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Holmium polysulfides: crystal growth, structure and properties

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Abstract

Crystals of holmium polysulfides, up to 3×2×1.5 mm in size, were grown by spontaneous crystallization from melted KI. A diversity in morphology was observed from thin transparent plates to polyhedrons with mirror-like surfaces. For crystals of different forms, the composition was determined, and density as well as refractory index was measured. Several phases crystallized, two of which were characterized using single-crystal X-ray diffraction as $HoS_{1.885(5)}$**(I)**, tetragonal, $P4/nmm$, $a=3.820(1)$, $c=7.840(3)$ Å, $V=114.40(6)$ Å^3, $Z=2$, $d_{cal}=6.542$ g/cm^3 and $HoS_{1.863(8)}$**(II),** monoclinic $P2_1/m$, $a=10.961(2)$, $b=11.465(2)$, $c=10.984(2)$ Å, $\beta=91.27(3)°$, $V=1380.0(4)$ Å^3, $Z=24$, $d_{cal}=6.486$ g/cm^3. Raman spectra reveals the characteristic band, corresponding to $S^-–S^-$ pair vibrations in the polyanionic layer. Crystals are transparent in the 0.65–25 μm spectral range, the bands with a fine structure in the transparency region being related to Ho^{3+}. The shortwave absorption edge is described by an exponential law (Urbach's rule) due to tails of state density for conduction and valence bands. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Holmium polysulfides; Crystal growth; Structure; Optical properties

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1. Introduction

The renewed interest in sulfides, including polysulfides of rare earth (RE) elements, is associated with their wide transparency range from visual to mid-IR and unextended phonon spectrum ($\nu<400$ cm^{-1}), which allows us to use them as active media of solid-state lasers operating beyond the 4 μm limit, where traditional laser matrices based on oxides and fluorides are ruled out [1]. A 'rule-of-thumb' indicates that to achieve acceptable quantum efficiency for emission from a given energy level, the energy gap to the next lowest level must span at least 4–5 (maximal energy) phonons [2]. Thus, for sulfides the spectral range until 6–6.5 μm is available and, indeed, room temperature laser action at 4.3–4.4 μm was already demonstrated in Dy:$CaGa_2S_4$ [3]. The advantage of RE sulfides and polysulfides is that they can be easily doped by other RE ions, they are non-hygroscopic and much more stable compared with chlorides as Pr:$LnCl_3$, where laser action at the record wavelength as 7.3 μm was realized [2,3].

A set of papers has been devoted to the study of polysulfides of RE, their structure and composition. In contrast to compounds containing light RE metals such as La, Ce, Nd et al., which form stoichiometric disulfides, the heavy RE polysulfides are not stoichiometric as was already shown for Dy and Er and thus their structure are different from that of disulfides [4,5]. In this work the attention has been focused to holmium polysulfides as representatives of heavy RE polysulfides. For preparation of holmium polysulfide crystals the method of spontaneous crystallization from a flux has been chosen since the synthesis from melted polysulfide is hardly possible because of the high melting point of polysulfides and high pressure of sulfur at these temperatures. The products of crystallization have been characterized and experimental results are discussed here. Some physical properties of holmium polysulfides are given in the present paper for the first time.

2. Experimental

2.1. Crystal growth

Solubility of holmium polysulfides in different fluxes was qualitatively estimated by watching the changing of a HoS_{2-x} crystal mass after keeping it in melted solvents at different temperatures. Solubility was found to decrease as

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$Na_2S_2 > Na_2S_{2,8} > Na_2S_4 > KCl > KI$. The triple compounds crystallized in the HoS_{2-x}–Na_2S_n system, and their formation was shown to occur through chemical interaction in solution. The halogenides were shown to be inert to holmium polysulfides.

KI with $T_{melt.} = 700°C$ was chosen for growing holmium polysulfide crystals by spontaneous nucleation from a flux. The technique combines synthesis of polysulfides and recrystallization from a flux. The δ-Ho_2S_3, rhombic S and KI were taken as starting compounds. The ampoule was 14 cm in a length and 2.8 cm in a diameter. The KI: Ho_2S_3 mass ratio was 10:1. Sulfur quantity was taken as needed for $Ho_2S_3 + 2S \rightarrow 2\ HoS_2$ reaction and to provide pressure of saturated vapor at 700°C, based on data of saturated sulfur pressure density [6]. Sulfur pressure was accounted to be about 16.4 atm. We suggest this pressure is enough to obtain the highest polysulfide without crushing quartz ampoule under these conditions. The temperature was 700 and 714°C for the cold and hot ends, respectively. Duration of crystallization of holmium polysulfide crystals was 4 weeks. Cooling was going at the 2°/h rate up to 690°C at the hot end, followed by further cooling in a switched-off furnace. The final product was treated by water for removing KI and boiled in toluene for extracting the sulfur, then washed with hot toluene and dried in the air. The crystals were characterized by morphology, size, color, chemical composition, crystal structure and spectroscopical properties. The refractory index was measured. Some details of experimental techniques are given below.

2.2. Characterization techniques

Micrographs of crystals were obtained using an optical microscope Nu-2E VEB Carl Zeiss Jena.

For determination of the composition the atomic emission spectroscopy with inductively-coupled plasma (ICP) was used. The weights 6–25 mg included one or several individual crystals (Table 2). The crystals were dissolved in $HNO_3 + Br_2$ mixture to convert all the sulfur (S^{2-} and S_2^{2-}) to SO_4^{2-}, and the contents of three elements, S, Ho and K were obtained.

Structural investigation was carried out for single crystals. Experimental set of intensities was obtained with the diffractometer Enraf Nonius CAD-4 by a standard technique (MoKα, graphite monochromator, consideration of absorption by transmission curves at azimuthal scanning of reflections, $2\theta_{max} = 70°$). $R = 0.0520$ for 184 $I_{hkl} > 2\sigma_I$ independent reflections from 979 I_{hkl} measured ones for the crystal **(I)** and $R = 0.0596$ for 5354 $I_{hkl} > 2\sigma_I$ independent reflections from 5354 I_{hkl} measured ones for the crystal **(II)**. Details of the technique have been discussed in [7]. Powder diffractograms were calculated by means of the program 'Polycrystall' [8] based on these data. The experimental diffractograms made from the ground crystals were obtained using the DRON-3 X-ray diffractometer with $\lambda = 1.5425$ Å and CuKα/Ni filtered radiation. They were compared with those calculated.

Densities were measured by the micro-burette technique with using ethanol as a liquid for measurements. The weights of 1–25 individual crystals, not less than $0.3 \times 0.3 \times 0.3\ mm^3$-sized, were from 7 to 23 mg. The accuracy was not less than $0.04\ g/cm^3$.

Raman spectra were recorded for individual crystals with a Triplemate, SPEX spectrometer equipped with a CCD camera in back-scattering geometry. The 632.8 nm, 50 mw line of an He–Ne laser was used for the spectral excitation. The IR absorption spectra were recorded both for powder of holmium polysulfides mixed with CsBr using the Bomem MBP-102 Fourier spectrometer and for holmium polysulfide crystals using the Comem Fourier transform spectrometer. The absorption spectra in the visible to near IR spectral region were obtained using set-ups based on diffraction MDR 2 monochromator with an incandescent lamp as a light source and cooled FEU-83 photomultiplier as a detector. The luminescence tests were made using a Hg 100 W lamp through color glass filters.

3. Results and discussion

3.1. Morphology and color

The crystallization product consisted of fine crystalline powder and crystals of different forms and up to $3 \times 2 \times 1.5\ mm^3$-sized. The total output of crystals was about 65 mass.%, about 30 mass.% among them being mm-sized crystals. The color of the powder changing from cherry to brown suggested the formation of polysulfides.

Microscopy studying showed that crystals looked like plates of different thickness having a form of whole or truncated rectangles or squares, stretched sharp-end pentagons (Fig. 1a) and 'spades' (Fig. 1b) or they represented bulk polyhedrons with, often truncated, rectangular or square extended side (Fig. 1c). Part of the crystals was observed to be splices or druses where different forms were mixed (Fig. 1d). The length of crystals from the second and the third group did not exceed 1.5 mm.

The crystals were observed to be as transparent as opaque. The color of thin transparent plates changed from yellowish-orange to deep cherry at a thickness increase up to ~40 μm. Opaque crystals were gray-colored with metallic luster and possessed mirror surfaces of the extended side. It was shown previously for the RE polysulfides that it was the side parallel to which S_2^{2-} layers lay [9].

When looking at lateral faces one could see that crystals were formed from a pile of layers. And at the smooth, at the first glance, the extended surface of thin transparent film steps of growth are clearly observed (Fig. 2). Evidently, disappearance of transparency is connected with the increase of defectness when the thickness grows since grown crystals are formed from layers.

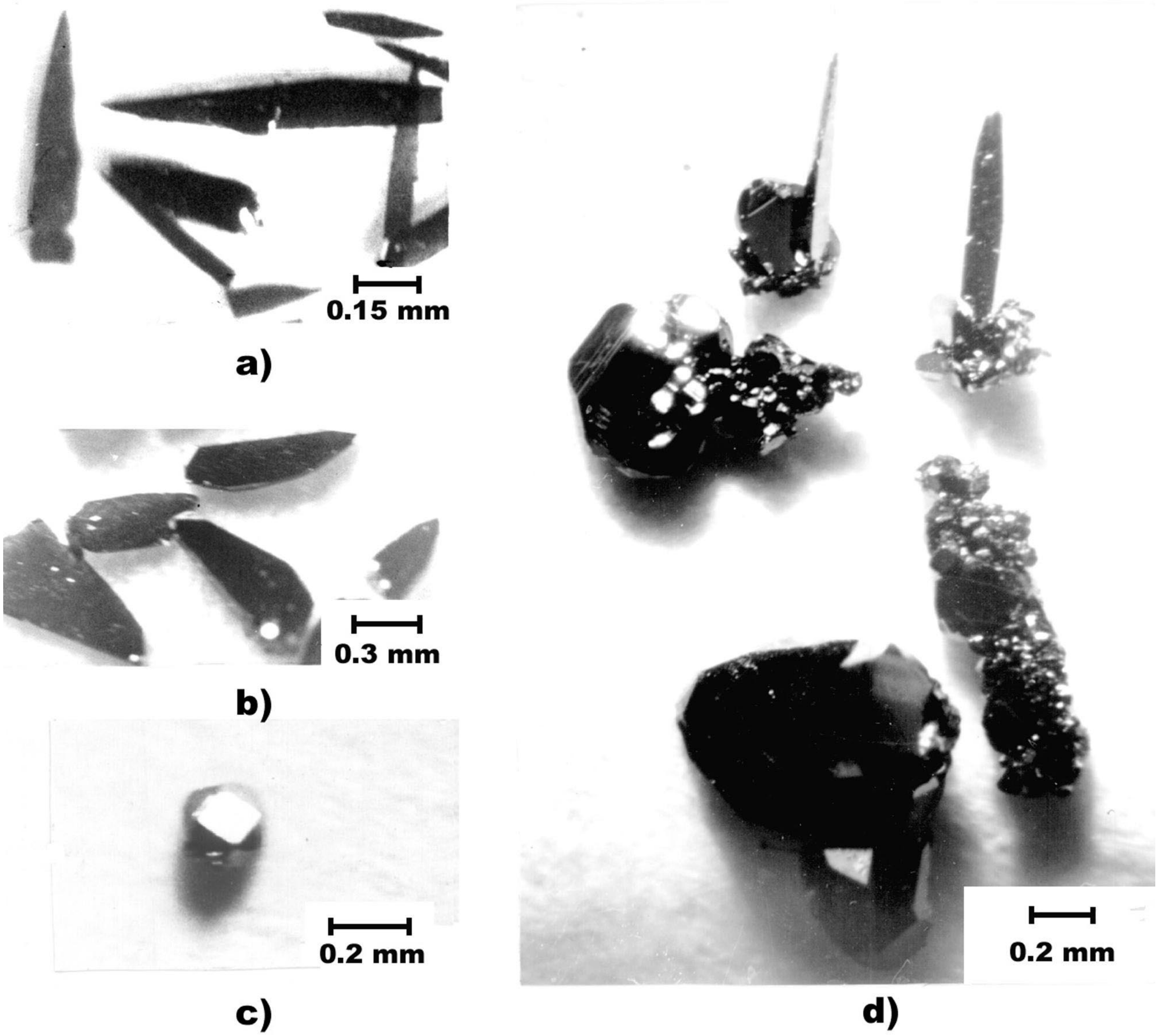

Fig. 1. Different morphology of holmium polysulfide crystals: (a) pentangles; (b) spade-like; (c) with square developed side and (d) splices and druses.

3.2. Structural characterization

To select single crystals meeting the requirements of single-crystal study was not a simple task because most of the crystals were of low quality, namely, they showed polycrystallicity, growing steps, twinning. From 30 to 50 crystals only 1 or 2 are suitable for these requirements. For two selected single crystals the structures were solved. From these structural studies the compositions were calculated to be $HoS_{1.885(5)}$(I) and $HoS_{1.863(8)}$(II) [7]. The first crystal had a form of thick square plate ($0.16\times0.24\times0.24$ mm^3), and its structure was established as tetragonal $P4/nmm$ with the cell parameters $a = 3.820(1)$, $c = 7.840(3)$ Å and $Z = 2$. The second one had a form of a thin transparent rectangular plate ($0.08\times0.14\times1.20$ mm^3), and the structure was determined as monoclinic $P2_1/m$ with the cell parameters $a = 10.961(2)$, $b = 11.465(2)$, $c = 10.984(2)$ Å, $\beta = 91.27(3)°$ and $Z = 24$. Atom coordinates are represented in Table 1.

It was shown previously [9] that structures of all the RE polysulfides have the structural type of the PbFCl [10] or anti-type of the Fe_2As [11] minerals, as the basic ones, with different orientation and parameters related to the parent substructure. The structure of RE polysulfides contains the common structural fragment $[LnS]^+$ which is a 4-layered package, consisting of alternating square nets . . . -[Ln — S — S — Ln]- . . . . Coordination of both of the atom sorts in the package is close to a tetragonal pyramid. The second layer, the so-called polysulfide layer, is a variable structural fragment. In contrast to disulfides having this layer consisting only of covalent connected sulfur atoms pairs $(S_2)^{2-}$, in polysulfides the conversion of a part of the pairs $(S_2)^{2-}$ to S^{2-} takes place, what results in changing (increasing) the cell parameters [9].

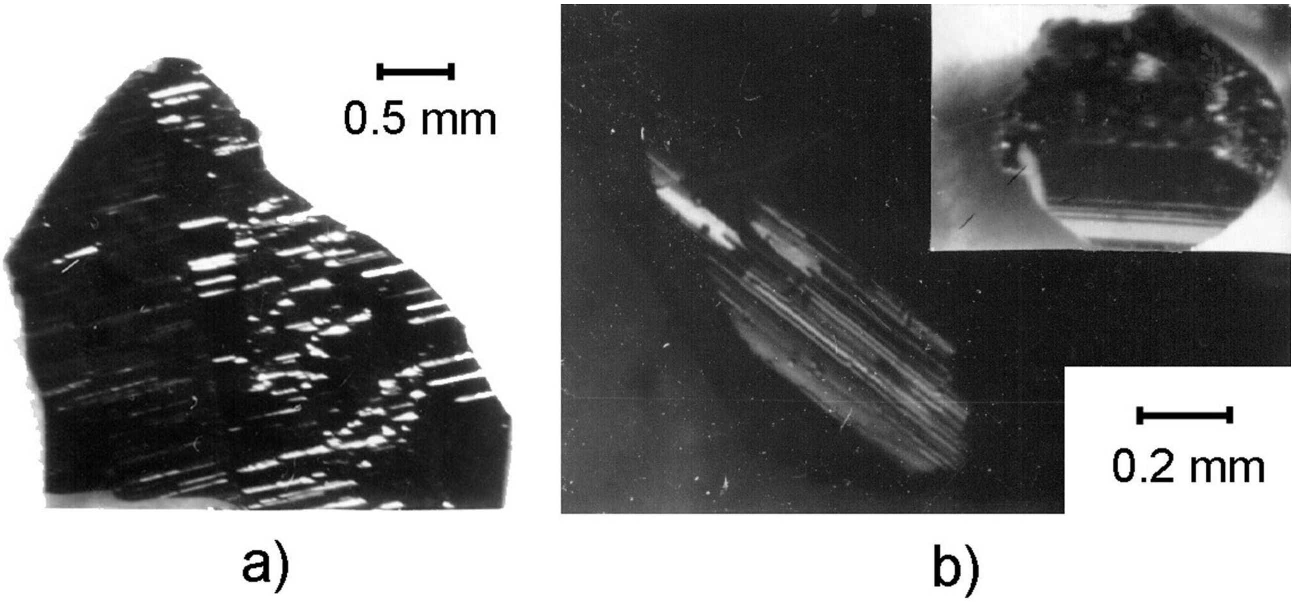

Fig. 2. Growth steps at deep red plate ($d = 35$ μm) (a) and lamination at the lateral side of bulk crystals (b).

Table 1
Atoms coordinates ($\times 10^4$) and equivalent thermal parameters (Å$\times 10^2$) for the crystals **(I)** and **(II)**

Atom	x	y	z	$U^{*}_{eq.}$	N	s.o.f.**
Crystal **(I)**						
Ho	2500	2500	2730(2)	18(1)	2	0.125
S(1)	2500	2500	6354(6)	11(1)	2	0.125
S(2)	2500	7500	0	83(6)	2	0.1108
Crystal **(II)**						
Ho(1)	8009(1)	2500	5667(1)	8(1)	2	0.5
Ho(2)	3399(1)	2500	313(1)	8(1)	2	0.5
Ho(3)	3189(1)	5826(1)	534(1)	8(1)	4	1
Ho(4)	9311(1)	7500	1888(1)	8(1)	2	0.5
Ho(5)	5691(1)	5835(1)	3119(1)	8(1)	4	1
Ho(6)	8361(1)	5855(1)	5405(1)	9(1)	4	1
Ho(7)	4272(1)	7500	−2974(1)	8(1)	2	0.5
Ho(8)	9220(1)	4143(1)	2047(1)	10(1)	4	1
S(1)	7510(3)	5834(2)	1234(3)	7(1)	4	1
S(2)	7416(3)	4172(2)	3817(3)	8(1)	4	1
S(3)	2440(3)	7500	−1205(3)	7(1)	2	0.5
S(4)	5031(3)	5852(2)	−1246(3)	8(1)	4	1
S(5)	4866(3)	7500	1418(3)	7(1)	2	0.5
S(6)	9901(4)	2500	3854(4)	13(1)	2	0.5
S(7)	10094(3)	5814(2)	3627(2)	8(1)	4	1
S(8)	7520(4)	7500	3768(3)	7(1)	2	0.5
S(9)	8160(3)	2500	8196(3)	8(1)	2	0.5
S(10)	6915(3)	4553(3)	6922(3)	15(1)	4	1
S(11)	5456(4)	2500	5473(3)	9(1)	2	0.5
S(12)	515(3)	9352(3)	510(3)	18(1)	4	1
S(13)	9045(5)	7500	8900(8)	34(1)	2	0.439(8)
S(14)	5884(3)	5857(3)	5909(3)	15(1)	4	1
S(15)	8117(20)	6387(20)	8027(20)	52(2)	4	0.497(8)
S(16)	7629(10)	7500	7334(10)	23(2)	2	0.240(10)

*$U_{eq} = 1/3(U_{11} + U_{22} + U_{33})$, **s.o.f. = statistic occupancy factors.

Thus, for the two investigated phases, the tetragonal (T) structure practically repeats the parent structure, while the monoclinic (M) structure is a derivative one. The connection of their unit cells parameters is realized according to the matrix (M) = 20–1| 030 | 201 (T). Fig. 3 demonstrates the correlation between unit cells of these two structures.

Comparison of powder diffractograms, experimental and calculated, shows that they could be attributed to the structure $HoS_{1.863}$ and not exclude a possibility of the presence of the $HoS_{1.885}$ phase. In comparing to X-ray powder data for the tetragonal $HoS_{1.67-1.72}$ ($a = 7.66$, $c = 7.84$) [12] the observed d_{hkl} values correspond closely to them. This finding leads us to the conclusion that powder diffractograms of these related structures hardly may serve for a precise identification for individual phases if they are in a mixture. The X-ray powder diffraction patterns, experimental and calculated for both phases are presented in Fig. 4.

The authors noticed, that the same parameters were measured for several crystals, but the dependence on a form of crystals was not observed.

3.3. The composition and density

The results obtained using the ICP technique leads to several compositions presented in Table 2. The content of K^+ which was determined for these weights varied from 0 mass.% in thin plates up to 0.14 mass.% in bulk crystals (see Table 2). Since the composition does not distort essentially because of impurities or inclusions, such as S, KJ or KS_x one can speak about three compositional phases with high, middle and low content of sulfur. The highest compositions do not seem to be right coming from the

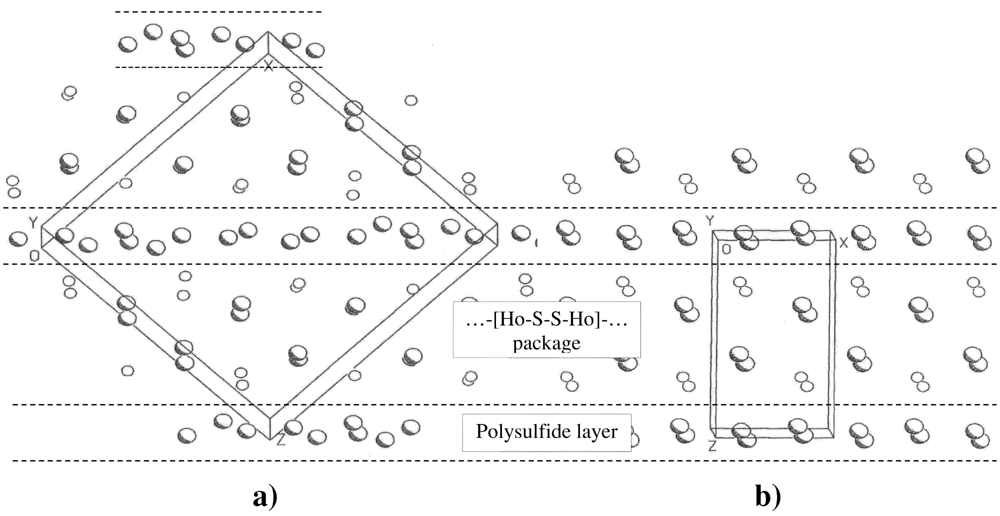

Fig. 3. Clinographic representation of $HoS_{1.863}$ (a) and $HoS_{1.885}$ (b) structures with comparison of their unit cells. ◯ – S, ○ – Ho.

suggestion that polysulfides of the heavy RE cannot exceed the composition $Ln_2S_{3.80}$ [13]. What is concerned is the middle compositions, they repeat the compositions found for Gd, Dy, Er [14,4,5] and are close to the structural data for holmium polysulfides. About the low compositions there is information in [12].

Experimental density values were within the range 5.95–6.40 g/cm^3 for different crystal weights, while the calculated values for the determined structures were found to be higher, i.e. 6.542 and 6.486 g/cm^3 for tetragonal and monoclinic phase respectively. Consideration of the known potassium content coming from K_2S_x or KI results in the changing of density values not more than in 0.04 g/cm^3 does not exceed the experimental error. The density values were most frequently concentrated near 6.16; 6.21 and 6.26 g/cm^3. The value 6.40 g/cm^3 is close to the density calculated for the $HoS_{1.863}$ phase, while the value 6.21 most likely characterizes the tetragonal phase $HoS_{1.67-1.72}$ [12]. Thus, according to the density measurements crystallization from a flux leads to formation of at least three phases. Further confirmation of their nature is in progress.

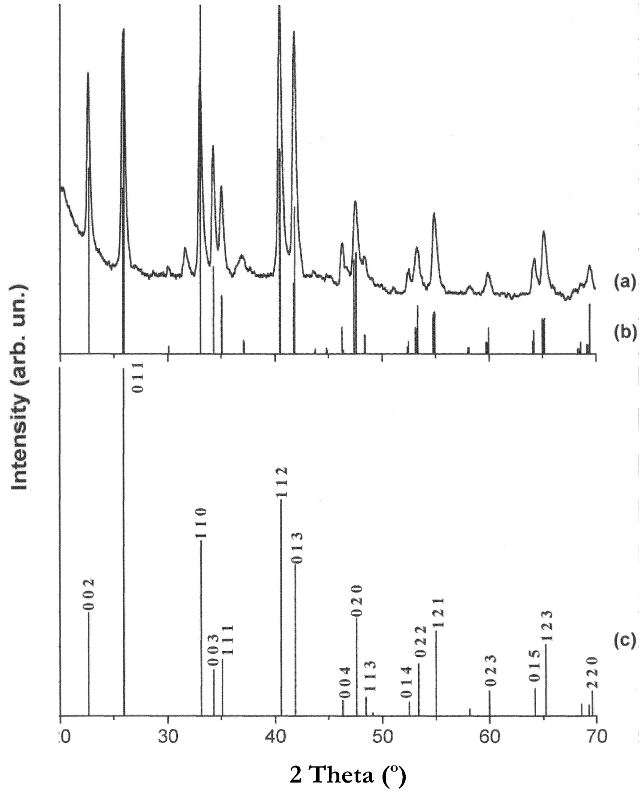

Fig. 4. Comparison of the experimental (a) and calculated powder diffractograms for $HoS_{1.863}$ (b) and for $HoS_{1.885}$ (c). The peak $2\Theta = 31.7°$ at (a) is attributed to the film which covered the sample under exposition.

3.4. Vibrational spectra

The Raman spectra for all crystal samples show three kinds of vibrations, which were previously identified in [15]: a clearly-expressed band of a high intensity in the range of 365–385 cm^{-1} corresponding to S–S bond vibration in S_2^{2-} pairs from a polysulfide layer, the set of bands of a middle intensity in the range of 65–140 cm^{-1} corresponding to the cation sublattice vibrations and several bands in the range of 170–320 cm^{-1} attributed to Ho^{3+}-S^{2-} bond vibrations.

The IR absorption spectra for holmium polysulfide powders have a broad band centered at 240–250 cm^{-1}, in general the spectra are similar to those obtained for polysulfides of other RE [16]: all phonon spectra are located at $\nu < 350$ cm^{-1} in IR absorption and at $\nu < 385$ cm^{-1} in Raman spectra. The IR spectra, recorded at 300 K for three 20-μm thick crystals of holmium polysulfides selected randomly were similar (Fig. 5). One can see the intense band with a fine structure, centered at 5000 cm^{-1} and related to electronic transitions in Ho^{3+}(see Section 3.5 below). The extended low energy part of the spectrum

Table 2
The data of the chemical analysis

No.	Weight, mg	Number of crystals *A*	Holmium content, mass. %	Sulfur content, mass. %	Potassium content, mass. %	Composition, in molar ratio S: Ho
1	19.31	6	75.79	23.74	0.06	1.61
2	21.78	21	74.47	24.87	0.06	1.72
3	8.01	1	73.10	25.84	0.13	1.82
4	9.06	15	73.08	26.52	0	1.87[a]
5	5.54	7	71.75	27.19	0	1.95
6	8.55	5	70.53	27.17	0.14	1.98

[a] Composition close to that calculated for the crystal **(II)**.

due to crystal vibrations is given in the inset: all typical features for both IR absorption (250 cm^{-1} broad band) and Raman (380 cm^{-1}) spectra are presented here.

The transparency range edge in the mid-IR is located at about 25 μm for 20-μm thick slices: one can see the intense absorption bands at larger wavelengths ($\nu<400$ cm^{-1}). For bulk crystals several millimeters thick this edge is expected to be at 14 μm.

3.5. Electronic transitions

The short wave edge of the transparency range, recorded for holmium polysulfide crystal having the composition $\mathrm{HoS}_{1.87}$ at 80 and 300 K is given in Fig. 6. The absorption edge is located at 590 and 650 nm for 80 and 300 K for the 100 cm^{-1} absorption level. The color of thin plates varies from red to cherry. The intense absorption bands (~100 cm^{-1}) at 540, 650 and 2000 nm (Fig. 6) and the weaker ones at 757, 895 and 1170 nm, about 20 cm^{-1} in intensity, are related to well-known transitions $^5\mathrm{I}_8 \rightarrow {}^5\mathrm{S}_2 + {}^5\mathrm{F}_4$, $^5\mathrm{F}_5$, $^5\mathrm{F}_7$ inside the 4f electronic shell of Ho^{3+} [16], respectively.

The position of the short wave edge for the holmium polysulfide is close to those obtained for other RE polysulfides from the diffuse reflection spectra for powdered LnS_2 compounds [15]. The density of band tail states was suggested to occur because of some localized disordered regions in the crystals grown. The analysis of the form of fundamental absorption edge shows that it is smooth enough and can be described by the Urbach's rule where an exponential law in ($k-h\nu$) coordinates, where k is the absorption coefficient and $h\nu$ is a photon energy (Fig. 6, inset), takes place [17]. The inclination angle of the straight line is usually dependent on crystal temperature. It is the case when the 'tails' of the state density function exist for conduction and valence bands [17]. In the case, when the 'tails' are due to some kind of charged impurity, the equation as

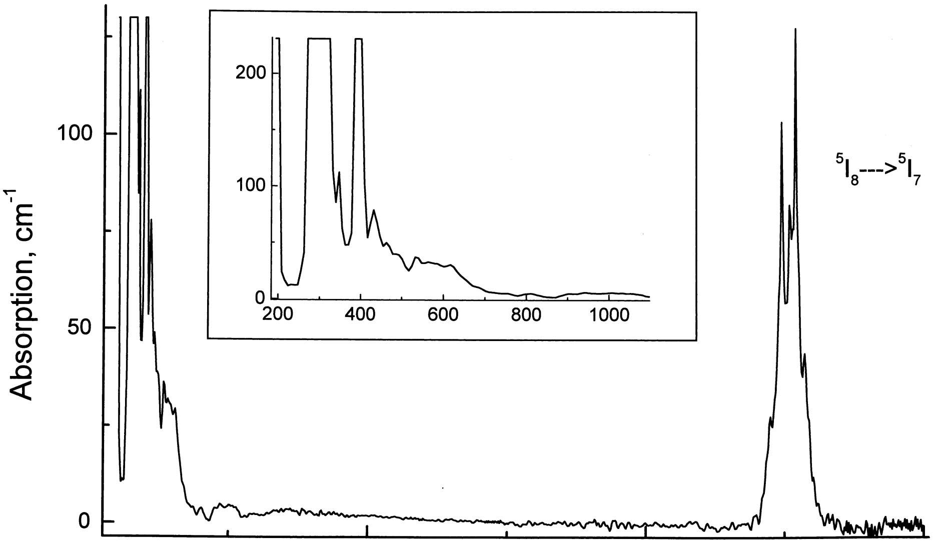

Fig. 5. The IR absorption spectrum for holmium polysulfide crystal, 20 μm thick, at 300 K. In the inset the low energy part of the spectrum is included.

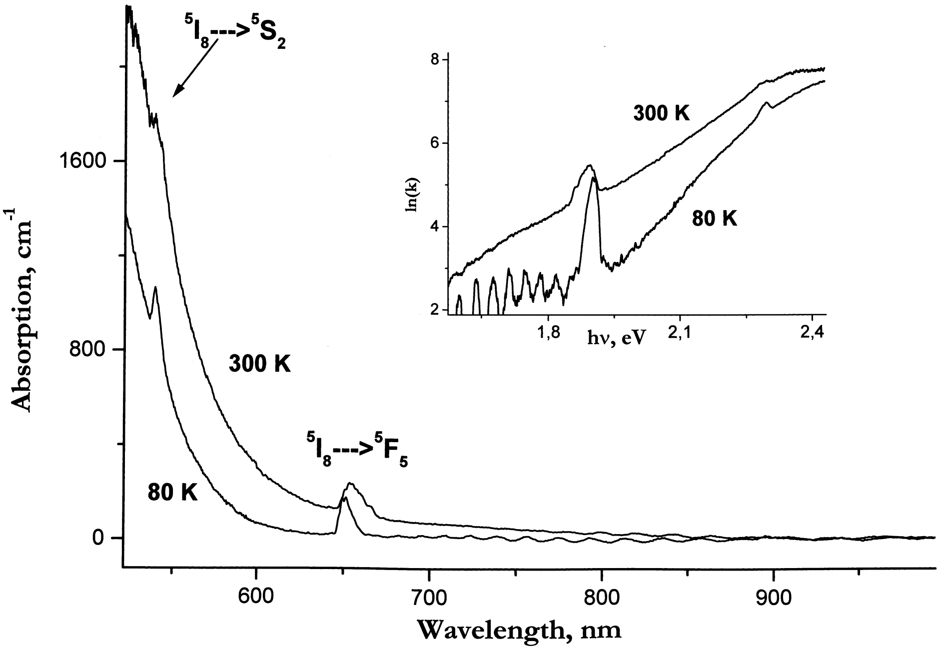

Fig. 6. The absorption spectra of the $HoS_{1.87}$ crystal in the visible and near-IR region at 80 and 300 K with identification of the RE transitions in Ho^{3+}. In the inset: the short-wave part of the same spectra represented in the (k-hν) coordinates. One can see that both spectra are approximated by straight lines with different inclination angles. Vibrations in the transparency range due to interference on natural parallel faces of the sample.

$$\frac{d(\ln k)}{d(h\nu)} = \frac{1}{k\mathrm{T}} \qquad (1)$$

with the Boltzmann constant k, is valid. In our case we have the experimental $d(\ln k)/d(h\nu)$ values equal to 1.05 and 0.72 for 80 and 300 K, respectively, which are considerably different from 147 and 38, calculated from Eq. (1). We can suppose that there are several reasons for such deviation for holmium polysulfide crystals grown from a flux. They are: possible colloidal impurities of KI and S, dislocations, even phase inhomogeneity in individual crystal.

No luminescence was found in holmium polysulfide crystals which can be understood taking into account that there is a large content of holmium ions in polysulfides and the adjacent holmium ions are quite near each other in the lattice: thus they form the continuous energy band with high density of states and dominating radiationless transitions when dissipating the excitation energy. It is obvious that it is necessary to incorporate a small enough amount (<1 mass.%) of other RE ions as Dy, Pr et al. with transitions of interest in order to have these ions as individual point defects. Taking into account $\nu_{\max} = 380$ cm^{-1} one could expect to have mainly radiative transitions up to 6–6.5 μm in the mid-IR. It is obvious also that for creating the mid-IR active media the most promising are the polysulfides of RE elements as La, Ce, Gd which have no transitions/absorption in the mid-IR.

The refractory index of holmium polysulfide, measured by the immersion technique, is equal to 2.2.

4. Conclusions

Crystals of holmium polysulfides were grown from a flux and characterized. Measured optical properties showed a perspective of using these compounds as optical materials for IR technology and, possibly, as laser media. It was shown that holmium polysulfides of close composition have a different structure because of different organization of the polysulfide layer. The data of chemical analysis and density measurements allowed the authors to suggest the formation of several phases, two of which were structurally characterized and identified from the previous work.

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References

[1] T.Yu. Shilkina, L.G. Gorbunova, I.G. Vasilyeva, Izv. Akad. Nauk. SSSR, Neorg. Mater. 23 (1987) 1103–1106.
[2] P.H. Page, K.I. Schaffers, S.A. Payne, W.F. Krupke, J. Lightwave, Technology 15 (1997) 786–797.

[3] M. Nostrand, P.H. Page, S.A. Payne, W.F. Krupke, P.G. Schunemann, Opt. Lett. 24 (No. 17) (1999) 1215–1218.

[4] N.V. Podberezskaya, D.Yu. Naumov, I.G. Vasilyeva, N.V. Pervukhina, S.A. Magarill, S.V. Borisov, Zhurn. Strukt. Khim. 39 (1998) 872–884.

[5] I. Vasilyeva, L. Gorbunova, Izv. AN. Neorg. Mater. 22 (1986) 897–899.

[6] H. Rau, T. Kutty, J. Guedes de Carvalho, J. Chem. Thermodynamics 5 (1973) 291–302.

[7] N.V. Podberezskaya, N.V. Pervukhina, S.V. Belaya, I.G. Vasilyeva, S.V. Borisov, Zhurn. Strukt. Khim. 42 (4) (2001) in press.

[8] L. Solovyeva, S. Tsybulya, V. Zabolotny, 'Polycrystall', Sistema programm dlya structurnykh raschetov, Novosibirsk, 1988, p. 122.

[9] N.V. Podberezskaya, S.A. Magarill, N.V. Pervukhina, I.G. Vasilyeva, S.V. Borisov, Zhurn. Strukt. Khim. 37 (1996) 1140–1170.

[10] M. Pasero, N. Perchiazzi, Min. Mag. 60 (1996) 833–836.

[11] H. Elander, G. Haegg, A. Westgren, Ark. Kem. Miner. Geol. 12B (1935) 1–6.

[12] S. Ring, M. Tecotzky, Inorg. Chem. 3 (1964) 182–185.

[13] J. Flahaut, M. Guittard, M. Patrie, Bull. Soc. Chim. Fr. 11–12 (1959) 1917–1920.

[14] I. Vasilyeva, L. Kurochkina, Zh. Neorg. Khim. 26 (1981) 1872–1874.

[15] B.A. Kolesov, I.G. Vasilyeva, Mater. Res. Bull. 27 (1992) 775–781.

[16] B.G. Wybourne, Spectroscopic Properties of Rare Earth Ions, Interscience, New York, 1965.

[17] F. Urbach, Phys. Rev. 92 (1953) 1324–1361.