Synthesis of ZnSe charge and growing methods of ZnSe single crystals

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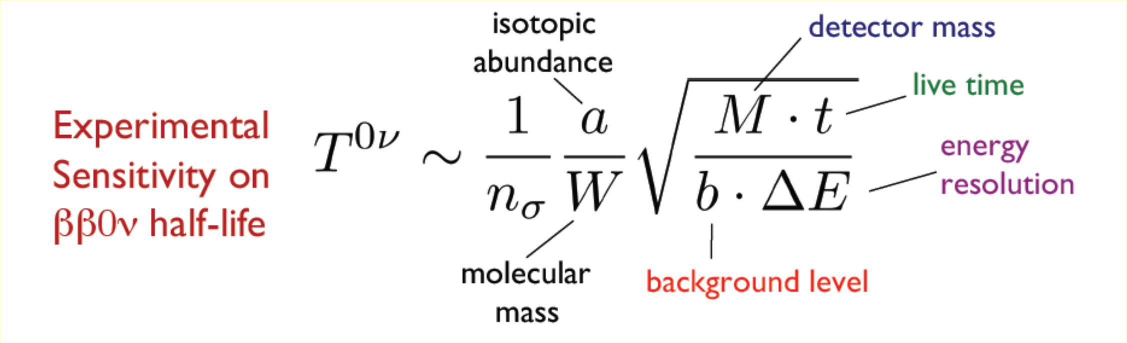
Outline

1. Introduction;
2. ZnSe^{82} synthesis methods;
3. Description of the ZnSe growing methods;
4. Analyses of defects formation caused ZnSe crystals growing process and thermal treatment;
5. Optical and luminescent characteristics of melt growing crystals;
6. Summary and future.

1.Introduction

Basic requirements to scintillation bolometers for studies of neitrinoless double beta-decay



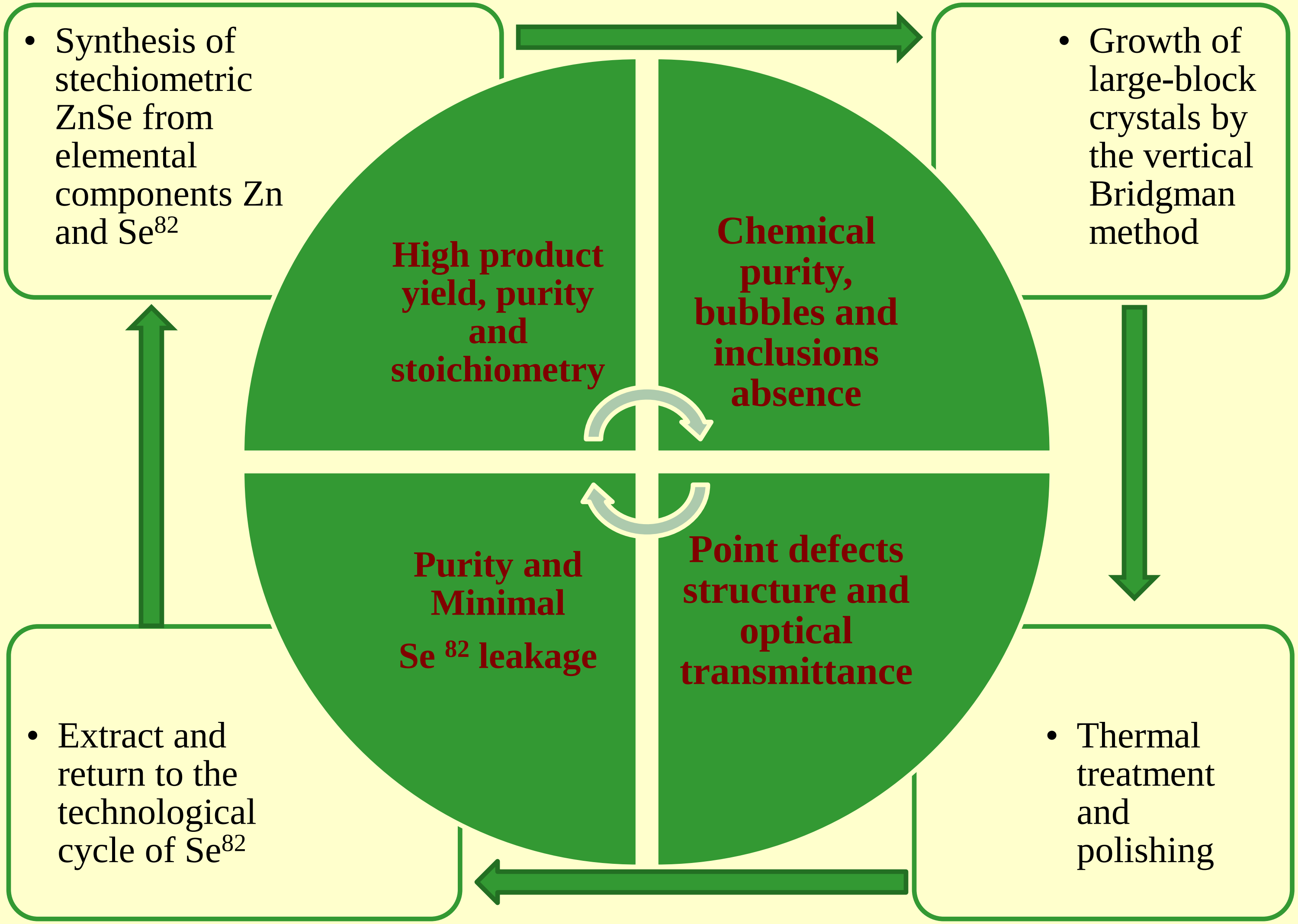
$$T^{0\nu} \sim \frac{1}{n_\sigma}\frac{a}{W}\sqrt{\frac{M\cdot t}{b\cdot \Delta E}}$$

ΔE-fundamental parameter, depend on luminescent intensity,

Requirements to ZnSe^{82} crystals:

1. **Low background level;**
2. **High intensity of luminescent signal;**
3. **High optical transparency in region of luminescence;**
4. **High thermal conductivity;**
5. **Reproducibility of crystal characteristics for multi element detector.**

Stages of ZnSe scintillation bolometers making



- Synthesis of stechiometric ZnSe from elemental components Zn and Se^{82}

High product yield, purity and stoichiometry

Chemical purity, bubbles and inclusions absence

- Growth of large-block crystals by the vertical Bridgman method

- Extract and return to the technological cycle of Se^{82}

Purity and Minimal

Se ^{82} leakage

Point defects structure and optical transmittance

- Thermal treatment and polishing

ZnSe^{82} synthesis methods

Synthesis methods	Modifications	Characteristics
Synthesis from elemental components	**1. Evacuated quartz ampoules;**	**Diffusion controlled method, high purity product**
	2. Microwave synthesis;	**Powder reagents, low stoichiometry**
	3. Reaction et high pressure	**Low stoichiometry**
	4. Self-propagating method	**Fast method, low purity**
H_2Se reactions with Zn-agents	$Zn + H_2Se = ZnSe + H_2$	**Wery hard in practicl using and high toxicity of hydrogen selenide**
	$ZnO + H_2Se = ZnSe + H_2O$	
	$Zn(Et)_2 + H_2Se = ZnSe + 2HEt$	
Reactions in liquid phase	$Na_2Se+ZnCl_2=ZnSe+2NaCl$	**Low purity**

Reasoning of ZnSe^{82} synthesis in evacuated quartz ampoules

1. Low temperature synthesis and high product yield;
2. Zn diffusion through ZnSe layer with possibility long time product conservation;
3. Low rate of synthesis is not problematical for limited product quantity;
4. Very allure provided the sublimation of ZnSe with crystal formation

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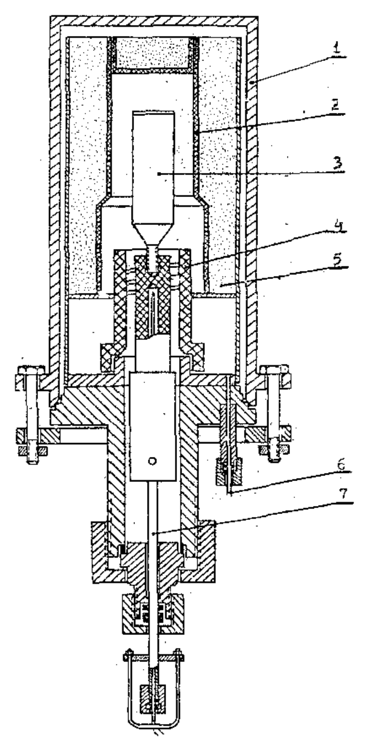
Content of impurities in ZnSe powder

Element	[at.%]	Element	[at.%]	Element	[at.%]	Element	[at.%]	Element	[at.%]
Li	1,1´10^{-5}	Sc	<1´10^{-7}	Y	<1´10^{-7}	Ce	<5´10^{-7}	Os	<5´10^{-7}
Be	< 10^{-6}	Ti	<1´10^{-7}	Zr	<1´10^{-7}	Pr	<5´10^{-7}	Ir	<5´10^{-7}
B	<5´10^{-7}	V	<1´10^{-7}	Nb	<1´10^{-7}	Nd	<1´10^{-7}	Pt	<5´10^{-7}
C	10^{-4}	Cr	2,4´10^{-6}	Mo	<2´10^{-7}	Sm	<1´10^{-7}	Au	<1´10^{-6}
N	1,2´10^{-4}	Mn	3,7´10^{-6}	Ru	<2´10^{-7}	Eu	<1´10^{-7}	Hg	<1´10^{-6}
O	3,4´10^{-5}	Fe	2,9´10^{-4}	Rh	<5´10^{-7}	Gd	<1´10^{-7}	Tl	<1´10^{-6}
F	< 10^{-6}	Co	5´10^{-7}	Pd	<5´10^{-7}	Tb	<1´10^{-7}	Pb	<1´10^{-6}
Na	1,9´10^{-5}	Ni	2,1´10^{-6}	Ag	<3´10^{-6}	Dy	<1´10^{-7}	Bi	<1´10^{-6}
Mg	9,4´10^{-5}	Cu	3,9´10^{-5}	In	<5´10^{-6}	Ho	<1´10^{-7}	Th	<1´10^{-6}
Al	1,5´10^{-4}	Cd	1,61´10^{-3}	Sn	<5´10^{-7}	Er	<1´10^{-7}	U	<5´10^{-8}
Si	9´10^{-5}	Ga	<3´10^{-7}	Sb	<2´10^{-7}	Tm	<1´10^{-7}	Ca	3,3´10^{-5}
P	<5´10^{-7}	Ge	<1´10^{-6}	Te	<1,3´10^{-5}	Yb	<1´10^{-7}	Rb	<1´10^{-6}
S	7,2´10^{-4}	As	<1,5´10^{-6}	I	<2´10^{-7}	Lu	<1´10^{-7}	La	<5´10^{-7}
Cl	1,1´10^{-6}	Sr	<5´10^{-8}	Cs	<2´10^{-7}	Hf	<1´10^{-7}	Re	<2´10^{-7}
K	<1´10^{-6}	Br	<2´10^{-6}	Ba	<1´10^{-6}	W	<3´10^{-7}		

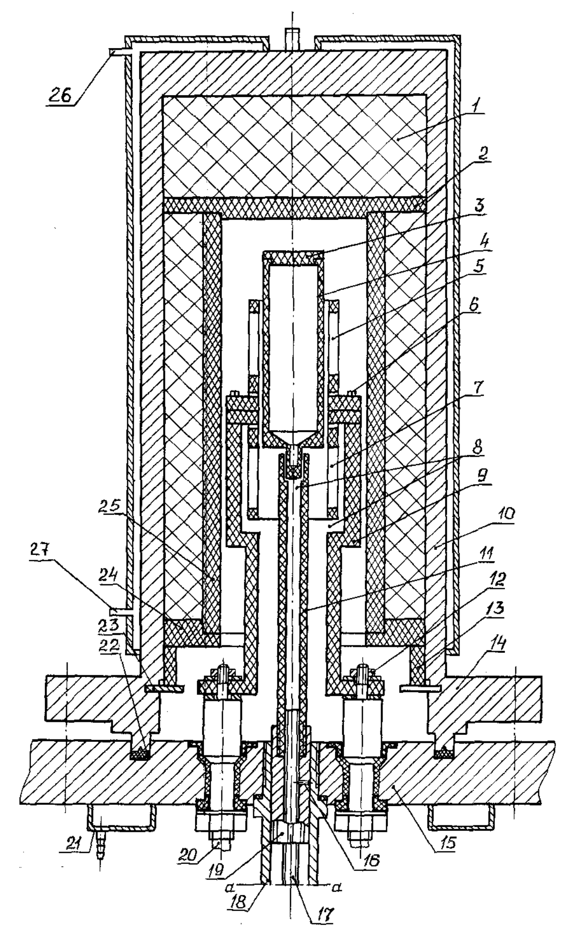
Modifications of Brigemann furnaces

Single zone furnace



1 – frame;
2 – thermal shield;
3 – crucible;
4 – heater;
5 – heat insulation;
6 – current lead;
7 – plunger.

Double zone furnace

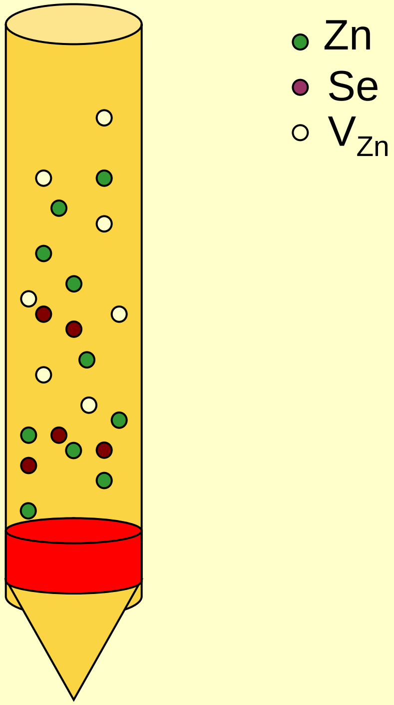


1 - graphite felt;
2 - disc;
3 - cover;
4 - crucible;
5 - upper heater;
6 - bolt;
7 - bottom heater;
8 - thermocouple;
9 - support;
10 - camera;
11 - extension cord;
12 - Nut;
13 - trumpet;
14 - flange;
15 - base plate;
16 - lock pin;
17 - plunger;
18 - the guide tube

19 - the slider;
20 - electrode;
21 - Water-cooled;
22 - O-ring;
23 - a lock ring;
24 - ring;
25 - trumpet;
26 - out of water;
27 - the entrance of water.

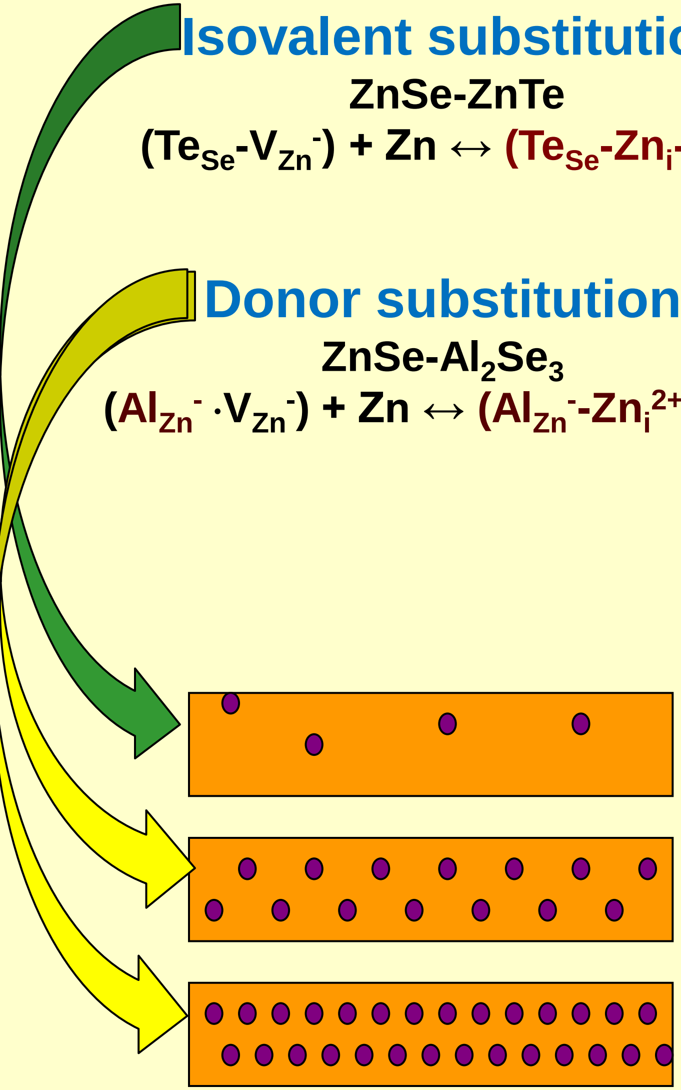
Photos of growing furnace and ZnSe crystals

Description of the ZnSe Brigemann-Stockbarger growing method



Increase concentration vacancies factors	Effects in ZnSe
Melt overheating	Stoichiometry disbalance
Isovalent substitution	Local deformation of crystal lattice
Donor doping	Vacancies generation in conformity with electric neutrality rule

ZnSe defect complexes formation



Isovalent substitution

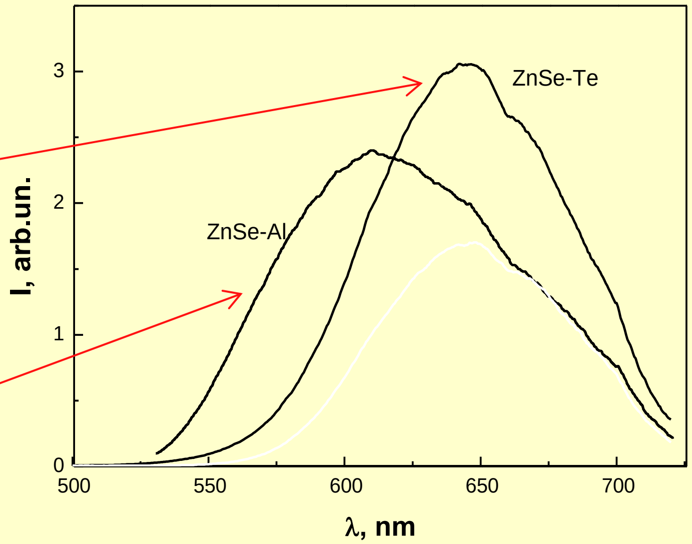
ZnSe-ZnTe

$(\mathrm{Te_{Se}}\text{-}\mathrm{V_{Zn}^{-}}) + \mathrm{Zn} \leftrightarrow (\mathrm{Te_{Se}}\text{-}\mathrm{Zn_{i}}\text{-}\mathrm{V_{Zn}^{-}})$

Donor substitution

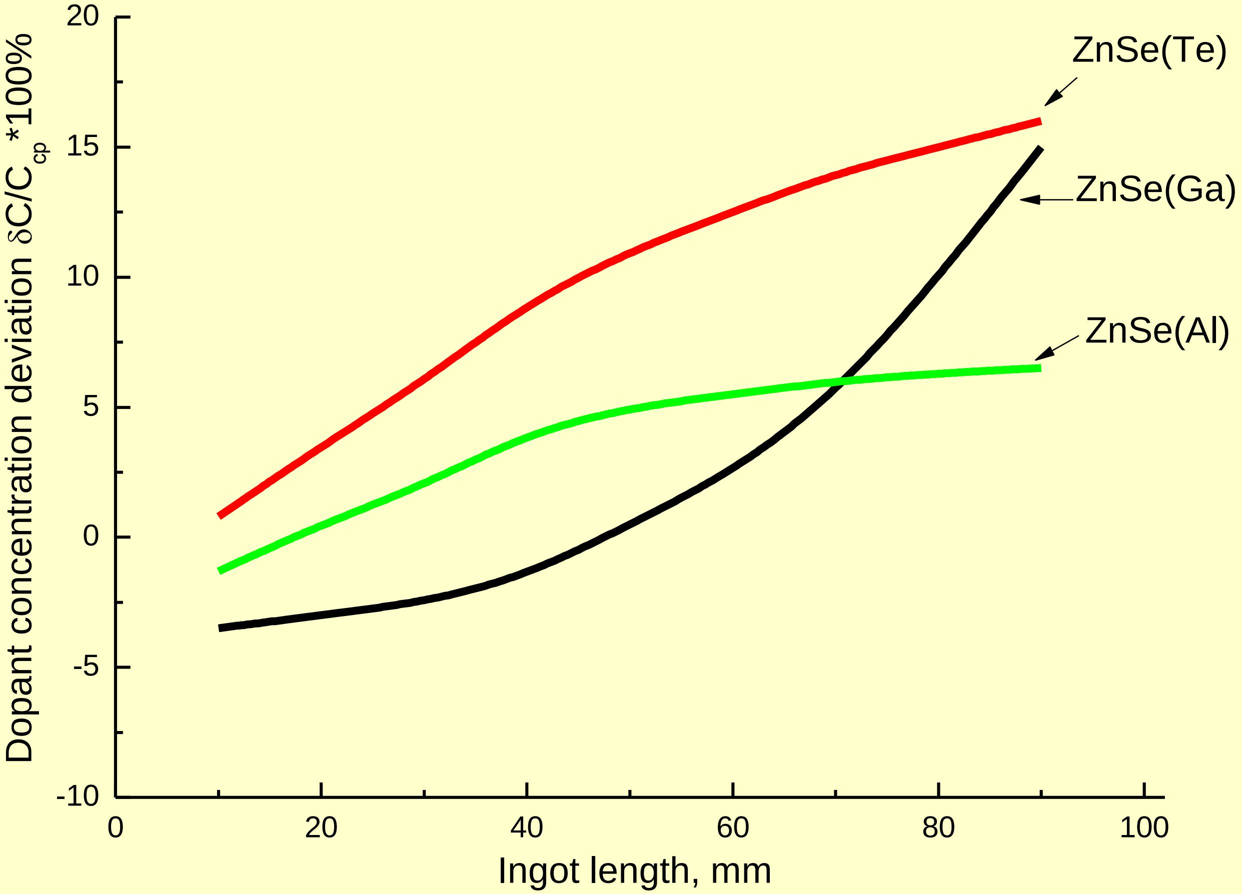
$\mathrm{ZnSe\text{-}Al_2Se_3}$

$(\mathrm{Al_{Zn}^{-}} \cdot \mathrm{V_{Zn}^{-}}) + \mathrm{Zn} \leftrightarrow (\mathrm{Al_{Zn}^{-}}\text{-}\mathrm{Zn_{i}^{2+}}\text{-}\mathrm{V_{zn}^{-}})$

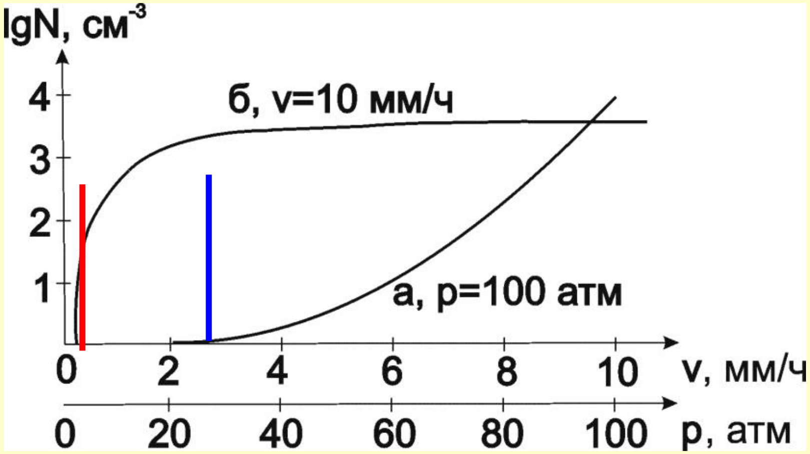


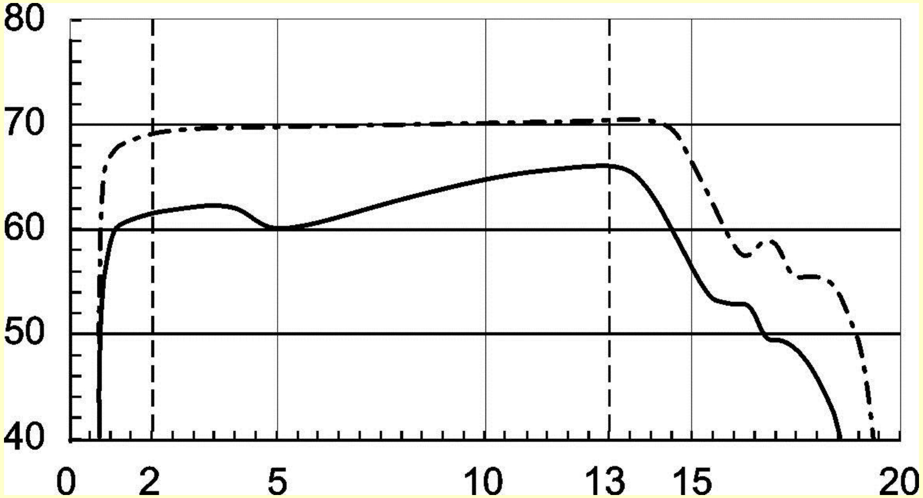
Defect complexes correlation	**Fracture strength**	**Optical absorption (600nm), cm-1**
No correlation	Medium	0.05
Medium correlation	High	0.1-0.2
Strong correlation	Low	0.3-0.5

The distribution of dopants along the length of the crystal



Defects formation at different Brigemann growing regimes





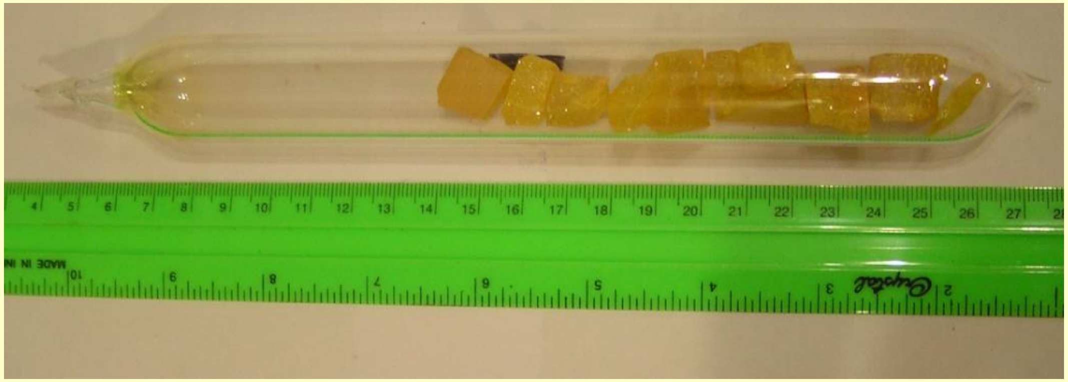
Experimental plot of the defects concentration (N) in the ZnSe crystals on the rate of growth at pressure of P = 100 kg/cm^2 – (curve-a).

The pressure dependence N, received at a growing rate v = 10 mm/h. (Curve–b)

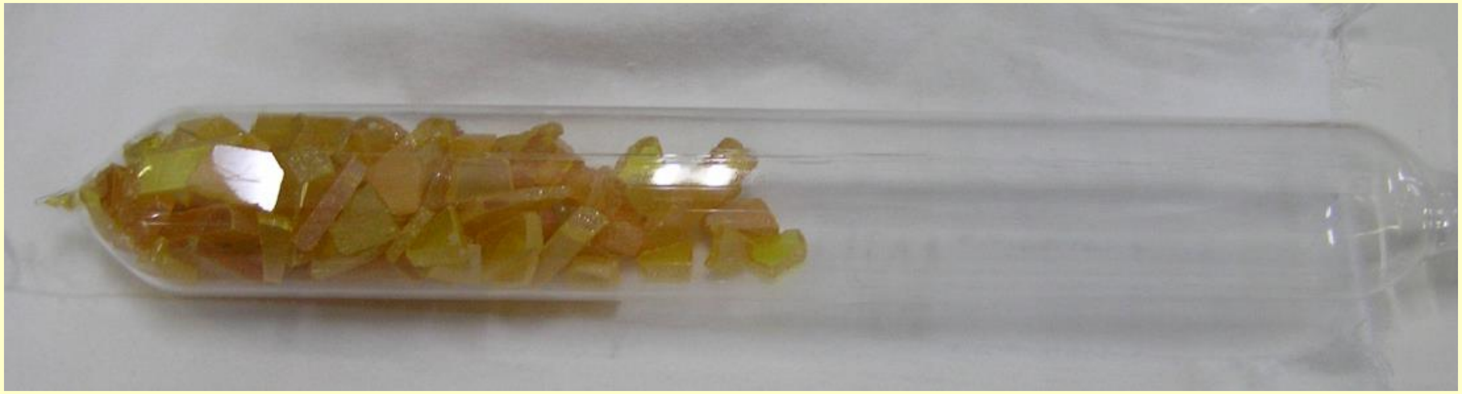
Reduction of sample transmission ZnSe with defects (solid line) relative to the theoretical bandwidth (dotted line).

Vacuum sublimation method

$$ZnSe_l \rightarrow Zn_g + 1/2Se_2$$

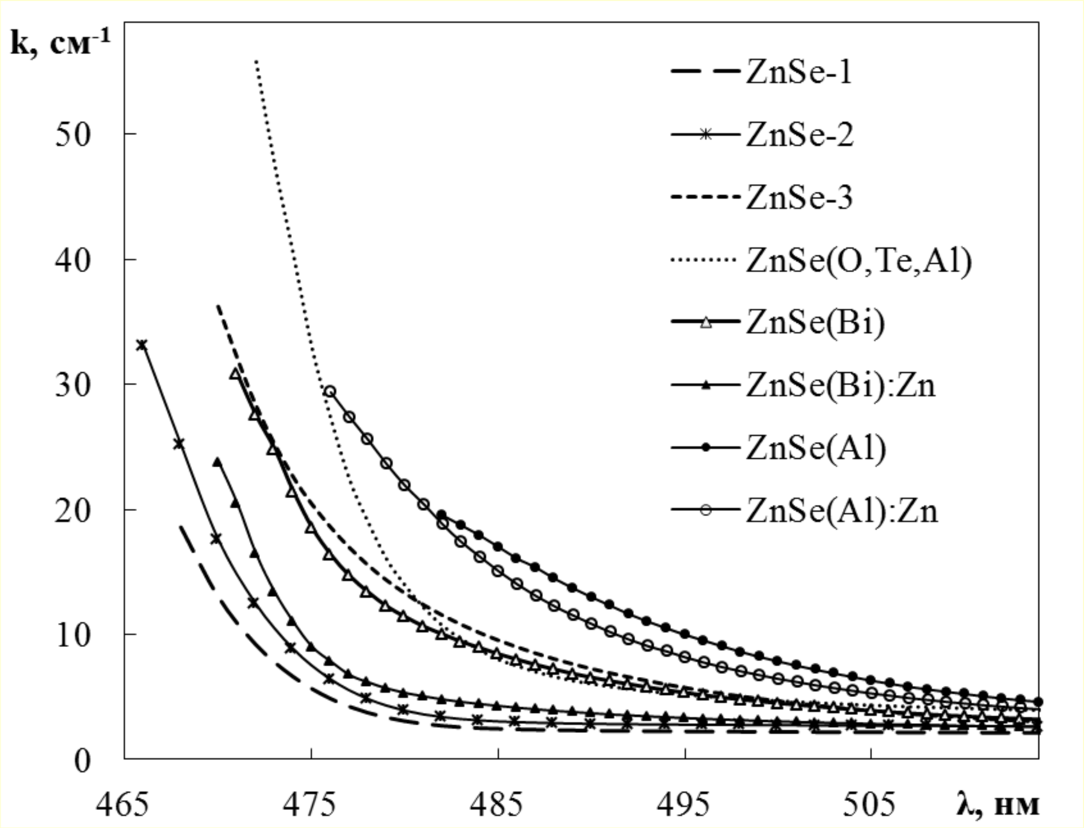


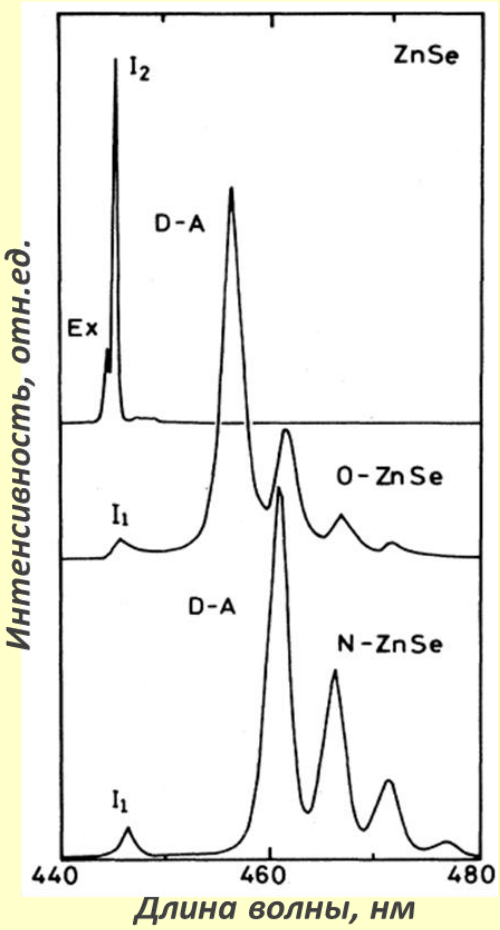
Quarts ampoule 25 mm dia., T=1150 C (source), 1120 C (crystal deposition)



Quarts ampoule 50 mm dia., T=1180 C (source), 1150 C (crystal deposition)

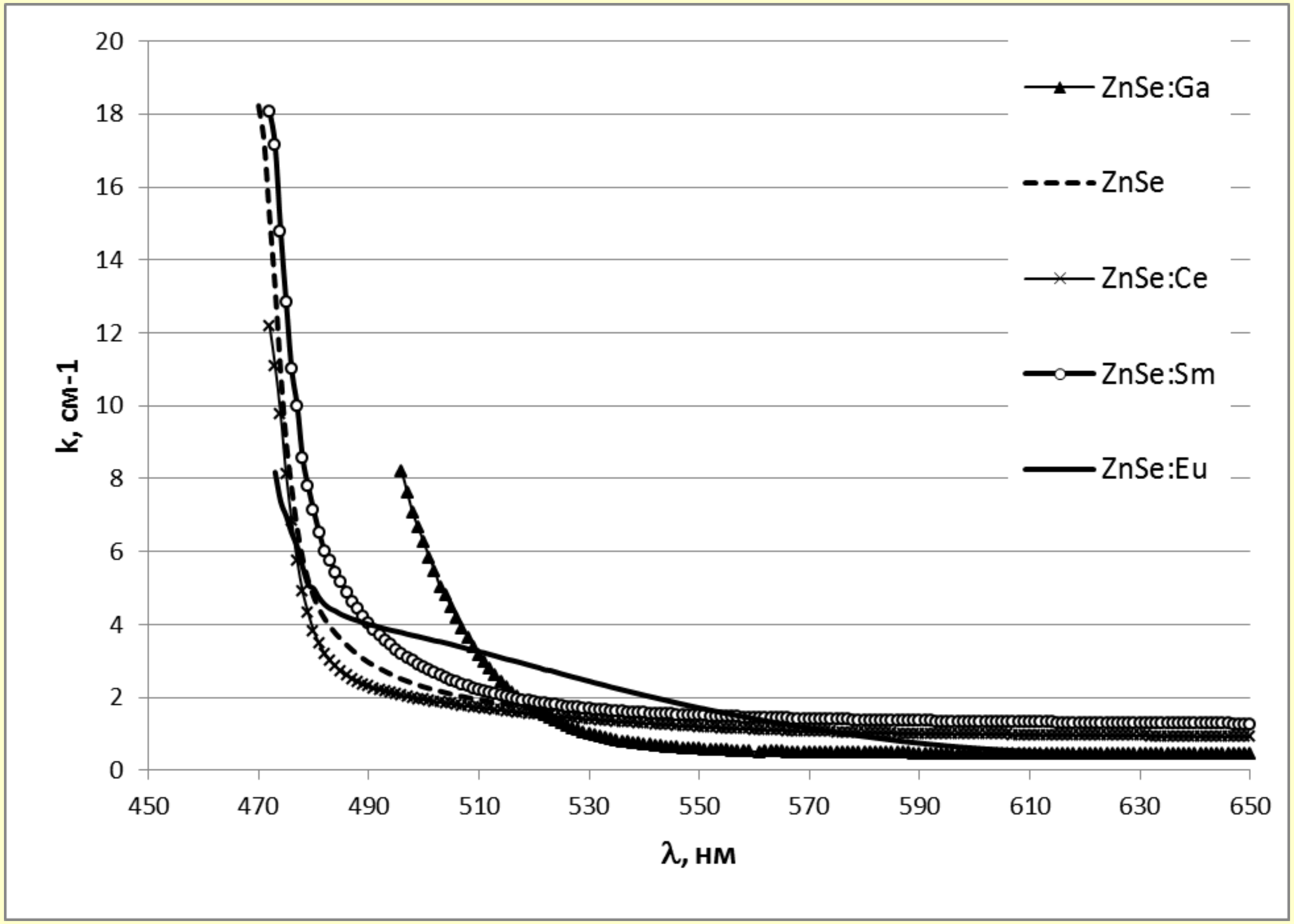
Absorption and luminescence regions of undoped and doped ZnSe crystals





Absorption specters of ZnSe samples at 300 K

Photoluminescence of pure ZnSe (top spectrum), oxygen and nitrogen doped crystals. T= 4 K



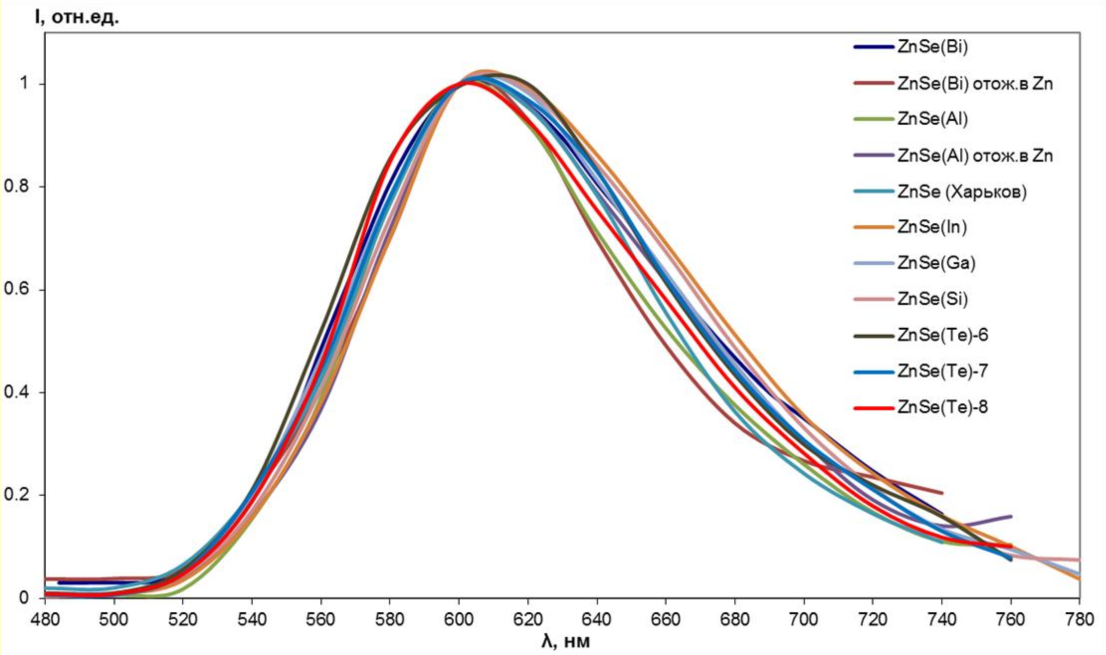
Absorption specters of ZnSe samples at 300 К

Determining the impact of various dopants on donor-acceptor radioluminescence in zinc selenide crystals

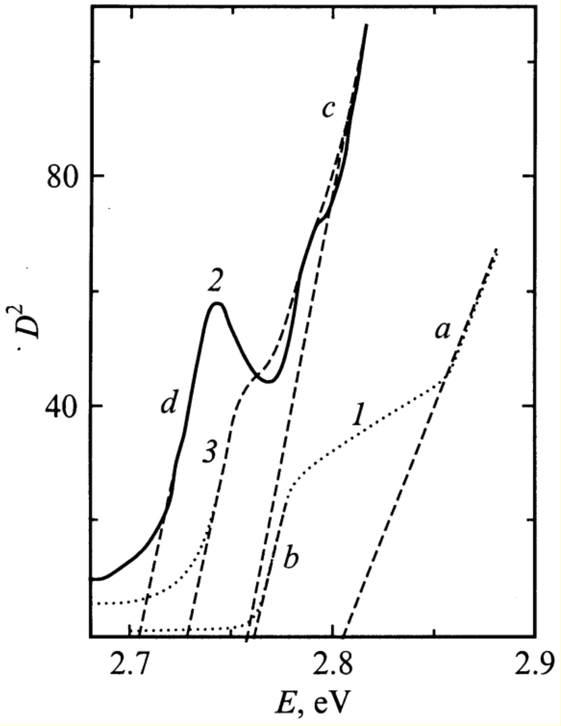
The relative luminescence intensity (λ = 610 nm) undoped and doped with different dopants ZnSe

crystals

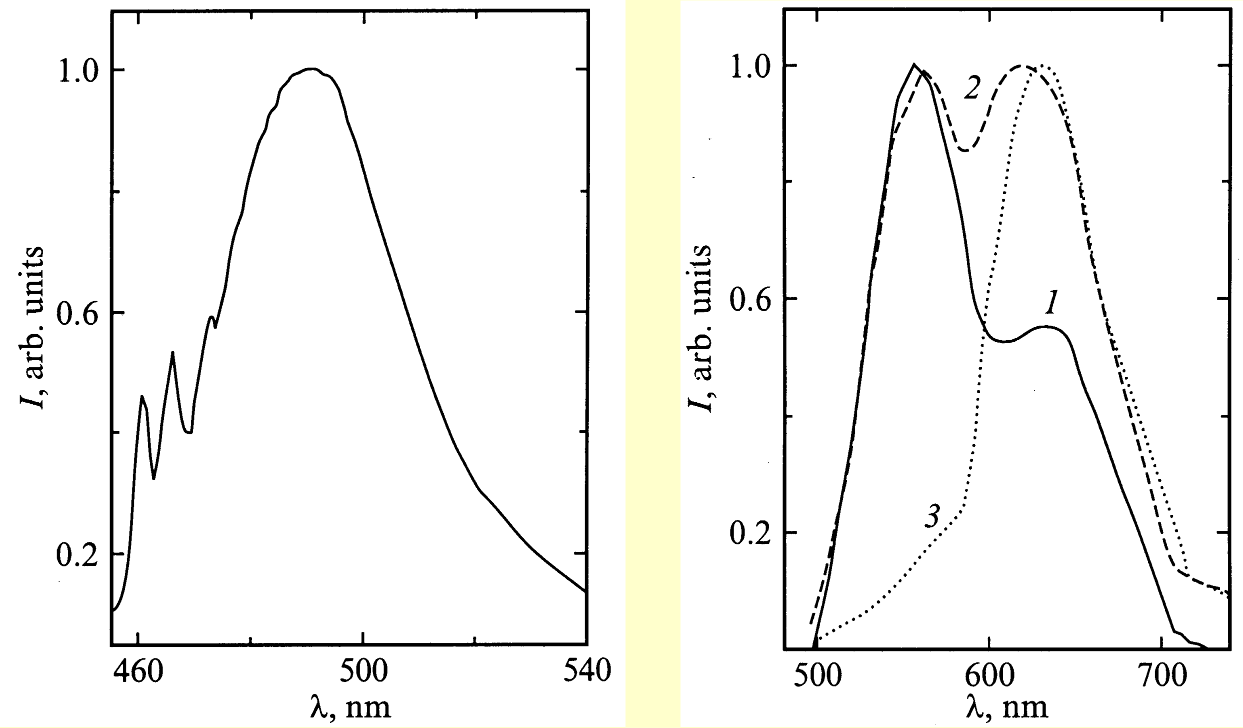
Crystal	I_{max}, arb. units
ZnSe -1	1
ZnSe -3	16
ZnSe(Ga)	63
ZnSe(Bi)	25
ZnSe(Bi):Zn	6
ZnSe(Al)	53
ZnSe(Al):Zn	271
ZnSe(In)	21
ZnSe(Si)	18
ZnSe(O,Te, Al)	109



X-ray spectra of ZnSe crystals doped with various dopants



Adsorption spectra of
ZnSe (*1*), ZnSe : In (*2*), ZnSe : In+Zn (*3*)



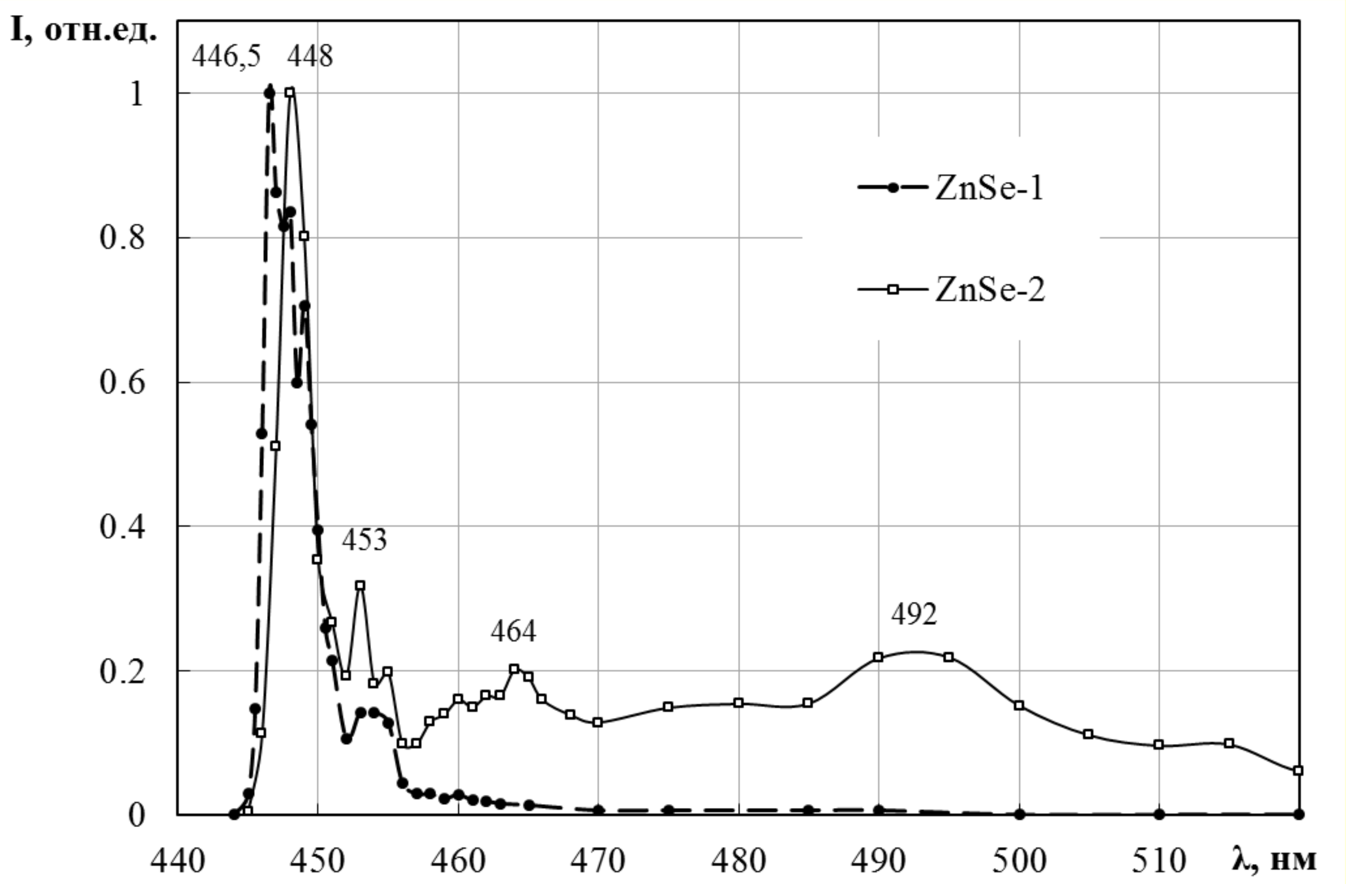
a

b

Photoluminescence of ZnSe : In at [In] = 4 10^{16} cm^{-3} (a) and ZnSe : In ([In] > 10^{17} cm^{-3} by different irradiation intense 100 (*1*), 50 (*2*), 20% (*3*).

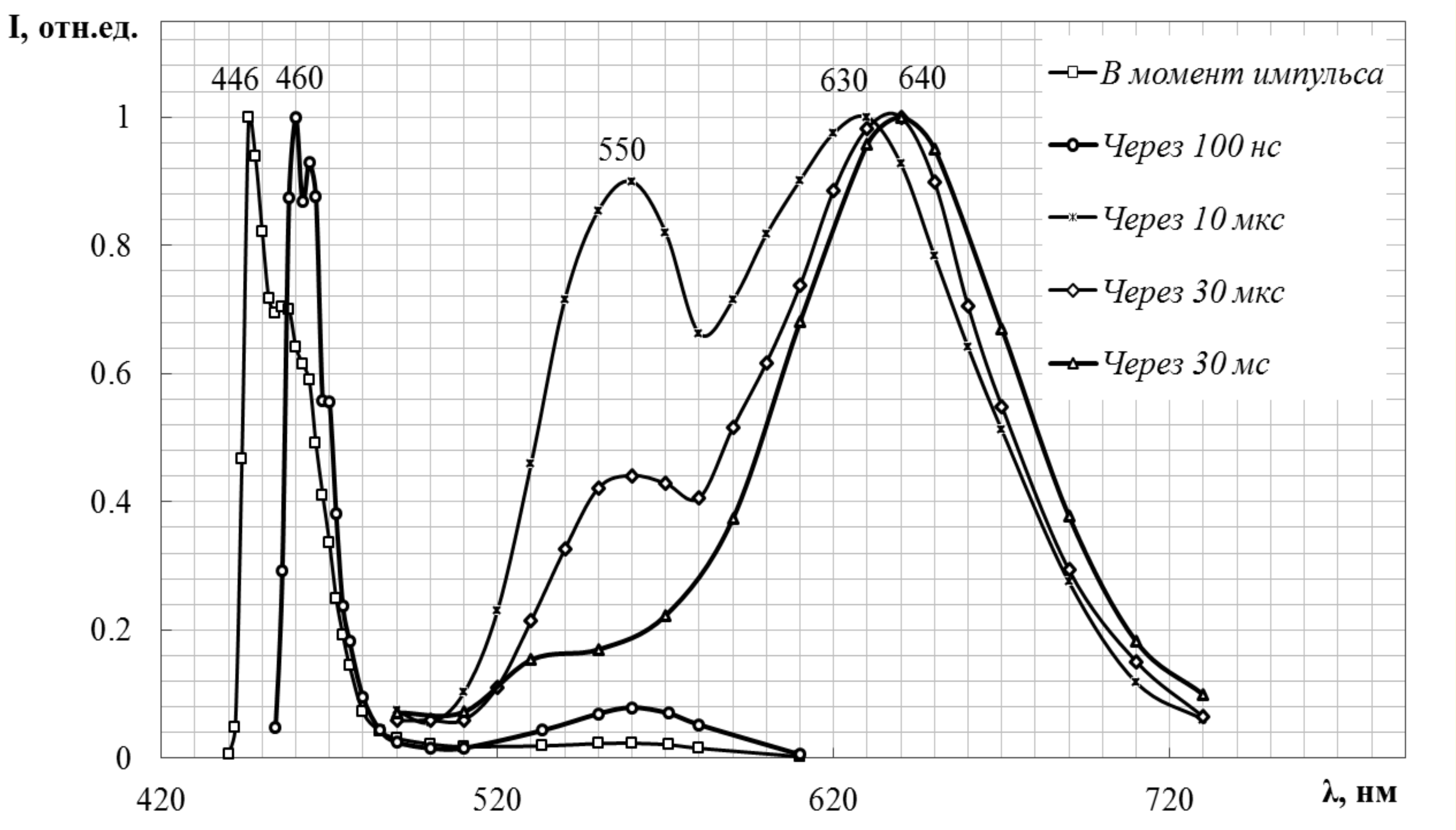
Physics and technique of semiconductors, 2001, v 35, Nb. 8

Edge luminescence of ZnSe-1 (sublimat) and ZnSe-2(melt growth)



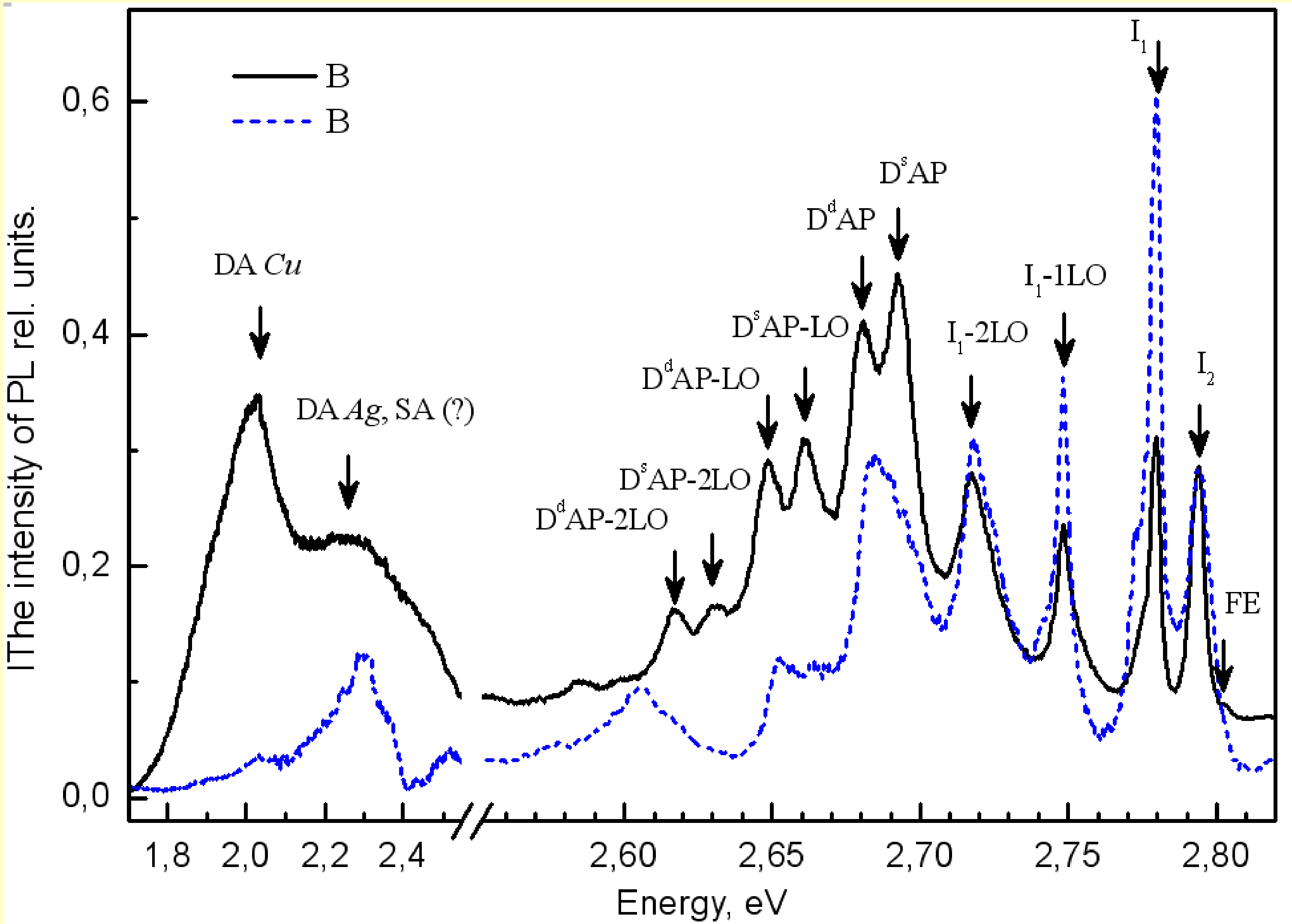
Normalize cathodoluminescense specters of ZnSe-1 and ZnSe-2.
(T=15K, t=10 ns after pulse)

Time evolution of ZnSe-Al luminescence

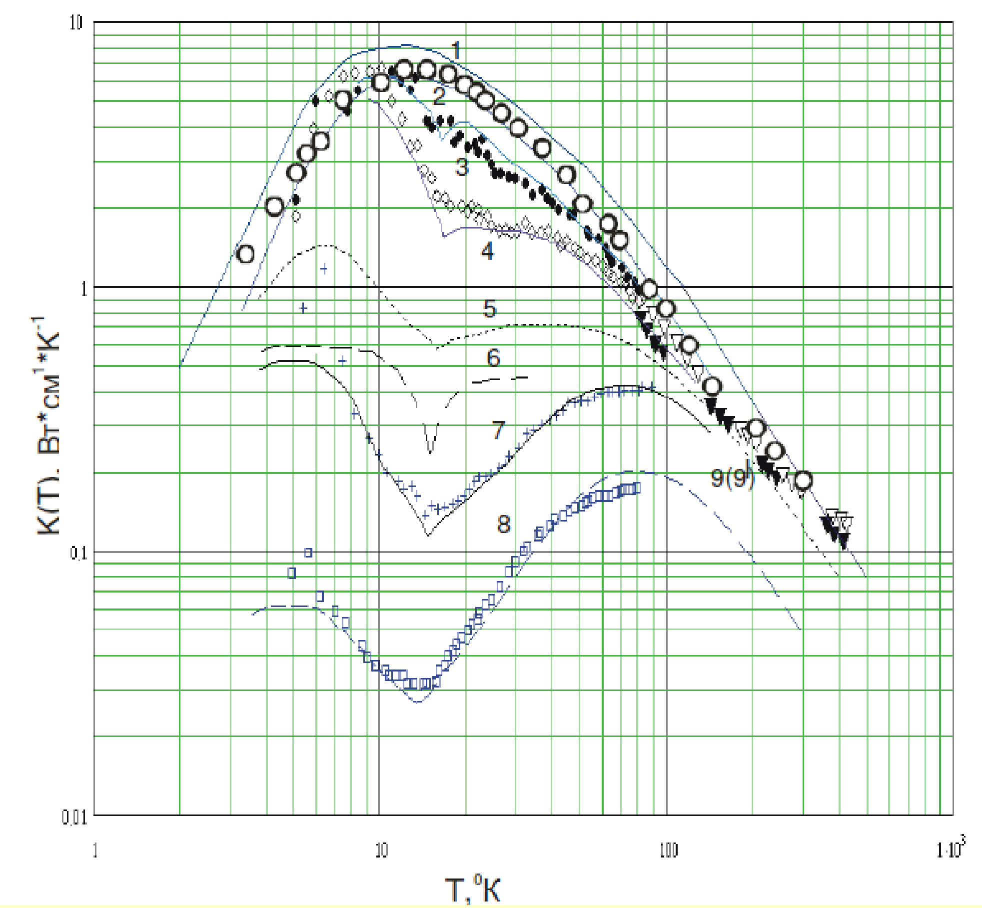


T = 15 K. Normalize to 1.

Influence of surface condition on low photoluminescence spectra crystals ZnSe (Al)



Thermo conductivity of d-element doped ZnSe crystals



Thermal conductivity of pure ZnSe crystals (1, 2), and Ni-doped (3-8).

Balandina N.V., Rostova A.T. Thermo conductivity of wide-band gap semiconductors

Conclusions

We propose a method for the synthesis of ZnSe charge, allowing to receive a high purity product.

Edge luminescence has a decisive contribution to the scintillating bolometers parameters ZnSe. It is therefore necessary to seek minimize concentration of ionized defects in crystalline material.

For optimization of thermal conductivity need a limitation of structural defects concentration in ZnSe crystals grown from the melt. Probably need a thermal treatment in selenium for stabilization of V_{Zn} concentration.

Thanks for attention !!!