Hydrothermal synthesis of oxide compounds

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Hydrothermal synthesis is widely used for growing oxide single crystals. The crystallization under hydrothermal conditions permits to vary thr Red/Ox conditions, temperature, pressure, the chemical composition of a medium on a wide scale. This technique enable to obtain both simple oxide materials with needed oxydation degree and complex oxygen-containing compounds. The present communication is, actually, a short review on synthesis and growth of some oxide materials under hydrothermal conditions based on the data obtained at the Institute of Crystallography, USSR Academy of Sciences.

Unlike crystal growth from solid phases, melts or flux, the synthesis of crystals from aqueous solutions at high temperatures and pressures provides quite a large set of crystalline phases. The specific feature of the hydrothermal synthesis is accounted for by both the composition of hydrothermal systems (the presence of a mineralizer) and the high temperatures and pressures applied which affect the kinetics of chemical processes. Changing the type of the mineralizer one can also vary the pH-Eh value of growth medium and chose the necessary Red/Ox regime for different compounds All these advantages of the hydrothermal technique permit one to vary within a wide range both extensive and intensive parameters of the experiments and to obtain in this manner a large number of solid phases using a comparatively small number of initial components

Oxide materials occupy a particular place in hydrothermal chemistry and hydrothermal crystallization. Large commercial single

crystals of silicon dioxide (quartz) are known to be the first oxide compound obtained by hydrothermal technique. Recently the stability fields and hydrothermal growth conditions have come known for a large number of different oxides - from the simplest ones (of the MO, M₂O₃, MO₂ types) to complex compounds of multicomponent systems.

Below we shall shortly describe the conditions for growing single crystals of some oxide materials.

Copper oxide, Cu₂O (cuprite)

The analysis of the Eh-pH diagram for the system $Cu-Cl-H_2O$ [1] leads to a conclusion that Cu_2O is a stable phase in feebly acidic, neutral and feebly alkalline media (Fig.1). The temperature rise decreases the stability field of Cu_2O as a result of the displacement of the equilibrium $Cu_2O - Cu^+$ into the region of neutral solutions:

 $2 \text{ Cu}^+ + \text{H}_2 \text{O} \implies \text{Cu}_2 \text{O} + 2 \text{ H}^+$

According to these data, a slightly acidic or a slightly alkalline solution may be used as a growth medium for Cu_00 [1].

The 200 cm³ - autoclaves with copper or silver cans were used for crystal growing (Fig. 2). The mass transfer increases with the increase of temperature, temperature gradient and mineralizer concentration. For different mineralizers the mass transfer of Cu₂O increased in the sequence $M_{\rm LiOH} < M_{\rm KOH} < M_{\rm NaCl}$ (Table 1). The growth rate of Cu₂O single crystals in NaOH solutions did not exceed 0.01 mm/day. The process follows the equation

$$Cu_{2}O + (2a-2)OH \implies 2CuO_{a}^{(2a-1)} + (a-1)H_{2}O$$

The Cu-containing alkaline solutions are characterized by low stability in respect to supersaturation (AT), and even a small variation of \mathcal{G} (AT) leads to a spontaneous crystallization of small Cu₂O crystals.

 Cu_2^{0} crystals can also be crystallized from slightly acid solutions(halogenides of alkali metals). The pH value of this solut: on was 4.5-5.5. At pH< 5.0 and at chlorine-ions concentration exceeding ~3 wt.%, copper chloride, CuCl, becomes a stable phase (Table 2).

From F, Br, J, Cl-containing solutions single crystals of cuprite were grown on seeds, the growth temperature was about 200°C, the temperature drop 20°C, the growth rate was 0.1 mm/day.

The hydrothermal method enables to obtain high-quality Cu_2O single crystals. The radiation of free exitons was determined for the first time on Cu_2O single crystals grown hydrothermally.

Optical characteristics of crystals obtained from different media show that optically better crystals are those grown from alkali metal hydroxide solutions.

Zinc oxide, ZnO (zincite)

Zincite crystals are grown from hydrothermal alkaline solutions (KOH, NaOH) doped with LiOH which affects crystal morphology, quality and growth rate. The growth of single crystals on seeds can be performed either at high [2] or at low [3] temperatures. The optimum conditions of crystal growth at low temperatures are as follows [3]:

crystallization temperature	260 - 290°C
temperature drop	40-50°C
KOH concentration	5-10 m
LiOH concentration	up to 1.5 m
seed orientation	(0001)

The type of the autoclave used for ZnO single crystal growth is shown in Fig.3.

Under the above conditions the growth rate along the [0001] polar axis is 0.1-0.25 mm/day which permits one to grow in long-term experiments bulk ZnO single crystals up to several cubic centimeters

in size (Fig.4). The crystals grown in these conditions are nonstoichiometric which is due to the reduction medium in the autoclave. Excessive zinc atoms (their number may reach $10^{15} - 10^{19}$ per cm³) occupy interstitial sites. The structure thus acquires some oxygen vacancies. The yellowish colour observed is due to the point defects and also to the presence of iron impurities. The above point defects are also responsible for high conductivity (which varies within the range 10^{-1} - 10^4 Ohm⁻¹cm⁻¹). Annealing in the presence of lithiu. salts at 700°C increases the resistivity up to 10^{11} Ohm · cm, providing thus a wide range of practical applications of this material. Some properties of synthesized zincite are given in Table 3.

Zincite single crystals are characterized by the maximum electromechanical coupling coefficient typical of nonferroelectrics. Piezoelectric properties of crystals are præserved in a wider temperature range than for other known materials (e.g. for quartz). This allows to use Li-doped ZnO crystals for designing efficient piezoelectric transducers operating at temperatures up to 1000 K. Synthetic ZnO crystals are also used as active elements in semiconductor electron-pumped lasers.

The lasing ZnO spectrum (Fig.5) has two lines at 375 and 383 nm with a halfwidth of 1.5-2 nm. The radiation power reaches 3-5 kWt in a 3-5 ns pulse at 80 K and at room ytemperature (at a voltage of 115 kV and electron beam density 60 A/cm² [3]).

Germanium dioxide, GeO2

Two polymorphs of GeO_2 (hexagonal one with \checkmark -quartz structure ty type and tetragonal with rutile structure type) can be obtained under hydrothermal conditions. In aqueous solutions hexagonal GeO_2 (high-temperature modification) transforms into a stable tetragonal

polymorph at T>150°C. According to the data on the behaviour of GeO₂ in aqueous solutions, feebly acid solutions were chosen for growing crystals, namely, alkali metal fluoride or ammonium fluoride solutions [7].

At the growth temperature (less than 150° C) the solubility of GeO₂ in weak fluoride solutions is practically the same as in pure water. Fluorine ions perform a role of a transport agent for Ge-O species.

The growth of \checkmark -GeO₂ occurs in the metastable region, according to the state diagram, and the growth is initiated by the introduction of a seed with the same structure type (\checkmark -quartz or \varpropto -quartz covered with a GeO₂-layer).

GeO₂ starts growing on the seeds with different crystallographic orientations: (0001), (1011), (0110) . No marked difference between the growth rates in different type of solvents (KF, NH₄F, RbF, LiF) with low concentration was noticed [7].

The best results were obtained on seeds cuy out from quartz crystals perpendicularly to the 3-axis. Worst quality material was grown on the seeds cut out parallelly to a large rhombohedron $\{10\overline{11}\}$ in LiF solutions. In this case the layer grown is of a bad quality and could be easily separated from the seed due to the weak adgesion with the substrate .

The sequence of growth rates for different faces was as following :

 $v_{(0001)} > v_{(10\bar{1}1)} > v_{(10\bar{1}0)} > v_{(10\bar{1}1)}$

The growth rate of the pinacoidal face (0001) was about 0.2 mm/day at $\Delta T \sim 7^{\circ}C$ (inside the autoclave) and it was ~ 0.04 at ΔT 2°C.

The morphology and growth mechanism of GeO_2 single crystals depends on the supersaturation in the growth zone and on the crystallographic orientation. At low supersaturation ($\mathbf{5}$ -0.1. Δ T 2°C)

for pinacoidal faces the specific cellular growth is typical ("cobbles"). The surface also shows round hills. For small rhombohedron the growth obeys the mechanism of layer growth.

At high supersaturation $(6\sim0.5)$ the morphology of different faces usually gives no information on crystellographic orientation of the growing surface. On the surface one can observe macrosteps and round vicinal hills with (or without) macrospirals. The hills with macrospirals are usually formed in the upper part of crystals (at vertical displacement of the seed) where the supersaturation of the solution is the highest. The step density goes fluently down from the upper to the lower part of the face . The polyhead growth is typical of pinacoidal faces. At V>0.2 mm/day the skeleton growth is observed.

Tellurium dioxide, TeO₂ (paratellurite)

Paratellurite (tetragonal TeO₂ modification) is of interest as a compound with very good piezoelectric and acousto-optic characteristics . TeO₂ single crystals can be obtained both by crystallazation from melt and by crystallization from hydrothermal solutions. Both techniques have their own advantages and disadvantages.

Under hydrothermal conditions paratellurite single crystals can be obtained from halogen-hygrogen acid solutions [8,9] the activity of acids in respect to the dissolution process and mass transfer of TeO₂ diminishes in the sequence:

HCl > HBr > HJ > HF

Paratellurite is highly soluble in these acids at rathe low temperatures. For example, the solubility of $T=0_2$ in 3% HCl is abou 2 wt.% at 200°C. The high temperature coefficient of solubility permits to obtain $Te0_2$ single crystals by direct temperature gradient method at temperatures 150-200°C. Low temperatures and

acid solutions allow to use transparent quartz autoclave for crystallization of TeO₂ (Fig.6).

The crystal growth takes place in chloride media, and Te passes into the solution in the form of different species: TeO(OH)^+ , TeO(OH)Cl, TeOCl_2 , TeOCl_3^- . The analysis of the data on solubility of TeO_2 in HCl-solutions showed that at 150°C main species of TeO_2 are TeO(OH)^+ (the concentration of HCl < 2.5 wt.%), TeO(OH)Cl(2.5-4 wt.%) and TeOCl_2 (>4 wt.%). This feature of dissolution of TeO_2 in HCl-solutions accounts for the possibility of growing simultaneously oxide TeO₂ and oxychloride $\text{Te}_6O_{11}Cl_2$ single crystals.

Only $\propto -\text{TeO}_2$ grows at $C_{\text{HCl}} < 1 \text{ wt.\%}$, only $\text{Te}_6 O_{11} \text{Cl}_2$ single crystals grow at $C_{\text{HCl}} > 6 \text{ wt.\%}$. In the intermediate region the growth of both phases is possible depending on the type of the seed (Fig.). At low temperature (150°C) and low fill degree the crystal growth c occurs in two-phase gas-liquid region. The crystallization at these conditions is similar to that from boiling solutions. The presence of gas bubbles promotes a better mixing of the solution. An important distinction of the process in two-phase region from classical hydrothermal crystallization from liquid phase is as follows. In the first case the increase of ΔT outside the autoclave may result in decrease of ΔT inside the autoclave due to the presence of gas bubbles and levelling of temperatures in the growth and dissolution zones.

Thus, at 100-200°C TeO₂ is stable at $C_{\rm HCl}$ 4 wt.%; at a higher concentrations the oxychloride of tellurium deposits, The growth rate of TeO₂ single crystals increases monotonously with the increase of HCl concentration up to 4 wt.%.

The conditions of stable growth of TeO_2 are : temperature 150-200°C ΔT 2 - 4°C HCl concentration 2.5-4 wt.% growth rate 0.05-0.3 mm/day.

Double oxides
$$ABO_4$$
 ($A^{3+} - Sb$, Bi, $B^{5+} - Nb$, Sb)

Double oxides ABO_4 where A - a 3-valent cation, B - a 5-valent one are interesting compounds as perspective pyroelectrics. Single crystals of these compounds were obtained by crystallization from mixed solutions containing H_2O_2 . Two different techniques were applied for crystal growth. They are : the classical hydrothermal synthesis at direct temperature gradient and the method of separation of nutrient components with the use of individual solvent [8].

Growth rates increase linearly with the increase of $C_{\rm KHF_2}$ (1 - 30 wt.%) and H_0O_2 (1-20 wt.%). The optimum growth conditions :

concentration of KHF	5-30 wt.%
concentration of H ₂ 0 ₂	5-6 wt.%
molar ratio Sb ₂ 03/Nb ₂ 05	1.3:1
volume ratio $V_{\rm KHF_2} / V_{\rm H_2O_2}$	2.5 : 1
temperature of dissolution zone	550°C
temperature gradient	1.2 deg/cm

Single crystals of $BiSbO_4$ were also obtained by the separation of nutrient components technique [8]. For Bi_2O_3 the solution KOH (8 wt.%) was used, for Sb_2O_3 the mixed solution KHF₂ (22 wt.%) + H_2O_2 (2.1 wt.%) was used as a solvent (Fig.9). The growth process follows the following scheme: dissolution of Bi_2O_3 and Sb_2O_5 in separate cells - transport of Bi- and Sb-species to the upper part of the autoclave - crystallization of double oxide $BiSbO_4$ in joint cell. The crystals grown shaped as prisms, maximum 3x4x18 mm in size.

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solution, concentration, wt.%		тос Дтос		mass transfer, g/day	crystal size, mm
LiOH	2%	300	35	0.15	1.0-1.5
LiOH	3%	300	35	0.20	1.0
NaOH	4%	300	25	0.13	0.1
NaOH	6%	300	35	0.9	1.5
NaOH	10%	200	40	0.3	3.0-4.0
NaOH	10%	250	50	1.0	2.0
NaOH	10%	300	60	3.0	2.5-4.0
NaOH	10%	350	75	3.5	2.0

Dependence of mass transfer and Cu_2O single crystals size on T, ΔT and solvent concentration (alkaline solutions) [1].

Table 2 Dependence of mass transfer and Cu_2O single crystals size on T, ΔT and solvent concentration (acidic solutions) [1].

goncen of X	ntration anion,	рĦ	T°C	∆t°c	mass transfer,	size of crystals,	Formation of X-con-
wt.%					g/day	mn	taining
							phase
F,	4	5.0	180	30	no	no	no
F ⁻ ,	4	5.0	200	30	0.15	4	no
F ⁻ ,	4	5.0	200	40	0.25	5	no
c1 ⁻ ,	2	5.3	275	50	0.5	22	no
01~,	3	5.1	300	50	1.05	4	no
c1 ⁻ ,	5	5.0	300	50	1.17	4	yes
Br ⁻ ,	3	5.1	300	50	1.1	4	уев
J ⁻ ,	3	5.1	300	50	0.2	1	yes

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Cherecteristics	Numerical value	Characteristics	Numerical value	
Sरू ₁	0.791	cFi	20.70	T
533	0.72	c.E.	20.95	
sT2	-0.33	ciz	11.77	
SE3	-0.235	cF3	10.61	1
355	2.23	c==	4.48	1
sE6	2.42	c ^E 6	54.46	I
s ^D 1	0.765	cP ₁	20.96	
5 ⁰ 3	0.56	c D ₃	22.1	1
SD2	-0.36	c12	12.04	ł
SP3	-0.17	cD ₃	10.13	
S-35	2.14	c ¹ / ₅	4.61	
ā31	-5.12	e31	-0.62	ł
ē33	12.3	e33	0.96	
₫15	-8.3	e15	-0.37	
<u></u> ¥31	0.181	٤ 7 1	8.67	
k33	0.466	٤33	11.26	
¥,15	0.199	٤ ^s	8.33	
k _t	0.229	٤ <u>5</u> 3	8.81	

Table 3 ZnO elastic, dielectric and piezoelectric constants at room temperature

<u>Cheracteristics:</u> elastic compliances S_{ik}^E · · 10 piezoelectric strain d_{ik} piezoelectric stress e_{ik} ²11 --2 10' m 1 1010 N ==-2 10-12 11 C-N-1 10 C•m-2



Fig. 1. Eh-pH diagram of the system Cu-Cl-H₂O at 300 C [1]. The activity of Cl⁻ anions is [1].





- Fig. 2. The scheme of the autoclave for Cu₂O single crystal growth. 1- plunger, 2- locking nut, 3- steel ring, 4- copper ring, 5- copper (silver) contact liner, 6- seeds, 7- baffle, 8nutrient.
- Fig. 3. The scheme of the autoclave for ZnO single crystal growing
 [5]. 1- autoclave body, 2silver insert, 3- copper glass,
 4- Teflon cap, 5- steel ring,
 6,7- baffle, 8,9- flanges, 10plunger, 11- bolt, 12- nut.



Fig. 4a





Fig. 4. Dependence of growth rate of ZnO single crystals on temperature (a) and on KOH concentration (b) [5]. C_{KOH} 5.15 m, C_{LiOH} 1.2 m;



Fig. 5. Lasing spectrum of ZnO single crystals [6].



Fig. 6. The scheme of the quartz reactor for visual observation of hydrothermal growth process [8].
1- corrugated cap (Teflon),
2- autoclave (fused quartz),
3- seeds, 4- baffles, 5-

heater.



Fig. 7. Growth rate of (010) $Te_6O_{11}Cl_2$ (1) and (102) α -TeO₂ (2) faces depending on HCl concentration [8].



Fig. 8. Growth rate of TeO₂ single crystals depending on supersaturation (growth in biphase region gas-liquid) [9].



Fig. 9. The scheme of the autoclave for ABO₄ single crystal growth [8]. 1,2- independent solution zones, 3- baffle, 4growth cell.