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High-resolution spectroscopy of $YAl_3(BO_3)_4 : Pr^{3+}$

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Received November 02, 2024
Revised November 08, 2024
Accepted November 14, 2024

Optical absorption spectra of $YAl_3(BO_3)_4 : Pr^{3+}$ crystals in the temperature range of 5–300 K in polarized light were studied by high-resolution Fourier spectroscopy (up to 0.1 cm^{-1}). The energies of crystal-field sublevels of 12 multiplets of the Pr^{3+} ion were determined. The observed splitting of a number of spectral lines corresponding to singlet-doublet transitions is due to the influence of random lattice deformations. The complex structure of the singlet-singlet transition line to the $^3P_0$ level is explained by the presence of additional centers „Pr^{3+} ion near a lattice defect". Presumably, such defects are uncontrolled impurities entering the crystal during its growth by solution-melt technique.

Keywords: $YAl_3(BO_3)_4 : Pr^{3+}$ in yttrium aluminum borate, crystal-field levels, high-resolution Fourier spectroscopy, deformation splitting.

DOI: 10.61011/EOS.2024.11.60318.7292-24

Introduction

Pr^{3+}-ion-activated crystals are used as phosphors [1–4] and laser media [5–9] and are being actively researched for their applicability as materials for quantum informatics devices [10–16]. Long coherence times of hyperfine structure levels required in this case have been reported for Pr^{3+} in oxide crystals Y_2SiO_5 [11,13,14,16] and $La_2(WO_4)_3$ [15].

Yttrium aluminum borate $YAl_3(BO_3)_4$ (YAB) belongs to the borate family with the structure of the natural mineral huntite (space symmetry group $R32$ [17]). This compound has a number of favourable physicochemical properties: mechanical, chemical and thermal stability [18], transparency over a wide spectral range, uniquely high thermal conductivity [19], high nonlinear optical coefficient [20]. Praseodymium-doped yttrium aluminum borate luminesces intensely in the yellow region of the spectrum and can be used in lighting devices [21].

Pr^{3+} ions isomorphically substitute for Y^{3+} ions and occupy a position with the D_3 point symmetry group. The information available in the literature on the crystal-field levels of Pr^{3+} ion in YAB:Pr^{3+} and on the crystal-field (CF) parameters is incomplete and contradictory [22,23]. The nature of the complex shape of some spectral lines observed in [23] study performed at high spectral resolution also remains unclear.

In this paper, the temperature-dependent absorption spectra of YAB:Pr^{3+} crystals have been investigated by high-resolution Fourier spectroscopy, and the scheme of crystal-field levels of the praseodymium ion in the YAB crystal field has been refined and substantially supplemented. These data form the basis for the subsequent correct calculation using the crystal-field theory. In this study the observed fine structure of some spectral lines is also discussed and its explanation is proposed.

Experiment

Single crystals of $YAl_3(BO_3)_4 : Pr^{3+}$ were grown at the L.V. Kirensky Institute of Physics of the Siberian Branch of the Russian Academy of Sciences by the solution-melt method with a flux based on the bismuth trimolybdate $Bi_2Mo_3O_{12}$ [24]. Samples for measurements were cut along the trigonal axis c of the crystal. Transmission spectra in the region 2000–23 000 cm^{-1} were recorded on a Bruker IFS 125 HR Fourier spectrometer with a resolution up to 0.1 cm^{-1}. Measurements were performed over a temperature range of 5–300 K using a Sumitomo SRP-082 closed-cycle cryostat. The temperature was monitored and stabilised using a Lake Shore Model 335 dual-channel thermocontroller. Transmission spectra were recorded in π ($\mathbf{k} \perp c$, $\mathbf{E} \parallel c$) and σ ($\mathbf{k} \perp c$, $\mathbf{E} \perp c$) polarizations. A KRS-5-based polarizer was used for the infrared region, and a film polarizer was used for the visible one.

Table 1. Splitting of levels of a free ion with an even number of electrons in a crystal field of symmetry D_3

J	Γ
0	Γ_1
1	$\Gamma_2 + \Gamma_3$
2	$\Gamma_1 + 2\Gamma_3$
3	$\Gamma_1 + 2\Gamma_2 + 2\Gamma_3$
4	$2\Gamma_1 + \Gamma_2 + 3\Gamma_3$
5	$\Gamma_1 + 2\Gamma_2 + 4\Gamma_3$
6	$3\Gamma_1 + 2\Gamma_2 + 4\Gamma_3$

Experimental results and discussion

A. Crystal-field levels of the Pr^{3+} ion in $YAl_3(BO_3)_4 : Pr^{3+}$

Fig. 1 shows the transmission spectrum of the $YAl_3(BO_3)_4 : Pr^{3+}$crystal in the regions of $f-f$-transitions from the crystal-field levels (1, 2, etc. in the order of increasing energy) of the ground $^3H_4$ multiplet of the Pr^{3+} ion to the crystal-field levels (A, B, C, etc.) of several excited multiplets. The designation 1A in Fig. 1 means that the line corresponds to the transition from the ground level to the lowest level of the excited multiplet.

The wave functions of the crystal-field levels of the Pr^{3+} ion occupying a position with point symmetry group D_3 in the YAB crystal are transformed according to two non-degenerate irreducible representations Γ_1, Γ_2 and one doubly-degenerate Γ_3. In Table 1 we show how the levels of the free ion (with an even number of electrons, as in Pr^{3+}) characterised by values of the total momentum J are split in the D_3-symmetry crystal field, and Table 2 gives the selection rules for electric dipole (ED) and magnetic dipole (MD) optical transitions for the Pr^{3+} ion in YAB. At sufficiently low temperature, only the ground level is populated, and the absorption spectrum is formed by transitions from it to excited levels. In this way the energies of the crystal-field sublevels of the excited multiplets were determined and are given in the third column of Table 3. Using the selection rules, from the experimental spectra we can also find the irreducible representations according to which the wave functions of the crystal-field sublevels are transformed (i.e., the symmetry of the levels).

Using Tables 1 and 2 and Fig. 1, *b* (transition $^3H_4 \rightarrow {}^3F_2$), let us first of all determine the symmetry of the ground state. The level of the free ion $^3F_2$ is split by CF into three crystal-field levels $\Gamma_1 + 2\Gamma_3$. The $^3H_4 \rightarrow {}^3F_2$ transition is forbidden in the free ion as an MD transition, and therefore for the ion in the crystal field the ED contribution will dominate. If the ground state is Γ_1, we can expect to see two σ-polarized lines in the spectrum, if Γ_2 — two σ-polarized and one π-polarized, if Γ_3 — one σ-polarized and two π-, σ-polarized. At 5 K, three transition lines from the ground state are observed: one in π polarization and two mostly in σ polarization, indicating the Γ_2 symmetry of the ground state. Thus in the $^3F_2$ multiplet, the lowest level A is Γ_3, the next level B is Γ_1, and level C is Γ_3. The energy of the first excited level 2 in the ground multiplet is 23 cm^{-1}, and the transition from it is clearly visible by the line 2A in the spectrum at 60 K. Level 2 has Γ_1 symmetry: the line 2B of the transition to level B with Γ_1 symmetry is not in the spectrum (the $\Gamma_1 \rightarrow \Gamma_1$ transition is strictly forbidden), in other multiplets there are also no lines of transitions from level 2 to Γ_1 levels. The experimentally determined level symmetries are also listed in column 4 of Table 3.

Note that the energies of the Γ_2 symmetry levels in excited multiplets were obtained from the lines of transitions to them from level 2 (Γ_1) ($\Gamma_2 \rightarrow \Gamma_2$ transitions from the ground level are strictly forbidden).

B. Pr^{3+} ions near structure defects

Figure 2 shows the absorption line 20 603 cm^{-1} in the YAB:Pr^{3+} (1 at.%) crystal. It corresponds to the singlet-singlet transition $1\Gamma_2$ ($^3H_4$) $\rightarrow$ $A\Gamma_1(^3P_0)$ but has a complex structure: satellites are observed near the main line. The authors of [23] observed a similar structure of this line in the yttrium aluminum borate spectrum with the same concentration of Pr^{3+} ions (1 at.%), but could not explain it. A comparison of our data (Fig. 2) and those of [23] (inset in Fig. 6 of [23]) shows that the intensity of the satellites in our case is about one and a half times smaller than in [23]. The crystals investigated in this study were grown with $Bi_2Mo_3O_{12}$ based flux, whereas in [23] $K_2Mo_3O_{10}$ based flux was used. In [25,26] it was shown that during crystal growth by the solution-melt method, the flux components enter the crystal. During YAB crystal growth using $Bi_2Mo_3O_{12}$, Mo^{3+} ions replace Al^{3+} ions, and the Bi^{3+} ion takes the place of Y^{3+} [25]. However, this flux binds molybdenum, it enters the crystal in smaller amounts than in the case of growth using $K_2Mo_3O_{10}$ [26].

Thus, the main line satellites are due to Pr^{3+} ions located near the defects „Mo^{3+} in place of Al^{3+}“ and „Bi^{3+} in place of Y^{3+}“. Based on the YAB structure and ionic radii, it can be assumed that the defects due to the presence of molybdenum are the most important.

C. Doublet structure of singlet-doublet transition lines

Praseodymium is a monoisotopic element having one stable isotope ^{141}Pr with nuclear spin $I = 5/2$. As a result of the hyperfine interaction, the non-Kramers Γ_3 doublets split into 6 hyperfine components. No hyperfine structure could be detected in the recorded spectra. Nevertheless, it should be noted that there is an obvious doublet structure of some spectral lines related to the singlet-doublet transitions $\Gamma_1(\Gamma_2) \rightarrow \Gamma_3$ (Fig. 3). The authors of the article [23] also reported the observation of the doublet structure of some absorption lines. The hyperfine structure intervals of the doublets calculated in [23] are significantly smaller than the observed splittings from 0.4 to 3.1 cm^{-1} for different lines.

Table 2. Allowed ED and MD transitions for ions with even number of electrons in the case of point symmetry group D_3

D_3	ED			MD		
	Γ_1	Γ_2	Γ_3	Γ_1	Γ_2	Γ_3
Γ_1	–	$d_z(\pi)$	$d_x, d_y(\sigma)$	–	$\mu_z(\sigma)$	$\mu_x, \mu_y(\pi)$
Γ_2	$d_z(\pi)$	–	$d_x, d_y(\sigma)$	$\mu_z(\sigma)$	–	$\mu_x, \mu_y(\pi)$
Γ_3	$d_x, d_y(\sigma)$	$d_x, d_y(\sigma)$	$d_x, d_y, d_z(\sigma, \pi)$	$\mu_x, \mu_y(\pi)$	$\mu_x, \mu_y(\pi)$	$\mu_x, \mu_y, \mu_z(\sigma, \pi)$

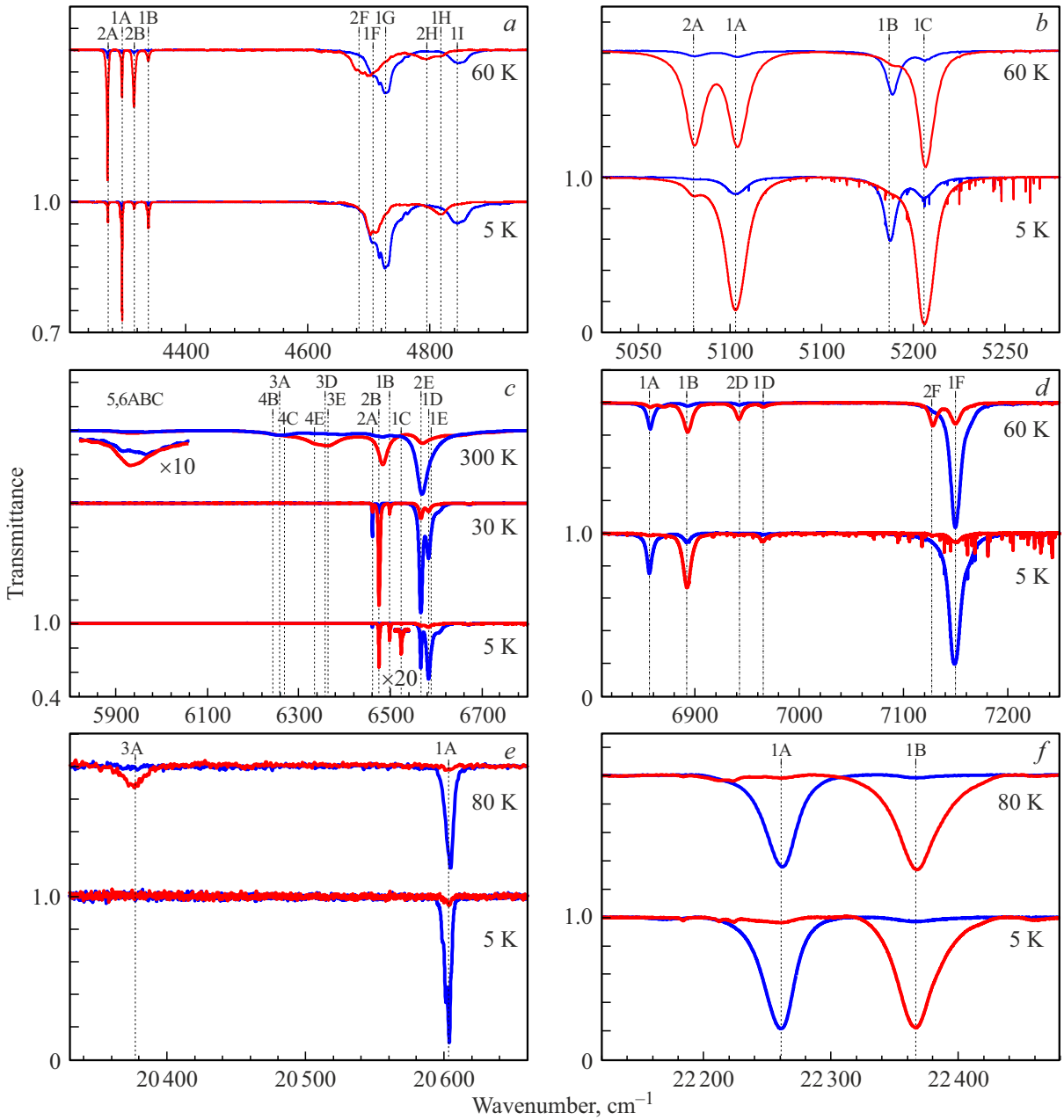

Figure 1. σ- (red) and π- (blue) polarized transmission spectra of a 4.15 mm thick $YAl_3(BO_3)_4 : Pr^{3+}$ (1 at.%) crystal at different temperatures in the region of transitions in the Pr^{3+} ion: (*a*) $^3H_4 \rightarrow {}^3H_6$, (*b*) $^3H_4 \rightarrow {}^3F_2$, (*c*) $^3H_4 \rightarrow {}^3F_3$, (*d*) $^3H_4 \rightarrow {}^3F_4$, (*e*) $^3H_4 \rightarrow {}^3P_0$, (*f*) $^3H_4 \rightarrow {}^3P_2$.

Table 3. E (cm^{-1}) energies of Pr^{3+} crystal-field levels in $YAl_3(BO_3)_4 : Pr^{3+}$ and the irreducible Γ_i representations of the D_3 point symmetry group that characterize them

$^{2S+1}L_J$	i	YAB:Pr					
		This paper		[22]		[23]	
		E	Γ	E	Γ	E	Γ
1	2	3	4	5	6	7	8
$^3H_4$	1	0	Γ_2	0	Γ_2	0	
	2	23	Γ_1	150	Γ_1	23	Γ_3
	3	226	Γ_3	231	Γ_3	139	
	4	255		332	Γ_3	226	Γ_3
	5	493–635		–	Γ_1	330	Γ_3
	6	493–635		560	Γ_3	560	
$^3H_5$	A	2196	Γ_3	–		–	
	B	–		–		2196.1	Γ_3
	C	2272		–		2272	
	D	–		–		–	
	E	–		–		2476	Γ_3
	F	–		–		–	
	G	–		–		–	
$^3H_6$	A	4295.5	Γ_3	–		4295.5	
	B	4338.7	Γ_3	–		4338.6	Γ_3
	C	–		–		–	
	D	–		–		–	
	E	–		–		–	
	F	4707	Γ_1	–		–	
	G	4727.8	Γ_3	–		4715	Γ_3
	H	4817.8	Γ_3	–		4845	Γ_3
	I	4845	Γ_1	–		–	
$^3F_2$	A	5103	Γ_3	5080	Γ_3	5103	
	B	5187	Γ_1	5178	Γ_1	5187	Γ_3
	C	5206	Γ_3	5200	Γ_3	5206	Γ_3
$^3F_3$	A	6484.3	Γ_2	6463	Γ_3	6465	Γ_3
	B	6498.6	Γ_3	6487	Γ_3	6485.1	
	C	6524		6528	Γ_2	6524	Γ_3
	D	6583.8	Γ_1	6555	Γ_1	6581	
	E	6589.8	Γ_2	6590	Γ_2	6607	
$^3F_4$	A	6855.5	Γ_1	6843	Γ_1	6855.5	Γ_3
	B	6891.3	Γ_3	6879	Γ_3	6891.3	
	C	6930	Γ_2	6928	Γ_3	6965	Γ_3
	D	6965	Γ_3	6980	Γ_2	–	
	E	–		7115	Γ_3	7150.4	Γ_3
	F	7150		7135	Γ_1	7160	
$^1G_4$	A	9707.4		–		9707.4	Γ_3
	B	–		–		9749	
	C	9909	Γ_2	–		9909	Γ_3
	D	–		–		–	
	E	10178		–		10178	
	F	10216		–		10216	Γ_3
$^1D_2$	A	16512	Γ_1	16525	Γ_1	16754	Γ_3
	B	16754	Γ_3	16769	Γ_3	–	
	C	17140	Γ_3	17156	Γ_3	17150	Γ_3
$^3P_0$	A	20603	Γ_1	20619	Γ_1	20603	Γ_1

Table 3. *Continued*

1	2	3	4	5	6	7	8
$^3P_1+$ $^1I_6$	A	21003	Γ_2	21176	Γ_3	20985	
	B	21014	Γ_1	21236	Γ_2	21008	
	C	21163	Γ_3	22274	Γ_1	21013	Γ_3
	D	–		–		21145	Γ_3
	E	–		–		21153	Γ_3
	F	–		–		21247	
	G	21330	Γ_1	–		21330	
	H	21353	Γ_3	–		–	
	I	–		–		–	
	K	21816	Γ_1	–		21816	Γ_3
	L	21858.6	Γ_3	–		21889	
$^3P_2$	A	22261	Γ_1	–		22365	
	B	22367	Γ_3	22379	Γ_3	22460	Γ_3
	C	22450	Γ_3	22418	Γ_3	22710	Γ_3

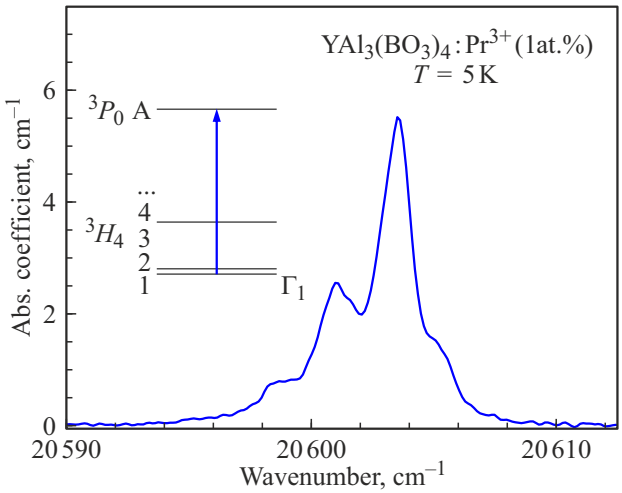

Figure 2. Absorption line 1A of π-polarized light in the $^3H_4 \rightarrow {}^3P_0$ transition region in the YAB:Pr^{3+} crystal (1 at.%).

No explanation for the observed doublet structure of the lines in the absorption spectra is given in [23].

As it follows from previous studies, the observed characteristic doublet shape of the lines corresponding to singlet-doublet transitions indicates the presence of low-symmetric local perturbations of the crystal field, which may be caused by point defects in the crystal lattice [27,28]. In YAB:Pr^{3+} crystals grown by the solution-melt method, such defects are both the Pr^{3+} ions themselves and uncontrolled impurities entering the crystal from the flux during growth. To find out which defects make the crucial contribution to the deformation splittings, further studies are required.

Conclusion

Transmission spectra of single crystals of $YAl_3(BO_3)_4$ activated by Pr^{3+} ions (1 at.%) have been measured. Pr^{3+} ions substitute for Y^{3+} ions at positions with point

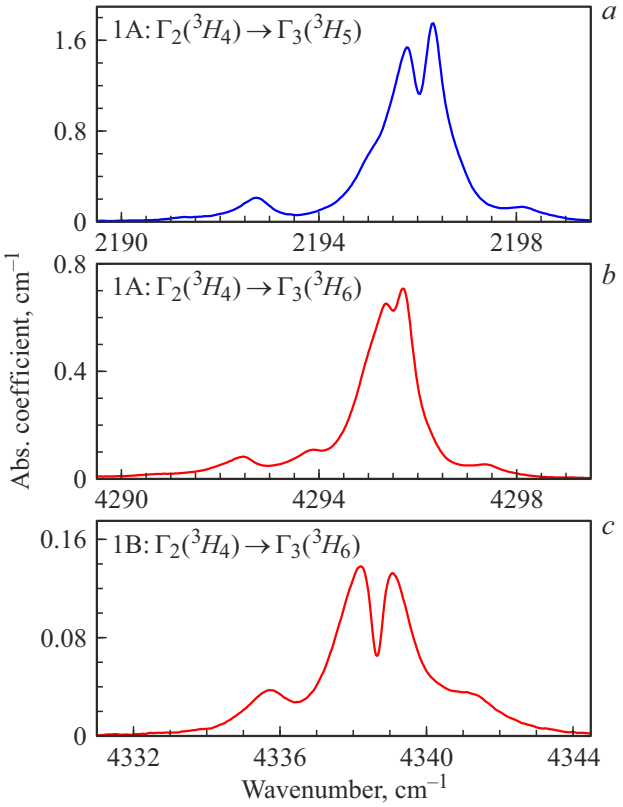

Figure 3. Spectral absorption lines in (a) π and (b,c) σ polarizations related to $\Gamma_2 \rightarrow \Gamma_3$ transitions in the YAB:Pr^{3+} crystal (1 at.%) at $T = 5$ K.

symmetry group D_3. The spectra were recorded in a broad spectral region (2000–23 000 cm^{-1}) by high-resolution Fourier spectroscopy (up to 0.1 cm^{-1}), which provides a highly accurate wave number scale. The crystal temperature was varied in a controlled manner from 5 to 300 K. As a result of analysing the spectra in π- and σ-polarized light, a scheme of crystal-field levels of the Pr^{3+} ion in YAB:Pr^{3+} has been constructed and the irreducible representations of the point group D_3 (Γ_1, Γ_2 or Γ_3), according to which the wave functions of the crystal-field levels are transformed, have been determined. These data form the basis for the subsequent correct calculation using the crystal-field theory.

The hyperfine structure caused by the interaction of electrons with the magnetic moment of the nucleus of the only stable isotope of praseodymium ^{141}Pr with nuclear spin $I = 5/2$ could not be observed in the spectra, but a characteristic doublet structure caused by the action of random lattice deformations was observed for a number of lines of singlet-doublet transitions. The spectral satellites of the $\Gamma_2(^3H_4) \rightarrow \Gamma_1(^3P_0)$ singlet-singlet transition line are attributed to transitions in Pr^{3+} ions close to the defects. Presumably, such defects are Mo^{3+} and Bi^{3+} ions, which enter the crystal from the flux during solution-melt growth and replace Al^{3+} and Y^{3+}, respectively.

Funding

This study was supported financially by the Russian Science Foundation (project No. 23-22-00433).

Conflict of interest

The authors declare that they have no conflict of interest.

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Translated by J.Savelyeva