Hydrothermal growth of $A^{II}B^{VI}$ semiconductors

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Abstract. Hydrothermal method is used for growing ZnO, ZnS and HgS single crystals. This method is more advantageous compared to the other ones and enables one to obtain large bulky crystals of technically convenient habit with low concentration of defects. Some physical properties of these single crystals were studied and active elements for the new advanced piezoelectric, electro-optic and laser devices are reported.

Keywords. Semiconductors; hydrothermal growth; piezoelectric; electro-optic; laser devices.

1. Introduction

$A^{II}B^{VI}$ semiconductors—zinc oxide and sulphide, mercury sulphide—are widely known as the advanced materials for different fields of technology due to the combination of various physical properties. Interest in these compounds was stimulated in recent years by the development of new methods of growth and possibilities of studying more profound properties. Thus, detailed investigation of zinc oxide elastic and electric characteristics puts this material in the forefront among the possible high-temperature piezoelectrics. Cubic ZnS is a potentially useful material for optical shutters and electro-optical modulators. Cinnabar, or mercury sulphide, can be used where a combination of acousto-optical and piezoelectric properties is required. Piezoelectric modulus of Cinnabar is greater by an order of magnitude, than that of quartz while electromechanical coupling coefficient is two times larger. The acousto-optical interaction coefficient (M_2) for $\lambda = 632$ nm, and longitudinal wave propagating along the optical axis with 2.45×10^5 cm/sec rate, is 690×10^{-18} sec³/g. This value is comparable with that of TeO₂, used in optoacoustical devices. The large value of rotation of plane of polarization and other interesting properties of Cinnabar are also well-known.

The new prospects of technical application of the above materials demand good crystals and methods for obtaining them. The crystal should possess: high optical homogeneity, perfect structure and technically convenient habit. Traditional methods of growing ZnO, ZnS and HgS single crystals (from a melt, vapour phase, flux) do not always meet these requirements.

Thus, the Stockbarger's technique, developed for growing zinc sulphide from the melt at 50–200 atm. of inertial gas pressure (Shternberg *et al* 1962; Kuznetsov 1964; Ananiev 1968; Kozielski 1967; Sysoev 1972; Obuhova *et al* 1977) enables one to obtain large ZnS crystals up to 40 mm in size (Kozielski 1967), (this method is not practically used for ZnO and HgS because of high melting point and high vapour pressure at melting point), but crystals grown by this method are structurally inhomogeneous—containing a high concentration of packing faults and the combination of the cubic and hexagonal ZnS modifications (the cubic one being larger in proportion). Under

crossed polarizers the crystal produces a pattern of alternating dark and light lines, indicative of its optical inhomogeneity, making it impossible for use in electrooptics.

In spite of numerous attempts, the flux method failed to provide large bulky ZnO, ZnS and HgS crystals. For ZnO the slow cooling of zinc oxide solution in lead fluoride melt (Kashyap 1973; Nielson and Dearborn 1960) from 1150 down to 800°C enabled to obtain large, but very thin ZnO plates. The same results were obtained by the other workers (Wolff and Labelle 1965; Chase and Osmer 1967; Timofeeva 1965; Wanklyn 1970). Besides the "inconvenient" habit, the flux grown ZnO crystals are non-stoichiometric, extremely heterogeneous and contain high concentration of impurities and melt inclusions.

The flux method yields only small zinc and mercury sulphide crystals of several mm in size (Harsy 1968; Babansky *et al* 1971; Chernyshev and Babansky 1977; Laudise 1963; Mita 1962; Parker and Pinnel 1968; Linares 1968; Samelson and Brophy 1961; Garner and White 1970; Nistor *et al* 1980). As a rule they are very faulty, contain large amount of melt inclusions and have dendrite morphology. However, ZnS obtained by this method proved to be perfect enough. Practically, ZnS crystals, grown at 575°C (Nistor *et al* 1980), were cubic. This fact shows, that on the contrary to melt methods, ZnS crystallization at low temperatures (much lower, than wurtzite-sphalerite phase transition point (1020°), enables to obtain crystals with high structure homogeneity.

This is clearly revealed when ZnS crystallizes from a vapour phase. At crystallization temperatures higher than 1000°C (Iwanaga *et al* 1979; Scharowsky 1953; Park and Reynolds 1967; Dodson and Savage 1968; Nielson 1968; Hirose 1971) the crystals were characterized by the high packing faults concentration like the melt grown ones. Under polarized light they produce the clear pattern of dark and light lines similar to the melt grown samples. Crystals were small, and only at maximum temperatures (1500–1600°C) samples of length 30–40 mm and diameter 10 mm were obtained.

The lowering of the crystallization temperature below 1000°C (Neviantseva *et al* 1972; Rabadanov *et al* 1970; Piper and Roth 1953; Green *et al* 1958) significantly improves the perfection of the crystals—packing fault concentration falls drastically—and there are even some evidences of pure cubic ZnS formation at 770–900°C (Piper and Roth 1953). However, large bulky crystals more than several mm in size at such low temperatures could not be obtained.

All attempts to obtain cinnabar crystals from vapour phase resulted in growing of either faulty and apparently inhomogeneous crystals up to 7 mm (at 580–750°C), or rather perfect, but small 1–2 mm crystals (at temperatures lower than 344°C) (Brafman *et al* 1964; Brafman and Steinberger 1966; Rumiantsev 1965).

Much progress was achieved in developing methods for growing ZnO from the vapour phase—(Rumiantsev *et al* 1965; Alexander *et al* 1970; Lendway 1971; Sasaki 1975; Shichiri *et al* 1978; Russel and Woods 1979; Pashkovsky *et al* 1961; Carloon 1967; Pottor and Barnes 1978; Faile 1978). These methods are based either on oxidation of zinc chalcogenides by oxygen or water vapour (Pashkovsky *et al* 1961; Carloon 1967), or on oxidation of zinc vapour by oxygen (Lendway 1971) at 1150–1350°C. The latter enabled to obtain some ZnO crystals of 7×7 mm² in size (Shichiri *et al* 1978; Russel and Woods 1979), but the yield of crystals was small, and the samples were mainly needles with the length not more than 10 mm. Moreover as grown ZnO crystals are highly nonstoichiometric.

Thus, each of the above methods results in specific faults in the crystals. None of them meets the requirements specified above. Crystallization at relatively high

temperatures results in noticeable nonstoichiometry (for ZnO) and structural inhomogeneity (for ZnS, HgS).

Lowering of the crystallization temperature significantly improves the crystal quality, but the small dimensions exclude their wide practical application. It is difficult to choose a versatile method which enables growth of crystals for all applications, but in the light of earlier discussion, combining low crystallization temperatures with the possibility of obtaining large crystals seems to be the most advanced one.

The present work discusses growth of ZnO, ZnS and HgS by the hydrothermal method. Relatively low crystallization temperatures—200–400°C (*i.e.* much lower than their melting and phase transition points) enable one to reduce the amount of faults which are characteristic for high temperature samples. Moreover, by varying chemical crystallization conditions, it is possible to control the defect structure and stoichiometry and by continuing of the process it is possible to obtain large crystals. Thus, the hydrothermal method seems to be the most advanced one meeting all the requirements.

2. Methods

The hydrothermal method is based on the crystallization of a substance from overheated aqueous solutions at pressures (usually 100–2000 kg/cm²) (Michaelski *et al* 1979). The process is carried out in the special steel autoclaves. In the more often used variant of 'direct temperature drop' method the initial charge is placed in the lower part of the vessel, where the temperature is maintained higher, than in the upper part. The latter contains a seed crystal. Temperature drop (ΔT) between the zones of growth and dissolution leads to a convection inside the autoclave: in the lower zone, the solution gets saturated with the charge, heats up and moves to the upper zone. It cools here, becomes supersaturated and the excess substance condenses on the seed. The cooled solution goes down and the process repeats until all the initial charge is transferred to the upper zone. We have used this method in this work. The parameters that are varied: supersaturation (expressed in terms of supercooling ΔT for convenience), composition and concentration of the solution, seed orientation and temperature. The experiments have shown, that pressure was not significant in our cases, except in some special situations.

2.1 Growth of ZnO crystals

The growth was performed in KOH and NaOH solutions, where ZnO solubility reaches a significant value at elevated temperatures (Laudise and Caporaso 1964; Anamov *et al* 1972; Kuznetsov and Lobachov 1972; Kuzmina *et al* 1970). The solutions contained the adding of LiOH, which influenced the morphology, growth rates and quality (Laudise and Caporaso 1964). Optimum solution concentrations, crystallization temperatures and temperature gradients were found experimentally. The initial charge contained chemical ZnO agent and polycrystalline ZnO, hydrothermally synthesized beforehand. The first seeds were grown from the flux according to Kashyap (1973) and Nielson and Dearson (1960) and later on replaced by the hydrothermal ones. In some cases ZnO needles and plates, grown by gas transport reactions, were used as seeds. Our preliminary studies have shown, that growth of the crystal is fastest in the (0001) direction. So, the plates oriented parallel to (0001) planes, were used as seeds. The

temperature range under study was 200–450°C. Figure 1 presents the concentration dependence of (0001) plane growth rate for ZnO at $T = 270^\circ\text{C}$, $\Delta T = 70^\circ\text{C}$ (ΔT is measured along the outside autoclave wall). The exponential form of the curve is universal, *i.e.* is not influenced by temperature and temperature gradients.

Figure 2 presents (0001), (000 $\bar{1}$), (10 $\bar{1}$ 0) growth rates *vs* temperature for two temperature gradients ($\Delta T_1 = 50^\circ\text{C}$, $\Delta T_2 = 75^\circ\text{C}$) in 5.15 m KOH + 1.2 m LiOH solution. One can see that the growth rates increase with temperature, but their relationship decreases. The values obtained for critical supersaturation (expressed in terms of ΔT_{cr}), have shown, that ΔT_{cr} is minimum for (0001) plane, which grows noticeably at low supersaturations (Lobachev *et al* 1982).

Since the growth rates in KOH solutions are higher than in NaOH solution under similar conditions, KOH solutions were used. ZnO growth kinetics was not practically influenced by the pressure changes within 100–600 kg/cm², however the crystal quality declined significantly at lower pressures (< 100 kg/cm²). The above experimental data show that the large growth rates of ZnO (> 0.1 mm/day) can be achieved within the wide temperature and solution concentration ranges. For better understanding of the

Figure 1. KOH concentration dependence of (0001) plane growth rate for ZnO.

Figure 2. Temperature dependence of (0001) (curves 1, 1'), (000 $\bar{1}$) (curves 2, 2') and (10 $\bar{1}$ 0) (curves 3, 3') growth rates for ZnO. ($C_{\text{KOH}} = 5.15$ m/kg, $C_{\text{LiOH}} = 1.2$ m/kg, $\Delta T = 75^\circ$ and $T = 50^\circ$ for curves 1–3 and 1'–3' respectively.).

crystallization conditions cathodoluminescence study of variously grown ZnO crystals was performed (Lobachev *et al* 1977). The spectral analysis, mainly of the half-width of narrow resonance cathodoluminescence lines and the possibility of their resolution, shows, that the crystals grown at 250–300°C, with supersaturations corresponding to $\Delta T = 40\text{--}50^\circ\text{C}$ have better perfection (Laudise and Caporaso 1964; Kuzmina *et al* 1970; Lobachev *et al* 1982). The crystal perfection declines, when the temperature lies outside the above range.

Assuming all the experimental data, we have optimized ZnO growth conditions: crystallization temperature = 260–290°C, $\Delta T = 40\text{--}50^\circ\text{C}$, pressure $\sim 600\text{ kg/cm}^2$, concentration of KOH = 5–10 m, LiOH = up to 1.5 m. (0001) growth rate was 0.1–0.25 mm/day under these conditions, which enabled one to obtain bulky ZnO crystals of several cm^3 in size in the prolonged experiments. Figure 3 represents one of such crystals.

Despite the low crystallization temperatures, hydrothermal ZnO crystals, as well as other grown ones, are not stoichiometric enough, which might be conditioned among other reasons by the reductional medium inside the autoclave. The excess zinc atoms (their concentration may reach $10^{15}\text{--}10^{19}\text{ cm}^{-3}$), located in the interstitials, and oxygen vacancies are fixed in the crystals. These point defects are responsible for the light yellow colouration of the crystals (also caused by Fe impurity) and the elevated

Figure 3. Hydrothermal ZnO crystal (natural size).

conductivity; usual ZnO resistance lies within 10^1 – 10^4 ohm. cm. The annealing at 700°C in the presence of lithium salts (Laudise and Caporaso 1964) leads to a significant rise of resistance. Lithium doping during the annealing increases the resistance up to 10^{11} ohm. cm which broadens their practical application.

The hydrothermal growing of large, isometric ZnO crystals, enabled to make first evaluations of their elastic, dielectric, piezoelectric and laser properties (Croxall *et al* 1974; Heiland *et al* 1959; Tokarev *et al* 1975; Kurbatov *et al* 1980). Table 1 presents the complete set of elastic, dielectric and piezoelectric constants of ZnO at room temperature.

The measurements have revealed the unique feature of ZnO crystallization—the slight dependence of the elastic characteristics and the electromechanical coupling coefficients on temperature (figure 4). Thus, the average temperature coefficient values of the elastic constants proved to be equal within 300 – 700°C range. (in grad^{-1}): $T_{s_{11}}^E = 7.5 \times 10^{-5}$, $T_{s_{12}}^E = 5.4 \times 10^{-5}$, $T_{s_{55}}^E = 7.1 \times 10^{-5}$, $T_{33}^D = 12.3 \times 10^{-5}$, $T_{55}^D = -6.9 \times 10^{-5}$.

Coefficients of dielectric constants, measured at room temperature (in grad^{-1}), are:

$$T_{\epsilon_{11}} = 4.3 \times 10^{-4}, T_{\epsilon_{33}} = 4.4 \times 10^{-4}.$$

Electromechanical coupling coefficients of ZnO are the largest among all the known nonferroelectrics and are practically constant up to 1000 K. Thus, piezoelectric properties of ZnO are preserved in a wider temperature range than those of the widely used materials (quartz, for instance). It enabled to construct high effective piezoelectric

Table 1. ZnO elastic, dielectric and piezoelectric constants at room temperature

Characteristics	Numerical value	Characteristics	Numerical value
s_{11}^E	0.791	c_{11}^E	20.70
s_{33}^E	0.72	c_{33}^E	20.95
s_{12}^E	-0.33	c_{12}^E	11.77
s_{13}^E	-0.235	c_{13}^E	10.61
s_{55}^E	2.23	c_{55}^E	4.48
s_{66}^E	2.42	c_{66}^E	54.46
s_{11}^D	0.765	c_{11}^D	20.96
s_{33}^D	0.56	c_{33}^D	22.1
s_{12}^D	-0.36	c_{12}^D	12.04
s_{13}^D	-0.17	c_{13}^D	10.13
s_{55}^D	2.14	c_{55}^D	4.61
d_{31}	-5.12	e_{31}	-0.62
d_{33}	12.3	e_{33}	0.96
d_{15}	-8.3	e_{15}	-0.37
k_{31}	0.181	e'_{11}	8.67
k_{33}	0.466	e'_{33}	11.26
k_{15}	0.199	e'_{11}	8.33
k_t	0.229	e'_{33}	8.81

$$(s - 10^{-11} \text{m}^2/\text{n}, d - 10^{-12} \text{q/n}, c - 10^{-10} \text{n/m}^2, e - \text{q/m}^2)$$

Figure 4. Electromechanical coupling coefficients temperature dependence for ZnO. 1. k_{31} ; 2. k_{15} ; 3. k_i (Tokarev *et al* 1975).

sound transducers on lithium doped ZnO crystals, worktable up to 1000 K (Tokarev *et al* 1975).

ZnO active elements for semiconductor electron pumped lasers in uv range have also been designed (figure 5) (Kurbatov *et al* 1980). ZnO lasing spectrum presents two lines with 375 and 383 nm maxima and 1.5–2 nm halfwidth (figure 6). The value of the radiation power reaches 3–5 kW in 3–5 ns pulse at 80 K as well as at room temperature (voltage $U = 115$ kV, electron beam density $j = 60$ A/cm²).

Figure 5. Pumping current I and accelerating voltage V dependence of radiation pulse power P for sealed lasers (Kurbatov *et al* 1980).

Figure 6. Lasing spectrum of ZnO laser targets at liquid nitrogen cooling. (Kurbatov *et al* 1980).

ZnO laser with an output power about 300 W allowing filtering, has been constructed. The lasing was observed at liquid nitrogen cooling with threshold electron beam density $j = 60 \text{ A/cm}^2$ and voltage $U = 34 \text{ kV}$.

2.2 Growth of ZnS crystals

The wide stability zone of ZnS in hydrothermal solutions provides the fundamental possibility of usage of various media when crystal growing, which enables wide variation of physical-chemical crystallization conditions. Two procedures for ZnS growth are the most applied ones: in the extremely acid (H_3PO_4) and alkaline (KOH, CsOH) solutions. The comparison of the crystals, grown under such different conditions, enabled to evaluate the influence of physical-chemical parameters on the faults present.

ZnS crystallization in H_3PO_4 solutions was performed at $380\text{--}450^\circ\text{C}$ with H_3PO_4 concentration up to 50 mass %. The seed crystal fast growing plane (111) growth rate reached $\sim 0.15 \text{ mm/day}$, which enabled to obtain $2\text{--}3 \text{ cm}^3$ ZnS crystals in prolonged experiments. Lowering of H_3PO_4 concentration leads to diminishing of growth rates, and its increase provides an extremely reducing condition in the autoclave (due to H_2S intensive releasing, when dissolving of the initial ZnS charge), which results in increasing amount of defects. First of all it caused the intense colouration of the crystals.

ZnS crystallization study in KOH and CsOH solutions was performed within $350\text{--}420^\circ\text{C}$ range, at concentrations up to 10 m. Figure 7 presents KOH concentration dependence of ZnS (111) plane growth rate. The dependence is the same in CsOH solutions. Temperature slightly influences ZnS crystallization rate, which practically does not change at constant temperature and with KOH concentration more than $\sim 4 \text{ m}$ (figure 7). The crystal growth was performed at 380°C , KOH and CsOH concentrations $\sim 8 \text{ m}$, $\Delta T = 5\text{--}10^\circ\text{C}$. Under these conditions (111) growth rate reached 0.1 mm/day in KOH solutions and 0.07 mm/day CsOH solutions. We preferred to use CsOH solutions, because the crystals grown in them were more perfect, although the growth rate in CsOH solution was less. One such as-grown ZnS crystal is presented in figure 8.

Figure 7. KOH concentrational dependence of (111) plane growth rate for ZnS ($T = 380^\circ\text{C}$, $\Delta T = 8^\circ\text{C}$).

Figure 8. Hydrothermal ZnS crystal ($\times 4$).

Optical and cathodoluminescence studies have shown a substantial difference in the defect structure of variously grown ZnS crystals (Shalimova *et al* 1974a, b; Morozova *et al* 1979; Galstian *et al* 1980). First of all, it is visually revealed in the different optical homogeneity of the materials. H_3PO_4 grown ZnS crystals are more optically homogeneous and as a rule look isotropic under crossed polarizers. Alkaline grown ZnS crystals are usually anisotropic. The reasons for this lie mainly in the different way of oxygen impurity trapping. Indeed, the chemical analysis showed that oxygen impurity containment in KOH grown ZnS crystals reached 0.7 at .%, while in CsOH — ~ 0.3 at .% (the quantity of oxygen impurity is correlated with that of the alkaline metal: K enters ZnS up to 0.3 at .% facilitating oxygen trapping according to the volumetric compensation principle, while Cs^+ concentration does not exceed ~ 0.1 at .%). Oxygen impurity concentration in H_3PO_4 grown ZnS crystals does not exceed 0.4 at .%. Cathodoluminescence spectra provide more detailed information concerning ZnS defect structure. The most characteristic spectral features of various ZnS crystals are as follows:

335 and 415 nm radiation and the intense edge luminescence are characteristic for H_3PO_4 grown crystals. Such a spectrum is indicative of the high concentration of point defects, practically no packing faults, and oxygen impurity, concentrating mainly on the specific defects (radiation at 415 nm).

338 and 368 nm radiation and the weak edge luminescence are characteristic of KOH and CsOH grown crystals. 415 nm radiation is not present. Such a spectrum is indicative of an elevated oxygen impurity concentration (sometimes it precipitates in the form of microscopic Zn(S, O) solid phase inclusions), the very low point faults

concentration, but higher (in comparison with 'acid' samples) packing faults concentration (not exceeding 1 %). The elevated presence of oxygen impurity in 'alkaline' ZnS and its precipitation in the form close to $\text{Zn}(\text{S}, \text{O})$ solid solution result in the above mentioned optical inhomogeneity of such crystals (Morozova *et al* 1979). Since oxygen is less trapped in CsOH solutions, the crystals obtained are more optically homogeneous.

Besides optical homogeneity, the differences in ZnS defect structure are revealed in some other properties also. Thus, the elevated point defects concentration in acid grown samples is responsible for their higher photoconductivity and lower resistance in comparison with alkali-grown samples ($\sim 10^{10}$ Ohm/cm against $\sim 10^{12}$ Ohm/cm). Acid grown samples are mainly greenish-brown, while alkaline grown ones are colourless and transparent within 0.23–12 nm (Shamburov *et al* 1970). All these distinctions are significant for usage of ZnS as electro-optic material.

Figure 9 presents the typical light transmission curves of 'alkaline' (111) ZnS cuts at transverse electro-optic effect under crossed polarisers *vs* voltage V (Shamburov *et al* 1970). One can observe the initial light transmission, characterizing optical homogeneity of the crystals, to be about 1.5–2 %. The measured halfwave voltage is ~ 10.5 kV at 630 nm and falls to ~ 8.5 kV at 500 nm (figure 10). The residual voltage of 'acid' crystals is lower than that of 'alkaline' ones, but the halfwave voltage varies from ~ 8 to ~ 15 kV. The latter might be conditioned by the screen effects due to the electric field application and higher mobility charge carriers in such crystals.

Thus, on account of the homogenous nature of ZnS obtained by hydrothermal method, the crystals can be used in optical shutters and light modulators within 0.4–13 nm. Note, that cubic ZnS, on the contrary to uniaxial crystals, enables to create wide angle modulators, necessary, *e.g.* in convergent beams modulation. So, it is possible to obtain 100% modulation depth for the beam converging at 12° , when applying the transverse electro-optic effect in (110) cut at $\langle 1\bar{1}0 \rangle$ field orientation; the crystals were 4 and 0.4 mm in light and field directions respectively (Shamburov *et al* 1970).

ZnS transparency in uv region enables their effective usage for overfrequency

Figure 9. Light transmission curve for transverse electro-optic effect in ZnS crystal (111) cut when crossed polarizers. The curve looks like a "butterfly" hysteresis loop (Shambunov *et al* 1970).

Figure 10. Wave length (λ) dependence of halfwave voltage $V_{\lambda/2}$ and electrooptical coefficient r_{41} (Shamburov *et al* 1970). 1. $V_{\lambda/2}$ (λ); 2. the extension of curve 1 linear part; 3. r_{41} (λ); 4. the curve 3 extension, corresponding to curve 2; 5, 6, 7, 8— r_{41} (λ) for natural ZnS.

Table 2. Optical characteristics of ZnS and ZnSe.

λ nm	$M_{\omega} \cdot \tau_{\lambda} \%$	
	ZnS	ZnSe
0.44	16	—
0.53	17	16
0.63	18	21

τ_{λ} —modulation depth; M_{ω} —crystal transparency.

modulation of the radiation with < 0.5 nm (Kuznetsov *et al* 1980). Table 2 compares the characteristics of ZnS and ZnSe, widely used for this purpose now. At 0.53 nm ZnS is more effective than ZnSe, and below 0.53 nm ZnSe is not used because of high absorption. So, ZnS enables to perform overfrequency modulation of the radiation with $\lambda < 0.5$ nm.

The spectra of electron pumped ZnS lasing have been studied (Kurbatov *et al* 1980). Laser target resonators have been specially made by spalling along the cleavage plane. Minimum ZnS lasing voltage was 40 kV at threshold electron beam density of 11 A/cm². A set of lines within 330–337 nm range with the most intensive one at 336 nm (~ 1.5 nm halfwidth (figure 11) was fixed in the lasing spectrum. The radiation power was 500–700 W in 3–5 ns pulse at 80 K. The lasing parameters are indicative of the high laser quality of ZnS, radiating in the most shortwave range in comparison with other known materials.

2.3 α -HgS crystallization

Unlike ZnS, the narrow stability zone of cinnabar substantially limits the solvents selection for crystal growth (Kuznetsov *et al* 1973; Tondic *et al* 1972). Rather intensive HgS recrystallization (without decomposition) was found to occur in sodium and potassium hydrosulphide solutions with pH 9–13 (Efremova *et al* 1976). HgS solubility

Figure 11. Lasing spectrum of ZnS laser targets at liquid nitrogen cooling (Kurbatov *et al* 1980).

Figure 12. α -HgS solubility within 8.5–12.5 pH range in NaHS solutions of different concentrations (Efremova *et al* 1976).

study in NaHS solutions enabled to choose two pH zones (figure 12): the one, where HgS solubility does not depend on pH (9–11.5), the other, where solubility rises when pH increases (pH > 11.5). Such solubility behaviour is conditioned by various compositions of the Hg complexes formed in solution (Efremova *et al* 1982).

Table 3. Growth rates of HgS on (0001) and (1010).

Solution	pH	V (mm/day)	
		(0001)	(1010)
$\text{Na}_2\text{S} + \text{H}_2\text{S}$	9–11	0.5	0.3
$\text{Na}_2\text{S} + \text{H}_2\text{S}$	12–13	0.1	0.05
$\text{Na}_2\text{S} + \text{NH}_4\text{Cl}$	12–13	0.05	0.02
$\text{Na}_2\text{S} + \text{NaHCO}_3$	12–13	0.2	0.07

(Temperature – 280°C; ΔT – 30°C)

Assuming the solubility data, cinnabar crystallization in NaHS solutions was performed within 9–11 and 12–13 pH intervals. The solutions with such pH values were obtained by: the saturation of Na_2S solution (pH > 13) with hydrosulphide, by addition of ammonium chloride or sodium bicarbonate or both to Na_2S solution. The latter was used for preparing only of 12–13 pH solutions. Table 3 presents HgS (0001) and (1010) growth rates in these solutions.

In Na_2S solutions, saturated with hydrosulphide up to pH = 9–11, HgS growth rates did not exceed 0.05 mm/day. At the same time, as-grown crystals were usually defective, with large amount of gas-liquid inclusions and obvious columnar crystallization traces. Moreover partial decomposition of HgS was sometimes found under these conditions, apparently due to the low redox potential, when considerable hydrosulphide was saturated into the initial Na_2S solution.

Within 12–13 pH interval cinnabar growth rates are noticeably higher in the same ($\text{Na}_2\text{S} + \text{H}_2\text{S}$) solutions; the amount of gas-liquid inclusions starts decreasing and columnar crystallization traces start vanishing. However, it was not always possible to avoid partial HgS decomposition. Moreover, saturation of Na_2S with hydrosulphide solution is rather technically complicated. So, in subsequent experiments we added ammonium chloride or sodium bicarbonate to Na_2S solutions to reach a pH of 12–13. In the first case HgS growth rate was lowered (see table 3). HgS decomposition with the formation of metallic mercury was found in none of the experiments. When sodium bicarbonate was added to Na_2S solution, the growth rates, on the contrary, increase, but HgS decomposes, indicating the considerable redox conditions change inside the autoclave in the presence of sodium bicarbonate. The best results were obtained using $\text{Na}_2\text{S} + \text{NH}_4\text{Cl} + \text{NaHCO}_3$ solutions (pH = 12–13). The growth rates in these solutions reached 0.1–0.15 mm/day without HgS decomposition. As-grown HgS crystals were 1.5 cm in size (see figure 13).

The samples of necessary orientation and shape for piezoelectric, elastic and dielectric constants measurements were made from the grown crystals. The bars and plates cut from the pure crystal did not exceed $4.8 \times 2.5 \times 1.5$ (–1.8) mm and $6 \times 4 \times 1.1$ mm in respective size. Maximum dimensions of the parallelepipeds were of $6 \times 4 \times 5$ mm³.

Piezoelectric properties of α -HgS are described by two independent moduli d_{11} and d_{14} . The resonance-antiresonance method was used for their measurements. The compression-tension oscillations of X-cut bar with the length along Y, excited by X-directed electric field and countour shear and thickness shear vibration of Y-cut plates were measured at room temperature.

Figure 13. Cinnabar (α -HgS) crystal, grown in the sulphide-chloride carbonate solution ($\times 2$).

The independently measured values of the electromechanical coupling coefficients and dielectric constants enabled to calculate the effective values of piezoelectric moduli d_{ik} .

The velocities of ultrasonic wave propagation along various crystallographic directions were measured by the pulse ultrasonic method. It enabled to calculate the effective value of elastic modulus and all its six independent constants, characterizing the elastic constant tensor of a crystal.

Table 4. Dielectric, elastic and piezoelectric constants of cinnabar and quartz crystals

Cinnabar	Quartz		
Piezoelectric modulus, 10^{-12} k/n	Our data	<i>a</i>	<i>b</i>
	$d_{11} = -21.3$	-19.0	-2.25
	$d_{14} = 15.43$	+2.0	+0.86
Elastic compliances, 10^{-12} m ² /n	$s_{11} = 42.82$	41.0	12.79
	$s_{12} = -17.8$		-1.535
	$s_{13} = -4.31$		-1.1
	$s_{14} = -32.2$		-4.46
	$s_{33} = 21.11$		9.56
	$s_{44} = 80.75$		19.78
	$s_{66} = 121.24$		28.65
Dielectric constants	$\epsilon_{11}^T = 17.6$	18.2	4.58
	$\epsilon_{33}^T = 27.8$		4.7

^a Data from Jaffe and Berlincourt (1965); ^b Physical acoustics (1964) data.

Table 4 presents the dielectric, elastic and piezoelectric constants. The analogous data for widely used quartz single crystals of the same modification and some literature data on constants (Physical Acoustic data 1964; Jaffe and Berlincourt 1965) are also given in the table.

α -HgS piezoelectric moduluses are almost an order of magnitude larger, than that of quartz. As for elastic properties, one can see their strong anisotropy. The crystal is soft, its Young's moduli ($E_{11} = s_{11}^{-1}$) and ($E_{33} = s_{33}^{-1}$) are 3.34 and 2.22 times less, than those of quartz. Note, that for HgS E_{33} is nearly two times larger than E_{11} .

Conclusions

For ZnO, ZnS and HgS crystals the hydrothermal growth method is preferable to high temperature methods. The main advantages offered by hydrothermal method are low crystallization temperatures and the possibility to realize prolonged growing cycles when using the oriented seeds. It enables to obtain convenient bulky crystals with low concentration of defects, characteristic for high temperature methods. For ZnS and HgS hydrothermal method seems to be the only convenient route for obtaining low-temperature modifications of these materials with homogeneous crystal structure. Appropriate techniques were developed and large single crystals of ZnO, ZnS and HgS, useful in piezoelectric, electro-optic and laser devices, were grown.

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