applications in optics, acoustics, electronics, nuclear physics etc. These compounds tend to have high mutual solubility and, therefore, based on solid solutions, one is able to readily synthesize new materials with specific band gaps, spectral ranges of transmission and other essential characteristics.

Among those currently in high demand are ZnSe-based materials, mainly used in multienergy detectors, X-ray scanners, computer tomographs and solar cells.^{6,7} For the initial charge synthesis of these materials, as a rule thermal methods, based on zinc and selenium interaction in the solid^{8,9} or in the gas¹⁰ phases, have been developed. In this case, special equipment for the synthesis is required, since the reaction between zinc and selenium is strongly exothermic.

Note, however, that zinc selenide can be also obtained in aqueous solution. Thus, cubic ZnSe nanoparticles with a diameter of 10 nm produced in alkaline solution from zinc and selenium interacting at 80 °C have been reported.¹¹ Maintaining hydrothermal conditions at 180 °C for 24 hours produces zinc selenide particles with a size of 70–100 nm.¹² Conducting the synthesis at 150 °C for 2 hours in 3.5 molar sodium hydroxide solution leads to the formation of particles of different sizes, depending on the Zn/Se molar ratio: for Zn/Se equal to 1, 1.5 and 2–2.5 particles of about 120 nm, large particles of a few μm and shaped particles of 5–7 μm in diameter are formed respectively.¹³

The reaction can be carried out using hydrazine hydrate as a reducing agent. During synthesis at 70 °C for 8 hours, ZnSe with a hexagonal structure is formed, but $\text{ZnSeO}_4 \cdot \text{H}_2\text{O}$

² M.F. Pereira and K. Henneberger. Microscopic theory for the influence of Coulomb correlations in the light-emission properties of semiconductor quantum wells. *Phys. Rev. B* **58** (1998) 2064–2076.

³ L. Jin, W.C.H. Choy, Y.P. Leung, T.I. Yuk, H.C. Ong and J.B. Wang. Synthesis and analysis of abnormal wurtzite ZnSe nanowheels. *J. Appl. Phys.* **102** (2007) 044302.

⁴ T.Y. Zhai, H.Z. Zhong, Z.J. Gu, A.D. Peng, H.B. Fu, Y. Ma, Y.F. Li and J.N. Uao. Manipulation of the morphology of ZnSe sub-micron structures using CdSe nanocrystals as the seeds. *J. Phys. Chem. C* **111** (2007) 2980–2986.

⁵ S.Y. Liu, W.C.H. Choy, L. Jin, Y.P. Leung, G.P. Zheng, J.B. Wang and A.K. Soh. Triple-crystal zinc selenide nanobelts. *J. Phys. Chem. C* **111** (2007) 9055–9059.

⁶ D.R. Vij (Ed.), *Luminescence of Solids*, pp. 95, 221. Plenum Press (1998).

⁷ J. Yang, C. Xue, S.H. Yu, J.H. Zeng and Y.T. Qian. General synthesis of semiconductor chalcogenide nanorods by using the monodentate ligand n-butylamine as a shape controller. *Angew. Chem.* **114** (2002) 4891–4894.

⁸ C.-L. Cheng and Y.-F. Chen. Low temperature synthesis of ZnSe nanowires by self-catalytic liquid–solid growth. *Mater. Chem. Phys.* **115** (2009) 158–160.

⁹ A. Colli, S. Hofmann, A.C. Ferrari and F. Martelli. Selective growth of ZnSe and ZnCdSe nanowires by molecular beam epitaxy. *Nanotechnology* **16** (2006) 139–142.

¹⁰ X.T. Zhang, Z. Liu, K.M. Ip, Y.P. Leung, Q. Li and S.K. Hark. Luminescence of ZnSe nanowires grown by metalorganic vapor phase deposition under different pressures. *J. Appl. Phys.* **95** (2004) 5752–5755.

¹¹ C. Wang, W.X. Zhang, X.F. Qian, X.M. Zhang, Y. Xie and Y.T. Qian. Aqueous approach to ZnSe and CdSe semiconductor nanocrystals. *Mater. Chem. Phys.* **60** (1999) 99–102.

¹² Q. Peng, Y. Dong, Z. Deng, X. Sun and Y. Li. Low-temperature elemental direct reaction route to II–VI semiconductor nanocrystalline ZnSe and CdSe. *Inorg. Chem.* **40** (2001) 3840–3841.

¹³ H. Gong, H. Huang, M. Wang and K. Liu. Characterization and growth mechanism of ZnSe microspheres prepared by hydrothermal synthesis. *Ceramics Intl* **33** (2007) 1381–1384.

impurities appear.¹⁴ Synthesis at 140 °C for 24 hours forms cubic ZnSe spherical particles with 200–300 nm diameter.¹⁵ As a precursor for the selenium, selenites^{16, 17} as well as sodium selenosulphite^{18, 19} can be used.

The present research was mainly focused on forming the nanoparticles; the quantitative yield of zinc selenide and impurity composition were not evaluated. Results for the influence of the conditions for zinc selenide deposition from alkaline solution on the morphological characteristics of the particles were used to obtain the charge for single crystals and are reported and discussed in this paper.

2. Experimental Procedure

2.1. Materials

Zn (97%), Se (99.9999%), ZnO (99.9999%), NaOH (reagent grade) and hydrazine hydrate (reagent grade) were purchased from “Reakhim”. All chemicals were used as received, without additional purification.

2.2. Synthesis

2.2.1. The interaction of zinc and selenium in alkaline solution

The calculated charges of zinc and selenium were placed into a 100 mL flask with 50 mL of sodium hydroxide solution and, subsequently, the solution was refluxed for 2–12 hours. Alkali concentration varied in the range 3–15 molar. In all cases, zinc and selenium were added in stoichiometric ratio. After synthesis, the resulting precipitate was separated on a glass filter, washed with distilled water and dried at room temperature for 12 hours.

2.2.2. The interaction of zinc oxide with selenium in alkaline solution in the presence of hydrazine hydrate

The calculated amounts of zinc oxide, selenium, and hydrazine hydrate were placed into a 100 mL flask with 50 mL of sodium hydroxide solution and the solution was refluxed for 2–6 hours. The alkali concentration varied from 3 to 6 molar. In all cases, zinc and selenium were added in stoichiometric ratio and hydrazine hydrate in twofold excess. The precipitate was separated on a glass filter, washed with distilled water and dried at room temperature for 12 hours.

¹⁴ P. Kumar and K. Singh. Wurtzite ZnSe quantum dots: synthesis, characterization and PL properties. *J. Optoelectronic Biomed. Mater.* **1** (2009) 59 – 69.

¹⁵ C. Jiang, W. Zhang, G. Zou, W. Yu and Y. Qian. Synthesis and characterization of ZnSe hollow nanospheres via a hydrothermal route. *Nanotechnology* **16** (2005) 551–554.

¹⁶ Q. Peng, Y. Dong and Y. Li. ZnSe semiconductor hollow microspheres. *Angew. Chem. Intl Edn* **42** (2003) 3027–3030.

¹⁷ Y. Jiao, D. Yu, Z. Wang, K. Tang and X. Sun. Synthesis, nonlinear optical properties and photoluminescence of ZnSe quantum dots in stable solutions. *Mater. Lett.* **61** (2007) 1541–1543.

¹⁸ S. Xiong, S. Huang, A. Tang and F. Teng. Synthesis and luminescence properties of water-dispersible ZnSe nanocrystals. *Mater. Lett.* **61** (2007) 5091–5094.

¹⁹ X. Wang, X. Chen, H. Zheng, J. Jin and Z. Zhang. Template-free solution approach to synthesize ZnSe hollow microspheres. *Appl. Phys. A* **80** (2005) 511–513.

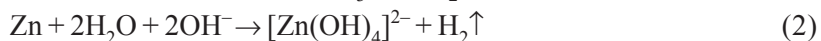
2.3. Characterization

The IR spectra were obtained with KBr tablets using a SPECTRUM ONE (Perkin–Elmer). Fourier transform infrared (FTIR) spectrometer. X-ray diffraction (XRD) patterns of the sample were measured on a Siemens D500 diffractometer using monochromatic Cu K $_{\alpha}$ radiation ($\lambda = 1.5418 \text{ \AA}$) at 40 kV and 100 mA. The scanning range was $10 < 2\theta < 90^{\circ}$ and the exposure 10 s per point. The X-ray rocking curve was obtained with a double crystal X-ray spectrometer with a Si monochromator adjusted to the (400) reflexion of Cu K $_{\alpha}$ radiation. The morphology and microstructure of as-prepared samples were analysed using a JSM–6390LV scanning electron microscope (SEM). Chemical analysis employed atomic emission spectrometry with an inductively coupled plasma using a TRACE SCAN Advantage instrument (Thermo Jarrell Ash, USA).

3. Results and discussion

3.1. The interaction of zinc and selenium in alkaline solution

In the preparation process of zinc selenide, investigation of the interaction of zinc and selenium in alkaline solution is focused on the effect of the synthesis conditions (concentration of alkali, reaction time) on the practical product output and the formation of oxygen-containing impurities. In the present, the alkali concentration in the solution varied from 3 to 15 molar and the synthesis duration from 2 to 12 hours. The interaction of the components takes place according to the following scheme:²⁰



Synthesis results are presented in Table 1. Regardless of the synthesis conditions, the formation of a powder with a reddish tint was observed. The alkali concentration had a significant effect on the formation of zinc selenide; i.e., higher concentrations of the alkali solution and synthesis times result in a greater product output, which reaches a maximum of 85% at an alkali concentration of 15 molar and does not change with further increase of the synthesis duration.

Low outputs were not acceptable for the charge (wasteful use of reagents); hence, samples with an output of at least 40 wt% were mainly considered. Regardless of the synthesis conditions, similar radiographs were obtained. According to the X-ray analysis results presented in Fig. 1, the nature of the synthesized powders is zinc selenide with the wurtzite structure.

Scanning electron micrographs of ZnSe powders are shown in Fig. 2. Regardless of the synthesis conditions, agglomerated spherical particles ranging in size from 0.1 to 0.3 μm are mainly formed. The changes in the concentration of alkali or synthesis duration had no significant effect on the primary particle size.

²⁰ B.B. Wang, X.Z. Xu. Study on effects of time and temperature on growth of nanocrystalline zinc selenide synthesized by hydrothermal method. *J. Crystal Growth* **311** (2009) 4759–4762.

Table 1. Results of the interaction of zinc and selenium in sodium hydroxide solution.

№	Concentration of NaOH / molar	Synthesis time / h	Output of ZnSe (wt%)
1	3	6	20
2	6	4	30
3	6	12	40
4	9	6	35
5	12	2	50
6	12	6	60
7	15	2	85

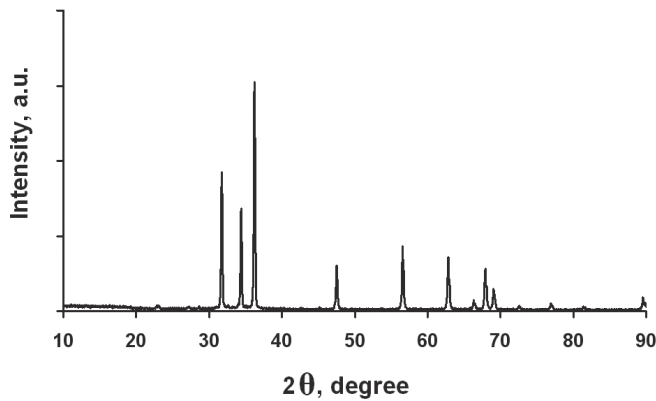


Figure 1. X-ray diffractogram of ZnSe powder synthesized from 6 molar NaOH solution for 12 hours.

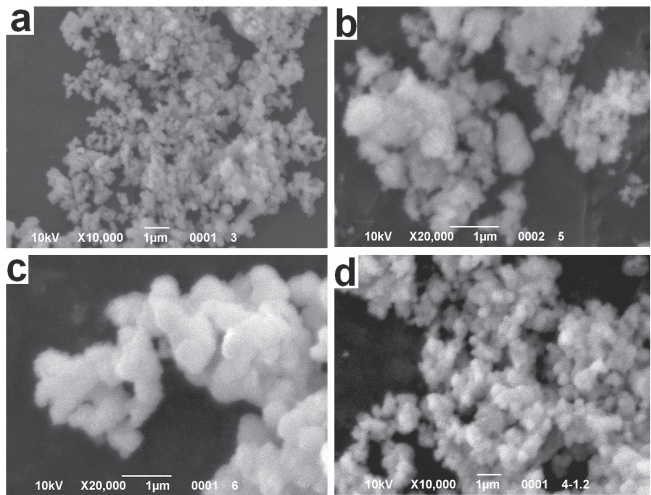


Figure 2. Micrographs of ZnSe powder particles synthesized with the indicated alkali concentrations in the solution and synthesis times: (a) 6 molar, 12 hours; (b) 9 molar, 6 hours; (c) 12 molar, 2 hours; (d) 15 molar, 2 hours.

Since one of the objectives of this work was the synthesis of zinc selenide suitable as a charge for crystal growth, the important point is the optimization of the impurity composition of the synthesized powders. Chemical analysis results are presented in Table 2. For comparison, a standard charge used for growing single crystals of zinc selenide is also shown in Table 2 (specimen №1). It is seen that the synthesized ZnSe (specimen №2) is characterized by a metal impurity content at the level of 10^{-4} – 10^{-5} wt%.

Table 2. Chemical composition of standard mixtures for synthesizing ZnSe powders as determined by atomic absorption spectrometry. See text for details of the specimens.

Specimen	Element (wt%)										
	Fe	Si	Mg	Ni	Sn	Pb	Cr	Al	Mo	Cu	Mn
№1	$1 \cdot 10^{-6}$	–	$2 \cdot 10^{-5}$	$5 \cdot 10^{-5}$	$1 \cdot 10^{-4}$	$4 \cdot 10^{-4}$	$1 \cdot 10^{-4}$	$1 \cdot 10^{-4}$	$5 \cdot 10^{-5}$	$2 \cdot 10^{-5}$	$2 \cdot 10^{-5}$
№2	$9 \cdot 10^{-5}$	$1 \cdot 10^{-3}$	$2 \cdot 10^{-4}$	$5 \cdot 10^{-5}$	$5 \cdot 10^{-5}$	$8 \cdot 10^{-4}$	$3 \cdot 10^{-5}$	$8 \cdot 10^{-5}$	$5 \cdot 10^{-5}$	$5 \cdot 10^{-5}$	$5 \cdot 10^{-5}$
№3	$5 \cdot 10^{-5}$	$1 \cdot 10^{-3}$	$2 \cdot 10^{-4}$	$2 \cdot 10^{-5}$	$2 \cdot 10^{-5}$	$8 \cdot 10^{-4}$	$1 \cdot 10^{-5}$	$2 \cdot 10^{-4}$	$5 \cdot 10^{-5}$	$5 \cdot 10^{-5}$	$3 \cdot 10^{-5}$

Infrared spectroscopy was used to investigate the effect of synthesis conditions on the formation of oxygen-containing impurities (Fig. 3). The IR spectrum of the powder, synthesized at 3 molar alkali for 6 hours, see Fig. 3(a), reveals absorption bands at 3410 and 1617 cm^{-1} , which are assigned to, respectively, the stretching and bending oscillation of water molecules. Furthermore, the observed absorption bands at 1150, 1050, 950 and 780 cm^{-1} are related to the SeO_3^{2-} ion oscillation²¹ and that at 550 cm^{-1} to the Zn–O oscillation²². For alkali concentrations up to 9 molar, the lack of absorption bands 950, 780 and 550 cm^{-1} and the weakening of the absorption bands at 1150 and 1050 cm^{-1} are indicated in the IR spectrum of Fig. 3(b), whilst the bands at 1546 and 1390 cm^{-1} may be attributed to changes in the carbonate ion.²³ A further increase in the alkali concentration in the solution leads to a weakening of the absorption bands, see Fig. 3(c). This effect (reducing the intensity of the absorption bands) can also be observed with increasing synthesis duration (not shown).

Note also that according to the IR spectroscopy data the synthesized ZnSe powders were contaminated by oxygen impurities and, therefore, vacuum annealing was used to clean them. For this purpose, the samples were placed in a quartz ampoule, which was evacuated at room temperature to a pressure of 10^{-2} Torr and, subsequently, heated in an annealing furnace to 800°C for 2 hours under constant evacuation and afterwards kept at this temperature for 1 hour. At the end of the annealing process, the pumping was stopped and the ampoule cooled to room temperature; all powders produced were yellow-orange in colour. As revealed from the IR spectrum (Fig. 3d), the absorption bands practically no longer exist, indicating removal of the impurities.

²¹ M. Tsuji. SeO_3^{2-} -selective properties of inorganic materials synthesized by the soft chemical process. *Solid State Ionics* **151** (2002) 385–392.

²² R.Y. Hong, J.H. Li, L.L. Chen, D.Q. Liu, H.Z. Li, Y. Zheng and J. Ding. Synthesis, surface modification and photocatalytic property of ZnO nanoparticles. *Powder Technol.* **189** (2009) 426–432.

²³ N. Kanari, D. Mishra, I. Gaballah and B. Dupré. Thermal decomposition of zinc carbonate hydroxide. *Thermochim. Acta* **410** (2004) 93–100.

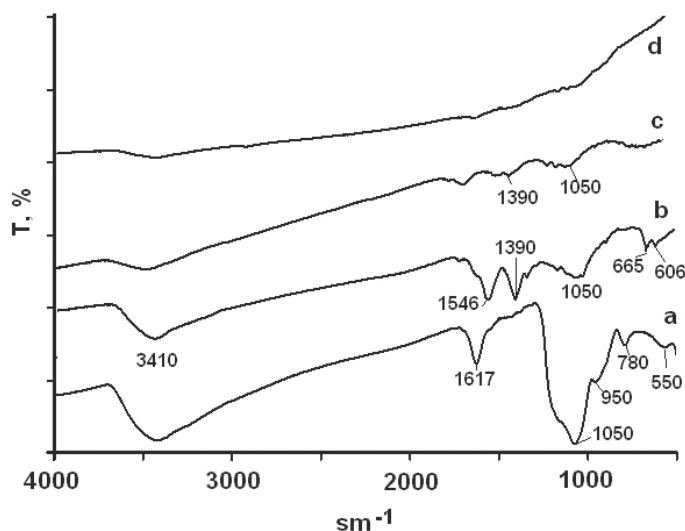
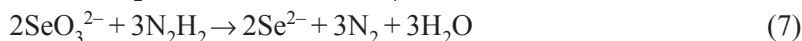
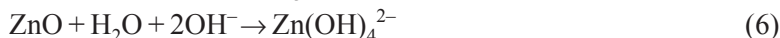


Figure 3. IR spectra of powders obtained by zinc and selenium interaction with the following alkali concentrations and durations of synthesis: (a) 3 molar, 6 hours; (b) 9 molar, 5 hours; (c) 15 molar, 2 hours; (d) 15 molar, 2 hours followed by annealing at 800 °C for 2 hours in a vacuum of 10^{-2} Torr.

Thus, the interaction of zinc and selenium in alkaline solutions is characterized by significant process duration and a maximum product output of 85%.

3.2. The interaction of zinc oxide with selenium in the presence of hydrazine hydrate

As in the previous case, in the process of synthesis of zinc selenide through the interaction of selenium with zinc oxide in alkaline solution in the presence of a reducing agent (hydrazine hydrate), attention is directed towards the influence of the synthesis conditions (concentration of alkali, deposition time) on practical product output and the formation of impurities, with the interaction of the components taking place according to:²⁴



Regardless of the synthesis conditions, a yellow powder with a reddish tint was obtained. It was found that variation of the alkali concentration from 3 to 6 molar had no significant effect on ZnSe output, which was 90–97 wt%, whilst the main factor affecting it was the duration of synthesis; i.e. the output increased with increasing duration reaching a maximum of 97 wt%. According to the X-ray diffraction, zinc selenide with the wurtzite structure was formed. Diffractograms of the powders produced in the presence of a reducing agent were identical with those of powders produced by the interaction of zinc with selenium in alkaline solution.

²⁴ X. Liu, J. Ma, P. Peng and W. Zheng. Ionic liquid-assisted complex-solvothermal synthesis of ZnSe hollow microspheres. *Mater. Sci. Engng B* **150** (2008) 89–94.

Micrographs of synthesized ZnS powder particles are shown in Fig. 4. For the 3 molar alkali solution, deposition of large spherical particles (with a size up to several μm) was observed. By increasing the NaOH concentration up to 4 molar, the size of the spherical particles was reduced to 0.5 μm , see Figs 4(b) and (c). A further increase of the alkali concentration up to 6 molar resulted in the formation of particles in the form of plates with dimensions up to 1 μm , see Fig. 4(d).

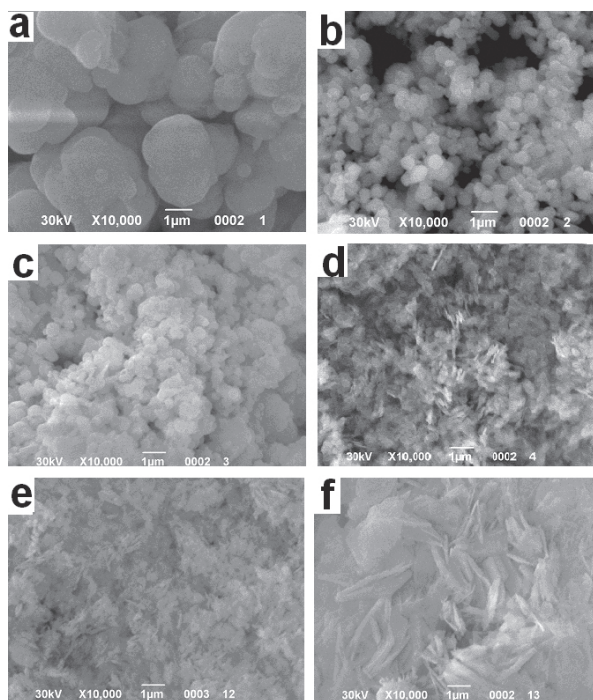


Figure 4. Micrographs of ZnSe powder particles obtained by precipitation with the following alkaline solutions in the presence of hydrazine hydrate and durations of precipitation: (a) 3 molar, 6 hours; (b) 4 molar, 2 hours; (c) 4 molar, 6 hours; (d) 6 molar, 4 hours; (e) 4 molar, 2 hours followed by vacuum annealing at 800 °C for 2 hours; (f) 6 molar, 4 hours followed by vacuum annealing at 800 °C for 2 hours.

According to the atomic emission spectrometry, synthesized ZnSe powders (specimen №3) are characterized by a metal impurity content at the level of 10^{-4} – 10^{-5} wt%.

The results of the infrared spectrometry are presented in Fig. 5. All the spectra reveal: weak absorption bands, among which the most intense are 3410 and 1624 cm^{-1} assigned to the stretching and bending oscillations of adsorbed water molecules; an absorption band at 1450 cm^{-1} and a broad absorption band at 950–1200 cm^{-1} with peaks at 1150 and 1050 cm^{-1} , which is probably connected with the SeO_3^{2-} ion oscillation,²¹ see Figs 5(a)–(c). After annealing in vacuum (10^{-2} Torr) at 800 °C for 2 hours, almost no absorption bands were observed in the IR spectrum, see Fig. 5(d), which indicates the removal of impurities.

Thus, the interaction of selenium with zinc oxide in alkaline solution in the presence of a reducing agent is characterized by a significantly shorter process duration as compared with the direct interaction of zinc with selenium and a maximum product output of 97%.

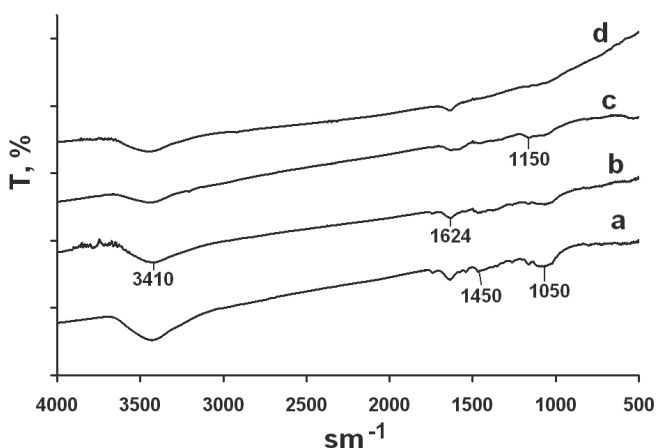


Figure 5. IR spectra of powders obtained by selenium and zinc oxide interaction in the presence of hydrazine hydrate with the following alkali concentrations and durations of synthesis: (a) 3 molar, 2 hours; (b) 4 molar, 2 hours; (c) 4 molar, 6 hours; (d) 4 molar, 6 hours followed by vacuum annealing at 800 °C for 2 hours.

3.3. ZnSe crystal growth

From the obtained ZnSe powder, ZnSe crystals were grown. The crystal growth was carried out by the Bridgman–Stockbarger standard method under pressurized inert gas and a load of 300 g of crystal mass;²⁵ orange crystals with a diameter of 30 mm and 30 mm height, consisting of large transparent single crystal blocks, were grown, see Fig. 6. The growth direction of the crystal coincides with the (331) crystallographic direction and the half-width of the rocking curves²⁶ obtained on the double crystal X-ray spectrometer was 34.5 arc s for the (331) reflexion.



Figure 6. Photograph of ZnSe crystals grown from the synthesized powder.

²⁵ V.K. Komar and V.M. Puzikov. Scintillation phosphors on the basis of A^{II}B^{VI} compounds: obtaining, properties and features of application. Kharkov: Institute for Single Crystals (2007) (in Russian).

²⁶ Refers to a method of rocking and rotating the sample used to determine the lattice constant along the crystallographic directions in a single crystal. In general this parameter is an indication of grown crystal perfection.

Thus, the synthesized zinc selenide powder is suitable for use as a charge for growing single crystals.

4. Summary and conclusions

From the results reported above pertaining to the effect of the synthesis conditions on the methods of obtaining a charge of zinc selenide from alkaline solutions by the direct interaction of zinc with selenium and the interaction of zinc oxide with selenium in the presence of a reducing agent, the following conclusions may be drawn:

(a) It was found that the interaction of zinc with selenium in alkaline solution results in an increasing output of ZnSe with increasing concentration of alkali and synthesis time. The output reaches a maximum of about 85 wt% in 15 molar NaOH for 2 hours. When using hydrazine, the ZnSe output is virtually independent of the concentration of alkali and the synthesis time.

(b) Regardless of the synthesis conditions, superspherical agglomerated powder objects, ranging in size from 0.1 to 0.3 μm , were formed. In the case of using hydrazine in 3 molar NaOH solution, the formation of large agglomerated superspheres with sizes up to a few μm was observed; an increase in the alkali concentration resulted in a diminution of the size of the superspheres to 0.5 μm .

(c) Regardless of the method of synthesis, oxide, carbonate and zinc hydroxide impurity phases were developed; they are readily removed during vacuum heat treatment.

(d) The optimal conditions for the synthesis of ZnSe powder suitable for use in crystal growth were 5 molar NaOH solution and stoichiometric amounts of ZnO and Se in the presence of a twofold excess of N_2H_4 for 4 hours followed by vacuum heat treatment at 800–900 °C for 1 hour.