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# SPECTROSCOPIC STUDIES OF PrBr<sub>3</sub> · 7H<sub>2</sub>O MONOCRYSTAL

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Single crystals of praseodymium tribromide heptahydrate were grown from aqueous solution. The IR, Raman, and high resolution absorption spectra were measured at room and low temperatures. The assignments of IR and Raman frequencies are reported. The temperature dependence of intensities was found and vibronic coupling in f-f transitions was analysed. Anisotropy of the intensities of optical lines was detected and taken into account in the Judd-Ofelt analysis of the f-f transitions probabilities. The results are compared to the available IR and electron spectroscopic data for other single crystals of lanthanide bromides.

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# 1. Introduction

The spectroscopic properties of  $NdBr_3 \cdot 6II_2O$  and  $EuBr_3 \cdot 6II_2O$  monocrystals were reported and compared by us to those of other neodymium and europium monomeric compounds [1].

Recently, Güdel et al. [2] published the spectroscopic results for the anhydrous lanthanide bromides and analysed the cooperative effect in those systems [3].

Single crystals of the 4f and 5f metals bromides are assumed to be isomorphic with  $LnCl_3 \cdot 6H_2O$  [4,5]. On the basis of X-ray data for  $GdCl_3 \cdot 6H_2O$  [6] and  $NdCl_3 \cdot 6H_2O$  [7] it was shown that in these chlorides two  $Cl^-$  anions are in the first coordination sphere. By analogy, in isomorphic NdBr<sub>3</sub>  $\cdot 6H_2O$  compound two Br<sup>-</sup> anions are inner-sphere ligands and the point symmetry of the Nd<sup>3+</sup> ion should be  $C_{2v}$ . Our spectroscopic studies of Nd and Eu tribromide hexahydrate monocrystals seem to confirm the above symmetry [1]. The X-ray structure of PrCl<sub>3</sub>  $\cdot 7H_2O$  differs from the heavier lanthanide trichloride hexahydrate [8]. The former compound is a dimer, in which two chloride bridges are formed, with coordination number (C.N.) = 9 for Pr<sup>3+</sup> ion: (H<sub>2</sub>O)<sub>7</sub>Pr  $\langle Cl_{1} Pr(H_2O)_{7}$ . The praseodymium tribromide heptahydrate, isomorphic with the corresponding chloride, is a dimer with bromide bridges linking two Pr atoms. It could be reflected in spectroscopic properties of PrBr<sub>3</sub>  $\cdot 7H_2O$  monocrystals.

# 2. Experimental

The monocrystals of praseodymium tribromide heptahydrate  $PrBr_3 \cdot 7II_2O$ were grown from aqueous solutions. The concentration of  $Pr^{3+}$  ions was determined complexometrically using xylenol orange as the end-point indicator [9]. The crystals were checked by X-ray diffraction (triclinic, a = 8.238(4) Å, b = 8.516(2) Å, c = 9.368(5) Å,  $\alpha = 71.9(3)^{\circ}$ ,  $\beta = 73.0(4)^{\circ}$ ,  $\gamma = 81.2(3)^{\circ}$ ). The density of  $PrBr_3 \cdot 7II_2O$  ( $\rho = 2.73$  g cm<sup>-3</sup>) was measured by the flotation method.

Absorption spectra at room and low temperatures were recorded on a Cary-Varian 5 spectrophotometer equipped with helium flow cryostat in the region 420-2200 nm. The room temperature spectra were obtained for different crystal orientations. The intensities of optical lines were calculated using TAUS program, transformed to the oscillator strength values and applied to calculate the  $\tau_{\lambda}$  parameters. The IR spectra were recorded in 50-4000 cm<sup>-1</sup> region using a Bruker FT-IR 113V spectrophotometer.

The Raman spectra were recorded at 300 K in the  $40-500 \text{ cm}^{-1}$  region. As the excitation source the 488 and 514.5 nm lines of Ar<sup>+</sup> laser were used. A double monochromator DFS 24 manufactured in the LOMO optical works (Russia) and a cooled GaAs photomultiplier with a computer detection of 2 cm<sup>-1</sup> resolution were applied in the measurements.

# 3. Results and discussion

Absorption spectra of  $PrCl_3 \cdot 7II_2O$  for two different orientations of crystals (at room temperature) and in one orientation (at 4 K) are shown in Fig. 1. The oscillator strength values of the f-f transitions are listed in Table I. A change of the single crystal orientation leads to significant fluctuations in the individual components of the f-f transition intensities (markedly detected in the bands corresponding to  ${}^{3}H_4 \rightarrow {}^{3}P_1$ ,  ${}^{1}D_2$  transitions), similar to those observed for NdBr<sub>3</sub> ·  $6II_2O$ monocrystals investigated by us previously [1]. The anisotropy effect of intensities is clearly seen in the changes of oscillator strengths collected in Table I. The mean values of oscillator strengths for two orientations of the crystal were used to calculate  $\tau_{\lambda}$  parameters from the Judd-Ofelt relation (in the form given by Carnall et al. [10]):

$$P = \sum_{\lambda=2,4,6} \tau_{\lambda} \sigma(f^{N} \Psi_{J} \parallel U^{(\lambda)} \parallel f^{N} \Psi_{J'})^{2} / (2J+1),$$

where  $U^{(\lambda)}$  are matrix elements of unit tensor operator of the order  $\lambda$ ,  $f^N \Psi_J$ and  $f^N \Psi'_J$ , are the initial and final states of electronic transitions, J is the total quantum number,  $\sigma$  is the wave number of the  $\Psi_J \to \Psi'_J$ , transition in cm<sup>-1</sup>.

The size of single crystals made impossible calculation of intensities for three orientations. The evaluated values of  $\tau_{\lambda}$  parameters are given in Table I, including also root mean square deviations.

The set of seven bands was considered in order to determine the Judd-Ofelt parameters. Unexpectedly good estimation of the parameters was obtained from oscillator strength values of f-f transitions evaluated from praseodymium single crystal spectra (set I). The variations of the transitions included into calculation procedure yielded three different sets of parameters. The best fit was reached when  ${}^{3}F_{3}$  and  ${}^{3}F_{4}$  transitions were eliminated (set II); in this calculation the  ${}^{4}G_{4}$  transition intensity was the worst determined. The results comparable to them could be obtained when excluding the  ${}^{3}F_{3}$  bands (set III). The fitting procedure used in the second and third variations of transitions gives almost ideal results for  ${}^{3}F_{2}$  band intensity. The errors of the estimation of  $\tau_{\lambda}$  parameters are relatively low compared to other reported results available for praseodymium systems [10, 11].

Decreasing temperature down to 4 K was accompanied by decreasing oscillator strength values. This effect was more pronounced than in single crystal spectra of other  $Pr^{3+}$  compounds reported recently [12]. Decrease in intensities with lowering temperature could be caused both by the changes in population of Stark components of  ${}^{3}H_{4}$  ground level of  $Pr^{3+}$  ion, as well as by vibronic coupling.

TABLE I

The oscillator strength values  $P \times 10^8$  at room (orientations *a* and *b*) and low (orientation *b*) temperatures, and the  $\tau_{\lambda}$  parameters for PrBr<sub>3</sub> · 7H<sub>2</sub>O crystal. Set I — all the transitions, set II —  ${}^{3}F_{3}$  and  ${}^{3}F_{4}$  transitions were excluded, set III —  ${}^{3}F_{3}$  transition was excluded.  $C_{\rm Pr^{3+}} = 5.427$  M.

	$P \times 10^8$							
Term	293 K				4 K			
	a		Ь			Ь		
$^{3}F_{2}$	889.67		1221.52			896.52		
${}^{3}F_{3}$ ${}^{3}F_{4}$	1509.26		1989.70			786.66		
$^1\!G_4$	57.61		59.64			33.05		
$^{1}D_{2}$	241.29		370.01			352.94		
${}^{3}\!P_{0}$	317.03		364.47			51.39		
${}^{3}P_{1} {}^{1}I_{6}$	758.41		952.75			478.52		
${}^{3}\!P_{2}$	1050.14			1414.78		588.13		
Set	RMS deviation	$ au_2  imes 10^9$		$ au_4  imes 10^9$		$ au_6  imes 10^9$		
I	$3.02 \times 10^{-6}$	$22.16 \pm 11.37$		$11.59 \pm 4.78$		$17.78 \pm 3.66$		
II	$0.83 \times 10^{-6}$	$20.73 \pm 3.12$		$10.64 \pm 1.32$		$33.28 \pm 1.24$		
III	$1.54 \times 10^{-6}$	$21.23 \pm 5.80$		$11.32 \pm 2.42$		$27.58 \pm 3.10$		
Term	$P_{\rm mean}$		$P_{\rm calc}({\rm I})$	$P_{\rm calc}({ m II})$	$P_{\rm calc}({ m III})$			
$^{3}F_{2}$	1055.60		1015.76	1056.07	1048.07			
${}^{3}\!F_{3}$	858.9 1740 5		1076 32		1078 75			
${}^{3}\!F_{4}$	$890.6 \int 1149.5$		1010.02		1010.10			
${}^{1}G_{4}$	58.63		89.75	132.15	116.79			
${}^{1}D_{2}$	305.65		222.01	370.08	316.71			
${}^{3}P_{0}$	340.75		459.90	422.21	449.36			
${}^{3}P_{1} {}^{1}I_{6}$	855.58		756.72	791.18	796.03			
${}^{3}P_{2}$	1232.46		703.86	1218.10	1032.08			

According to vibronic transitions probabilities [13, 14], one would await relatively strong vibronic coupling for lanthanide bromides, since f-d transition is located at low energy. The measurements of absorption spectra in the UV region (for powder PrBr<sub>3</sub> · 7II<sub>2</sub>O in oil) located the first f-d transition at  $\approx 42600 \text{ cm}^{-1}$  (see Fig. 1), and at somewhat higher energies than it was detected by Nugent et al. [15] for PrBr<sub>3</sub><sup>3-</sup> complexes.

The absorption spectra at 4 K are presented in Fig. 1. Complex structure of bands was recorded. Since the number of strong optical lines exceeds that expected from X-ray results, one could assume some deviation in the crystal structure with temperature lowering. The observed phenomenon could be also given by cooperative absorption in system with dimeric structure, with two praseodymium ions being coupled [2, 12, 16, 17]. Careful analysis of the absorption spectra of diluted crystals should help in explanation of the obtained results. It is worth noting that  ${}^{3}P_{0}$  band is composed of two components at 4 K. Confrontation of the low temperature absorption spectra with the frequencies detected in the Raman ones (at 67 and 89 cm<sup>-1</sup>) seems to confirm the above assumption.

Temperature dependence of  ${}^{3}H_{4} \rightarrow {}^{3}P_{0}$  transition (see Fig. 2) allowed to determine partially the scheme of energy levels of the ground state  ${}^{3}H_{4}$  term. The successive Stark components could be noticed as energies 12(a), 21(b), 34(c), 45(d), 67(e?), 80(f?), 116(g?), and 147(h?) (all in cm<sup>-1</sup>).



Fig. 1. The absorption spectra of  $PrBr_3 \cdot 7H_2O$  monocrystal at room temperature for different orientations (I) and at 4 K (II). III — the f-d transition for  $PrBr_3 \cdot 7H_2O$  in oil compared to that for  $LaBr_3 \cdot 7H_2O$  in oil.



Fig. 2. Temperature dependence of  ${}^{3}H_{4} \rightarrow {}^{3}P_{0}$  transition for PrBr<sub>3</sub> · 7H<sub>2</sub>O crystal.  $P \times 10^{8}$  — the oscillator strengths values.



Fig. 3. The Raman spectra of PrBr<sub>3</sub> · 7II<sub>2</sub>O crystal.

The IR and Raman spectra for the compound studied were discussed on the basis of real structure of the complex. The triclinic unit cell of the  $P\overline{1}(C_i^1)$  symmetry consists of 2 formula units comprising 50 atoms. The coordination number of praseodymium is 9 and the site symmetry  $C_1$ . Because of the dimeric structure of the complex,  $(II_2O)_7 \Pr \langle \frac{Br}{Br} \rangle \Pr(II_2O)_7$ , the symmetry of this cation is  $C_i$ , i.e. the same as the factor group one. The factor group analysis (FGA) predicts that the 150 unit cell modes decompose into  $3A_{\rm u}$  acoustic and  $75A_{\rm g} + 72A_{\rm u}$  optic phonons. 147 optical zone-centre modes contain  $9A_u$  translatory lattice modes of the bromide anions (T'(Br)),  $3A_u$  translatory lattice modes of the complex ion (T'(Pr/Pr)), and  $3A_g$  libratory lattice modes of the cation. The internal vibrations of the dimer,  $72A_g + 60A_u$ , could be further distributed into the following normal modes:  $\nu(\text{OII})$ :  $14A_g + 14A_u$ ,  $\delta(\text{IIOII})$ :  $7A_g + 7A_u$ ,  $\nu(\text{PrO})$ :  $7A_g + 7A_u$ ,  $\nu(\Pr \langle \frac{Br}{Br'}, \Pr): 2A_g + 2A_u, \ \delta(\Pr \langle \frac{Br}{Br'}): A_g + A_u \text{ and } \delta(OPrO) + \delta(OPrBr): 27A_g + \delta(OPrBr): 27A_g$  $15A_{\rm u}$ . The odd symmetry modes are IR active only and those of parity ones are Raman scattering active only. It means that each vibrational mode has its Raman and IR counterpart. The vibrational spectra obtained in this work are given in

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TABLE II

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Vibrational frequencies	of IR and	Raman	active	modes	for	the	PrBr <sub>3</sub>	• 7H <sub>2</sub> O
complex.								

IR $[cm^{-1}]$	Raman [cm <sup>-1</sup> ]	Assignment
$\approx 3500 \text{ sh}$	3437 sh	$\nu_{\rm s,as}({ m IIOII})$ of the
	3390 vs	coordinated water
3366 vs, vb	3370 s	
	3320 sh, b	
$\approx 3200 \text{ sh}$	3270 sh,w	
	3201 w	
	2931 m	
	2875 m	
2174 m	2138 w	${}^{3}\!H_{4} \rightarrow {}^{3}\!H_{5}$ of the Pr <sup>3+</sup> ion
	2006 m	
	1975 sh	
1640 sh		$\delta$ (IIOII) of the
1618 vs	1615 s	coordinated water
1600 sh	1569 w	
	1507 w	
	1479 sh	
	1439 s, b	
1180 m		$\delta(Pr-OII)$
1075 m		· · · · ·
566 vs, vb	672 w	$\omega(\mathrm{II}_2\mathrm{O})$
(in 500–900 contour)	534 w (554,531)	
451 s	462 w, vb	
428 s		
402 s		
305 s	300 w	$\nu(Pr-OII_2)$
270 s, vb	282 w	
225 s	218 w	$\nu_{\rm as}(\Pr \langle \frac{Br}{Br} \rangle \Pr)$
213 s	189 w	
168 m	150 sh	$ \nu_{\rm s}(\Pr \langle {{\rm Br} \atop {\rm Br}'} \Pr) $
130 m	136 w	$\delta(\Pr \stackrel{Br}{Pr} \Pr)$ and $\delta(OPrO)$
110 m	115 w	or/and
70 s	89 m	lattice modes
	67 s	
	45 s	

1...\*

TABLE III

	Energy [cm <sup>-1</sup> ]	$\Delta E$ (from 0-phonon line) [cm <sup>-1</sup> ]
${}^{3}P_{2}$ 1	22353	0-phonon line
2	22380	
3	22429	
4	22476	
5	22488	
6	22503	
7	22523	
8	22534	
9	22580	227 $\nu_{as} \Pr \left\langle \frac{Br}{Br} \right\rangle \Pr$
10	22623	$270 \downarrow \mu(\text{Br}=0)$
11	22658	$305\int \mathcal{V}(11-\mathcal{O})$
12	22769	$416$ (u(II_aO) of the Pr(OII_a) - polyhedron
13	22813	$460 \int \omega(1120)$ of the 11(0112)7 polyhedron

The electronic and vibronic components in absorption spectrum of  $PrBr_3 \cdot 7H_2O$  crystal at 4 K.

Fig. 3 and discussed in Table II. The energetic position of these phonons agrees with Nakamoto et al. report [18] for lanthanide halides and Wells et al. studies [19] for lanthanide trihalides. The vibrations of the coordinated water appear at the standard frequency regions [20].

Table III includes both energies of electronic components and vibronic side bands. The vibronic components were assigned after confrontation of the energy level position in the absorption spectra with those of IR and Raman data. It is important to note that the vibronic transitions were associated with the modes of first coordination sphere of  $Pr^{3+}$  ions, i.e. with oxygen involved and bromide modes. These modes play the role of energy promoting phonons in the electron-phonon coupling mechanism.

## 4. Conclusions

1. The IR, Raman and electronic spectra of  $PrBr_3 \cdot 7II_2O$  are consistent with the triclinic crystal structure and  $C_i$  symmetry of the complex dimer formed.

2. Judd-Ofelt intensity analysis gave a set of  $\tau_{\lambda}$  parameters evaluated with quite small standard deviation.

3. On the basis of IR and Raman spectra, the vibronic components of  ${}^{3}H_{4} \rightarrow {}^{3}P_{2}$  electronic transition were determined and identified.

4. The presence of two components (with the same intensity separated by 87 cm<sup>-1</sup>) of  ${}^{3}\!H_{4} \rightarrow {}^{3}\!P_{0}$  transition at 4 K, compared to Raman data, gave an opportunity to suppose about cooperative absorption mediated by phonon.

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