Zinc oxide: hydrothermal growth of nano- and bulk crystals and their luminescent properties

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Hydrothermal growth, crystal chemistry and catodoluminescence of ZnO single crystals were studied. Zinc oxide was grown as bulk crystals so as crystalline films and powders with different form-factors (size and shape of the particles). The dependence of form-factor on the growth conditions was studied. Growth morphology and spectra of impulse cathodoluminescence (ICL) were analysed for the samples depending on growth conditions. Two emission bands were registered in ICL-spectra with band lengths ~385 and 600 nm. The shift of the band in visible part of spectrum (VIS-band) was found depending on KOH concentration in starting solutions. © *2006 Springer Science + Business Media, Inc.*

1. Introduction

Zinc oxide, a wide-band gap semiconductor ($\Delta E \cong$ 3,37 eV at 300 K), possesses by an unique set of mechanical, electrical, optical properties. Combination of high stability, very high melting point with valuable physical characteristics makes zinc oxide by an attractive material for applications in various regions of modern technologies (low-voltage and short wavelength electro-optical device, piezoelectric transducers, chemical sensors, varistors, lasers etc.). ZnO has the highest value of exiton binding energy among the binary semiconductors ($\cong$ 60 meV), it provides the existence of UV band of the luminescence due to direct recombination of exitons up to 500 K. Due to bright UV luminescence, zinc oxide is a perspective material for manufacture of UV light emitting diodes, UV lasers operating at room temperature and display devices.

As was mentioned in recent publications, ZnO is a functional material that maximally adapted for obtaining laser radiation in UV region at room temperature [1]. The effective generation in UV region for disordered nanosized polycrystalline ZnO powders and films was one order higher in comparison with bulk crystals [2]. This fact explains growing interest to manufacture of ZnO low-dimensional powders and films.

Single crystals, low-dimensional powders and films may be obtained using various techniques. Among them, the hydrothermal synthesis is of special interest due to following reasons:

(a) it operates at rather low temperatures;

(b) it allows to vary the crystal size and properties in a wide range due to varying the growth media composition, temperature, pressure;

(c) it allows to input various elements into the crystals at rather low temperatures,

(d) hydrothermally obtained crystals have shown much higher efficiency of UV-luminescence in comparison with crystals grown from the gas phase [3].

Goals of this work were growth of ZnO bulk single crystals; synthesis of low-dimensional crystalline powder of zinc oxide (nominally pure and doped); study of the effect of growth conditions on the ZnO yield and size of microcrystallites in the powders, composition of the final product; study of the luminescence characteristics of materials obtained.

2. Experimental

ZnO single crystals were grown under optimal hydrothermal conditions found earlier [4]: temperature in the growth zone was 230–300°C, ΔT between the dissolution zone and growth zone was 50–75°C (measuring along outer wall of the autoclave), and pressure was 30-50 MPa. Alkaline solution of mixed composition was used as a solvent (5.14 mol/l KOH +1.2 mol/l LiOH). Crystals were grown on the seeds parallel to (0001); seed surfaces were preliminarily chemically treated to remove the defect layer formed during the cutting.

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Zinc oxide thin powders were synthesised by soft hydrothermal chemistry methods at low temperatures. Experiments were carried out under isothermal conditions and under conditions of temperature gradient.

Varying parameters of synthesis:

Zn-precursor   ZnO (A-precursor),
            as-prepared amorphous $Zn(OH)_2$
            $\cdot nH_2O$ ($B-$, $C-$ precursors), Zn;

Solvent	H_2O, LiOH, KOH + LiOH;
Seed-substrate	Zn, Si(100), SiO_2(0001), ZnO;
Dissolution temperature	$120-250°C$
Temperature gradient	0.5 degree/cm;
Fill coefficient	$0.75-0.9$;
Experiment duration	$10-48\ hours$.

$Zn(OH)_2 \cdot nH_2O$ was prepared using the interaction between MOH (M = Li, K, NH4) and Zn-acetate (B-precursor) or between MOH and Zn-nitrare solutions (C-precursor). Final products of the synthesis were analyzed by the following methods: X-ray powder diffraction (Diffractometer Rigaku D-max III-C, λCu Kα); thermal analysis DTA, TGA; scanning electron microscopy SEM (JEOL JXA-840); optical microscopy (Neophot-32); impulse catodoluminescence (ICL) spectroscopy ("KLAVI-1", energy of electrons in the beam 180 $\pm$ 20 keV, current density 700 $\pm$ 100 A/cm$_2$, $\tau \approx 2$ ns); photoluminescence at the exitation by 4th harmonics of YAG:Nd^{3+} ($\lambda \sim 266$ nm, $\tau \sim 10$ ns).

3. Results and discussion
3.1. Crystallographic characteristics
Zinc oxide has hexagonal symmetry, sp. gr. P6$_3$mc, unit cell parameters are $a = 3.249$, $c = 5.207$ Å. The structure is built by the [ZnO$_4$]-tetrahedrons sharing their vertices. The absence of center of symmetry determines the polar character of the compound along [0001] axis and as a result the polar character of the growth along this direction.

The (0001) monohedron has on its interface Zn^{2+}-ions, while the negative monohedron is terminated by O^{2-} ions, so these faces are different in their effective charge on the surface. Along C-axis there exists the following sequence of planar nets which construct the monohedra: Zn / O / Zn [5].

For $\{10\ \bar{1}1\}$ and $\{11\ \bar{2}0\}$ prisms, elementary layers are built by the nets with mixed composition (Zn, O) / (Zn, O). For $\{10\ \bar{1}1\}$ and $\{10\ \bar{1}2\}$ pyramids more complicated structure is characteristic: the corrugated layers (Zn, O) and O are alternated along the direction perpendicular to the face of these simple crystallographic forms.

Theoretically for spontaneous crystallization, growth rates must change in consequence:

$$(000\ \bar{1}) < \{11\ \bar{2}0\} \sim \{10\ \bar{1}0\} \sim \{10\ \bar{1}1\} \ll (0001).$$

For directional seeded growth this sequence may change depending on seed orientation.

Analysis of polyhedral structure model allows to make some preliminary conclusions on the relative growth rates of the faces of different simple crystallographic forms in accordance with [6]. The faces looking at the interface with the vertices of the polyhedrons have the largest growth rates (in our case there is positive monohedron), and the faces looking at the interface with the faces of polyhedrons have the minimal growth rates (negative monohedron). For prism and pyramid, [ZnO$_4$]-polyhedrons are inclined to the interface at different angles. Structures of the interfaces for the faces of basic crystallographic forms are shown in Fig. 1.

Of course such "geometric" approach gives only the preliminary imaginations about the growth rates of individual faces of the crystal. The final crystal habit will defined by the relations between the chemical composition of the interface, chemical composition of growth species in growth media, temperature of the process and so on.

Thus, analysis of the construction of the simple crystallographic forms allows to make the following conclusions:
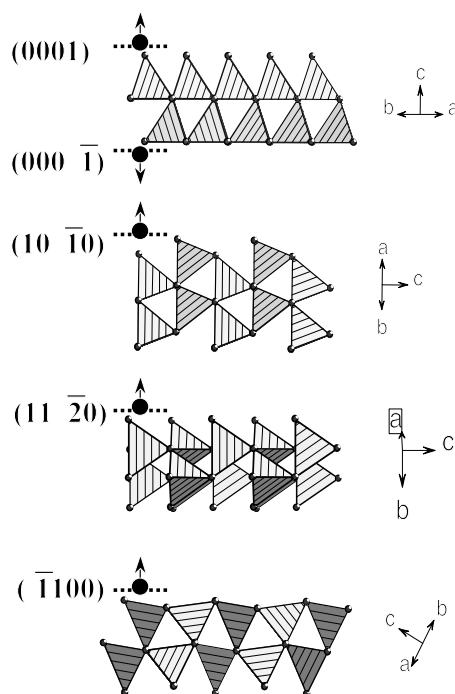

Figure 1 Structures of the interfaces for the faces of monohedra (0001) and (000 $\bar{1}$), hexagonal prisms $\{11\ \bar{2}0\}$ and $\{10\ \bar{1}0\}$, hexagonal pyramid $\{10\ \bar{1}1\}$. Arrows show the growth directions.

(a) polar growth must be pronounced in grown crystal habit;

(b) V(0001) >> V(000 $\bar{1}$) in aqueous media (negatively charged species are characteristic of such media);

(c) V{11 $\bar{2}$0}∼V{10 $\bar{1}$0} due to similar construction;

(d) V{10 $\bar{1}$1} will be defined mainly by growth conditions (chemical composition, temperature).

3.2. Bulk single crystal growth

High quality single crystals with mass up to 200 g were grown under the conditions mentioned above (vessel capacity ∼800 cm^{-3}). Crystals are faceted by the faces of positive monohedron (0001); negative monohedron (000 $\bar{1}$), prism of the 1st kind {10 $\bar{1}$0}; prism of the 2nd kind {11 $\bar{2}$0}, pyramid {10 $\bar{1}$1}. Preliminary investigations have shown the following sequence of the growth rates for the seeded growth:

$$V\{11\,\bar{2}0\} \sim V\{10\,\bar{1}0\} < V\{10\,\bar{1}1\}$$
$$<< V(000\bar{1}) < V(0001).$$

Maximal growth rate is characteristic of the growth in $+C$ direction. Under the chosen conditions, growth rates of the other simple crystallographic forms are very low (<0.05 mm/day). Growth pyramid of the positive monohedron has light yellow tint, while growth pyramid of negative monohedron is coloured into greenish colour. This difference is explained by different colour centre formation, different capture of Li^{+} and, as a result, by different stoichiometry in growth pyramids of these simple crystallographic forms. Dislocation density is 10^2–10^3 cm^{2-} (calcutated using chemical etching) for the faces of positive monohedron; for negative monohedron it is several times higher.

3.3. Crystalline powder synthesis

Dehydration of starting Zn-hydroxide due to temperature increase or recrystallization of starting ZnO resulted in the formation of ZnO crystalline powders. The dimensions and crystal habit of crystallites depend on growth conditions. XRD analysis confirmed the formation of hexagonal ZnO (wurtzite structure type) for all samples under study.

Well-faceted crystallites have dimensions in the range ∼100 nm – 20 μm depending on growth condition. In accordance with X-ray evaluation, typical mean dimensions of the crystallites are 40–100 nm. Typical crystal habit is prismatic or platy, main simple crystallographic forms are positive (0001) and negative (000 $\bar{1}$) monohedra, hexagonal prism {10 $\bar{1}$0} and pyramid {10 $\bar{1}$1}.

Temperature effect. At low temperatures (110–130°C) final product consists of the mixture of ZnO, precursors and some intermediate compounds in short-time experiments (2–3l h). The full recrystallization of the precursors (100% ZnO yield) takes place already at temperatures
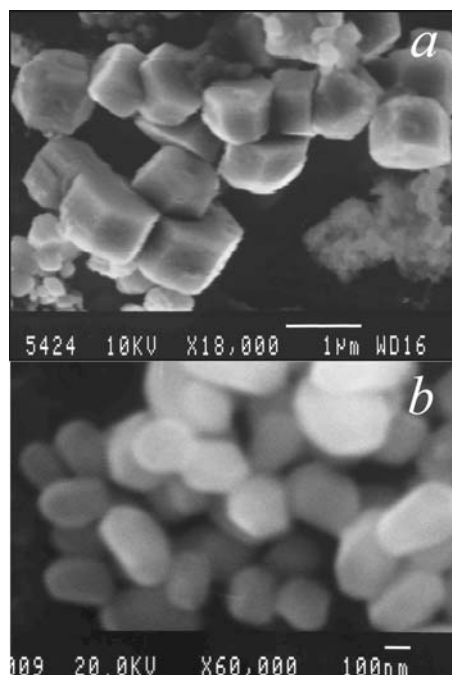

Figure 2 Scanning microscopy images of ZnO crystallite morphology a) after heat treatment at T = 450°C (run No. 135, temperature of the synthesis 120°C, *B*-precursor, H$_2$O);
b) typical crystal habit (run No 47, *C*-precursor, KOH 10%).

∼150°C at experiment duration ∼40 h. Temperature increase in 50–70°C results in the shortening of experiment in 4–5 times. The longer is the hydrothermal treatment the larger crystallites are being formed. In the case of low-temperature experiment, well faceted crystallites of ZnO with size about 1 μ are forming only after heat treatment (Fig. 2a).

Precursor effect. In pure water as a solvent, more uniform distribution of crystallites on their dimensions are observed when ZnO-precursor are represented by Zn(OH)$_2$·nH$_2$O which was as-prepared from acetate solutions (B-precursor). Crystallites have shortly-prismatic or platelet-like habit when as-prepared zinc hydroxide is used as ZnO-precursor. Typical morphology is shown in Fig 2b. Crystallites with prismatic habit and maximal *c/a* ratio (∼3 : 1) are formed when ZnO is used as starting nutrient (*A*-precursor).

For crystallites obtained in pure water, faceting is less pronounced when precursor Zn(OH)$_2$·nH$_2$O is prepared using zinc acetate; uniform distribution of crystalline dimensions is characteristic of this series; crystallites are smaller in comparison with *C*-series. Crystalline powders obtained in another series (precursor is Zn(OH)$_2$·nH$_2$O prepared using zinc nitrate) are characterized by better faceting with well-developed faces of monohedra. When ZnO was used as starting material, the final crystalline powder is characterized by non-uniform distribution of crystallites on their dimensions. In this case new crystallites are forming due to two processes:

spontaneous nucleation in the solution and crystallization on the ZnO particles as nucleus in the nutrient.

Solvent effect. Introduction of alkali (KOH, LiOH) into the growth system leads to decrease of crystallite growth rate in *c*-direction (as well as for bulk crystal growth) due to change of the growth mechanism [7]; crystalline habit changes from prismatic to platy one. The higher is KOH concentration the less *c*/*a* ratio is observed for ZnO-plates.

3.4. Polycrystalline film growth

When various seeds (Zn, Si, SiO$_2$, ZnO) are introduced into the growth system, disordered polycrystalline films are forming on their surfaces. If metallic Zn serves as a substrate-seed, ZnO crystallites have thin platy habit. Such plates are of 150–500 nm in size with large prevalence of monohedron faces in their habit (growth takes place in [10 $\bar{1}$0] direction). Plates are usually located normally to the substrate (*c*-axis is parallel to substrate surface). Introduction of metallic Zn into the growth system results in the change of Red/Ox potential in the system (especially near the Zn-plate). Chemical reaction between Zn and solvent leads to the formation of hydrogen which introduces into ZnO lattice very easily changing the stoichiometry of the material and its properties. ZnO crystals are known to be characterised by Zn-excess independently on growth method, and nonstoichiometry can be decreased at partial substitution of Li$^+$ or H$^+$ for Zn^{2+}.

3.5. Spectroscopic characteristics

Zinc oxide may show a bright luminescence in several regions of spectrum (orange luminescence, $\lambda \approx 600$ nm, green luminescence, $\lambda \approx 520$ nm, UV luminescence, $\lambda \approx 385$ nm). The ratio of the intensities of these bands depends on many factors (various quenching centres, various impurities, preliminary treatment, pre-history of the samples, crystallographic orientation etc.). It is known that different crystallographic forms entrapped different impurities [4] and, as a result, the samples which were cut from different growth pyramids of single crystals demonstrate different properties. ICL spectra for ZnO single
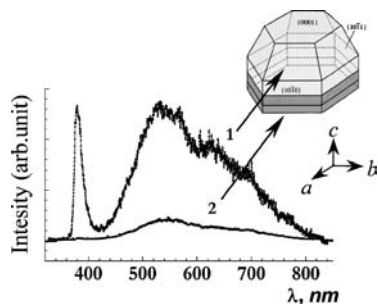

Figure 3 ICL spectra of ZnO single crystals registered on the samples cut from growth pyramids of positive <0001> (curve 1) and negative <000 $\bar{1}$> (curve 2) monohedrons.
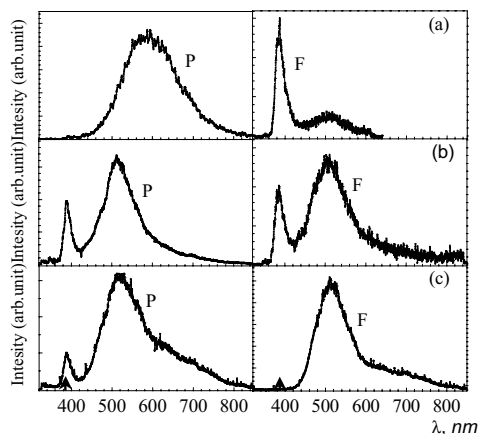
Figure 4 ICL spectra of ZnO polycrystalline films (left row) and nanocrystallte powders (right row) synthesised at 180°C.
(a) precursor ZnO, solvent KOH 10%;
(b) precursor ZnO, solvent H$_2$O;
(c) precursor Zn(OH)$_2$nH$_2$O precipitated from acetate solutions; solvent H$_2$O.
Solid arrow shows the UV-band position.

crystal (Fig. 3) demonstrates this peculiarity. In the spectrum of the sample cut from positive monohedron there are two typical bands of emission with close intensities. Narrow band lies in UV region ($\lambda \sim 385$ nm, $\triangle \sim 15$ nm) and wide one ($\lambda \sim 500$ nm, $\triangle \sim 200$ nm) is in visible part of spectrum. Intensity of UV emission is very low (I$_{UV}$/I$_{VIS} \sim 0.1$) for the sample cut from negative monohedron due to another quality and type of quenching centres. For polycrystalline materials, I$_{UV}$/I$_{VIS}$ depends mainly on stoichiometry of crystallites and impurities. ICL-spectra of polycrystalline films demonstrate the dependence of ZnO spectroscopic characteristics on precursor for ZnO deposited onto the Zn-plates and type and also the difference between the position and intensity of emission bands for ZnO deposited onto the Zn-plates and ZnO crystallized in the nutrient in bottom part of the vessel in the same experiment (Fig. 4). Some spectroscopic characteristics of ZnO powders and films are shown in Table I.

Thin films on Zn-substrates demonstrate the UV luminescence, I$_{UV} \gg$ I$_{VIS}$ in the case when we used *B*-precursor and pure water as a solvent. For ZnO powders (obtained in the same experiment) only wide VIS-band is observed in ICL-spectra (Fig. 4a). When ZnO (chemical) is used as a ZnO-precursor, both film and crystalline powders show the similar ICL-spectra (Fig. 4b).

When KOH is introduced into the growth media, the intensity of UV band decreases (as for film so as for powder) up to disappearing the band (Fig. 4c and 5). Simultaneously the VIS-band is shifted into long-wave region. The VIS-band of luminescence consists of at least three overlapping bands ($\lambda \approx 510$ nm, ≈ 570 nm and ≈ 600 nm). Their intensities change independently,

TABLE I Spectroscopic characteristics of ZnO powders and films (impulse cathode exitation)

Starting nutrient /solvent	Substrate	UV band, 385 nm (ICL)		I_{UV}/I_{VIS}	
		film	powder	film	powder
ZnO/ H_2O	Zn	+	+	0.7	0.6
ZnO/ 10% KOH	Zn	−	+	−	0.3
$Zn(OH)_2 \cdot nH_2O^*$ (gel) / H_2O	Zn	+	−	5	−
$Zn(OH)_2 \cdot nH_2O^*$ (gel) / H_2O			+		No VIS-band
$Zn(OH)_2 \cdot nH_2O^{**}$ (gel)/ H_2O	Zn	+	−	1.4	−
$Zn(OH)_2 \cdot nH_2O^{**}$ (gel)/ H_2O			+		No VIS-band
$Zn(OH)_2 \cdot nH_2O^*$ (gel)/5% KOH	Zn	+	−	0.05	−
$Zn(OH)_2 \cdot nH_2O^*$ (gel)/ 10% KOH	Zn	−	−	−	−
$Zn(OH)_2 \cdot nH_2O^*$ (gel)/ 25% KOH	Zn	−	−	−	−
Zn(CH3COO)₂/ KOH 8.2%	Zn	+	−	1.6	−
$Zn(OH)^2 \cdot nH^2O^*/H^2O$	No substrate	−	+		No VIS-band (laser exitation,λ 266 nm)

* — Zn-hydroxide synthesized on acetate technology (*B*-precursor);

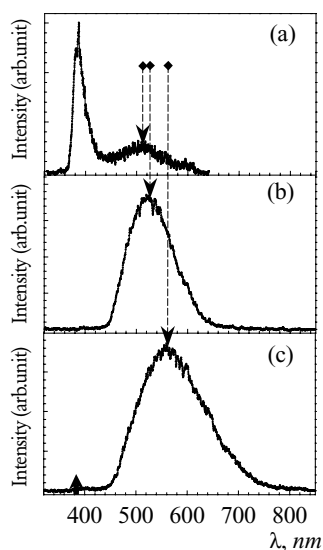**— Zn-hydroxide synthesized on nitrate technology (*C*-precursor);

Figure 5 Shift of VIS-band in ICL spectra of ZnO polycrystalline films grown on Zn-seeds in H_2O (a), KOH 5% (b), KOH 25% (c) using *B*-precursor.

and we explain this fact by the presence of at least three types of quenching centers. The shift of VIS-band may be explained by the change of type and quantity of quenching centers in the samples grown from solutions with different concentrations.

4. Conclusion
High quality bulk single crystals were grown from KOH+LiOH alkali solutions under hydrothermal conditions.

Low-dimensional ZnO crystalline powders were synthesized in polycomponent systems $Zn(OH)_2 - H_2O -$ AOH; $Zn(OH)_2 - H_2O - Zn - AOH$, where A is Li^+, K^+, with 100% yield of final product at temperatures 120–

250°C. Increase in temperature by 50–70°C results in the increase of the rate of crystallization process in 4–5 times. The powders consist of faceted microcrystallites (100 nm – 20 μm in size). Crystallites are faceted with the faces of monohedra (0001) and (000 $\bar{1}$), hexagonal prism $\{10 \bar{1}0\}$, hexagonal pyramid $\{10 \quad \bar{1}1\}$. The development of these faces is defined by the growth conditions. Crystal habit changes from prismatic to platy depending on solvent concentration. presence of impurity and temperature.

Polycrystalline films were obtained using Zn, Si, SiO₂ or ZnO as substrates.

The samples obtained were characterized by the methods of X-ray diffraction, SEM, ICL.

Spectra of ICL were registered for bulk single crystals, powders and polycrystalline films. Luminescent characteristics of ZnO depend on the growth conditions (type of precursor, solvent, Red/Ox potential) and they are different for powders and polycrystalline films ZnO obtained in the same run. The probable reason of such difference is the appearance of different quenching centers in the crystals obtained at different conditions.

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