Spectroscopic peculiarities of a trigonal $TbAl_3(BO_3)_4$ single crystal

A.V. Peschanskii[1] and A.Yu. Glamazda[1,2]

[1]*B. Verkin Institute for Low Temperature Physics and Engineering of the National Academy of Sciences of Ukraine, 47 Nauky Ave., 61103 Kharkov, Ukraine*

[2]*V.N. Karazin Kharkiv National University, 4 Svobody Sq., 61022, Kharkov, Ukraine*

In recent years, the physical properties of rare-earth aluminoborates $RAl_3(BO_3)_4$ (R is yttrium or a rare-earth ion) have been actively studied. The interest in these crystals is caused by their nonlinear optical properties, which, combined with their high chemical and mechanical strength, make it possible to use them for frequency doubling, laser and other devices. Yttrium and gadolinium aluminoborates with addition of Nd are used in optoelectronics and development of mini-lasers.

The crystal structure of $TbAl_3(BO_3)_4$ is characterized by the space group $R32\ (D_3)$ and presented in Fig. 1. The structure of the crystal can be represented in the form of layers perpendicular to the crystallographic axis c and consisting of distorted TbO_6 prisms, AlO_6 octahedra, and two types of BO_3 groups (Fig. 1).
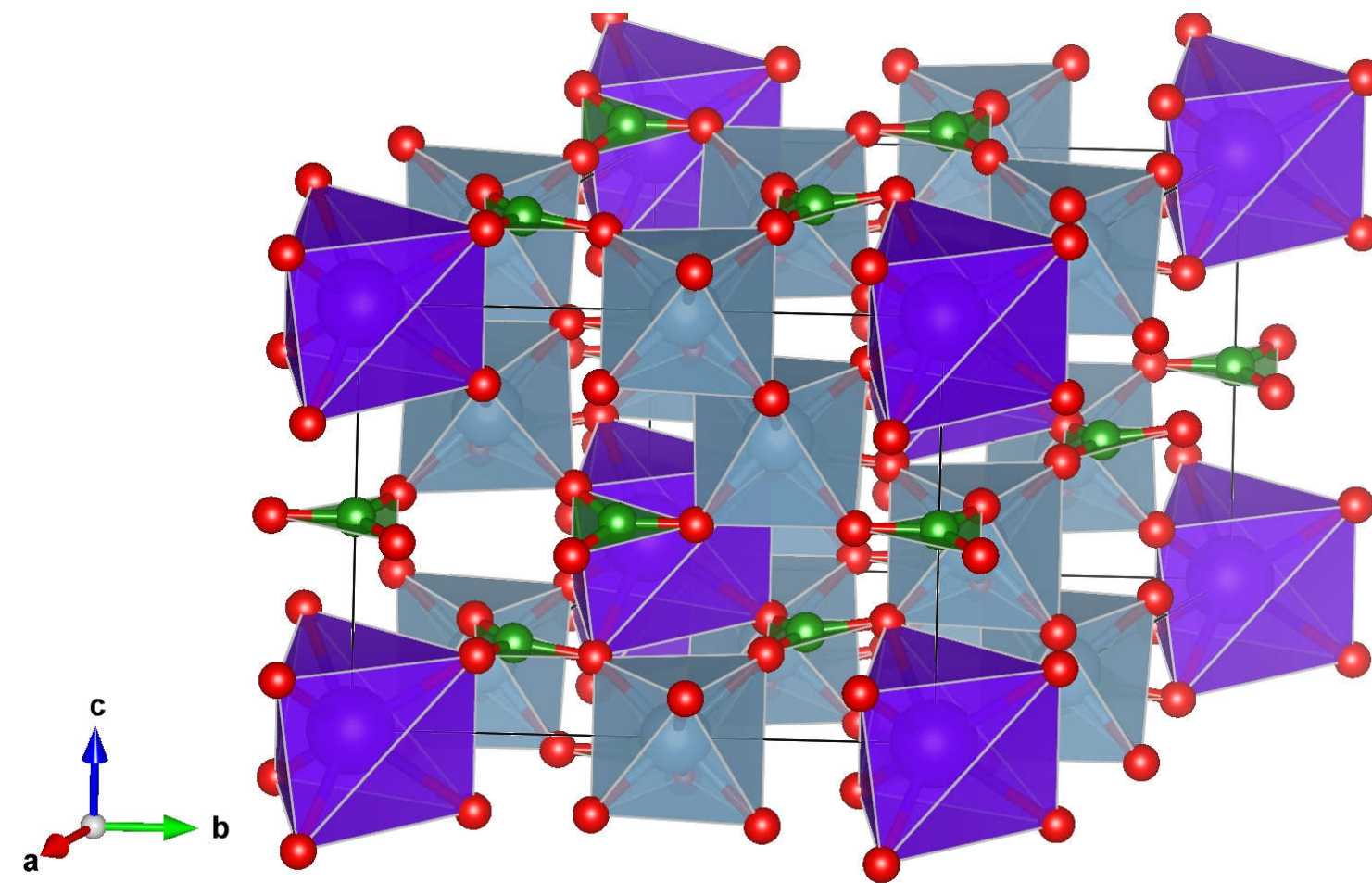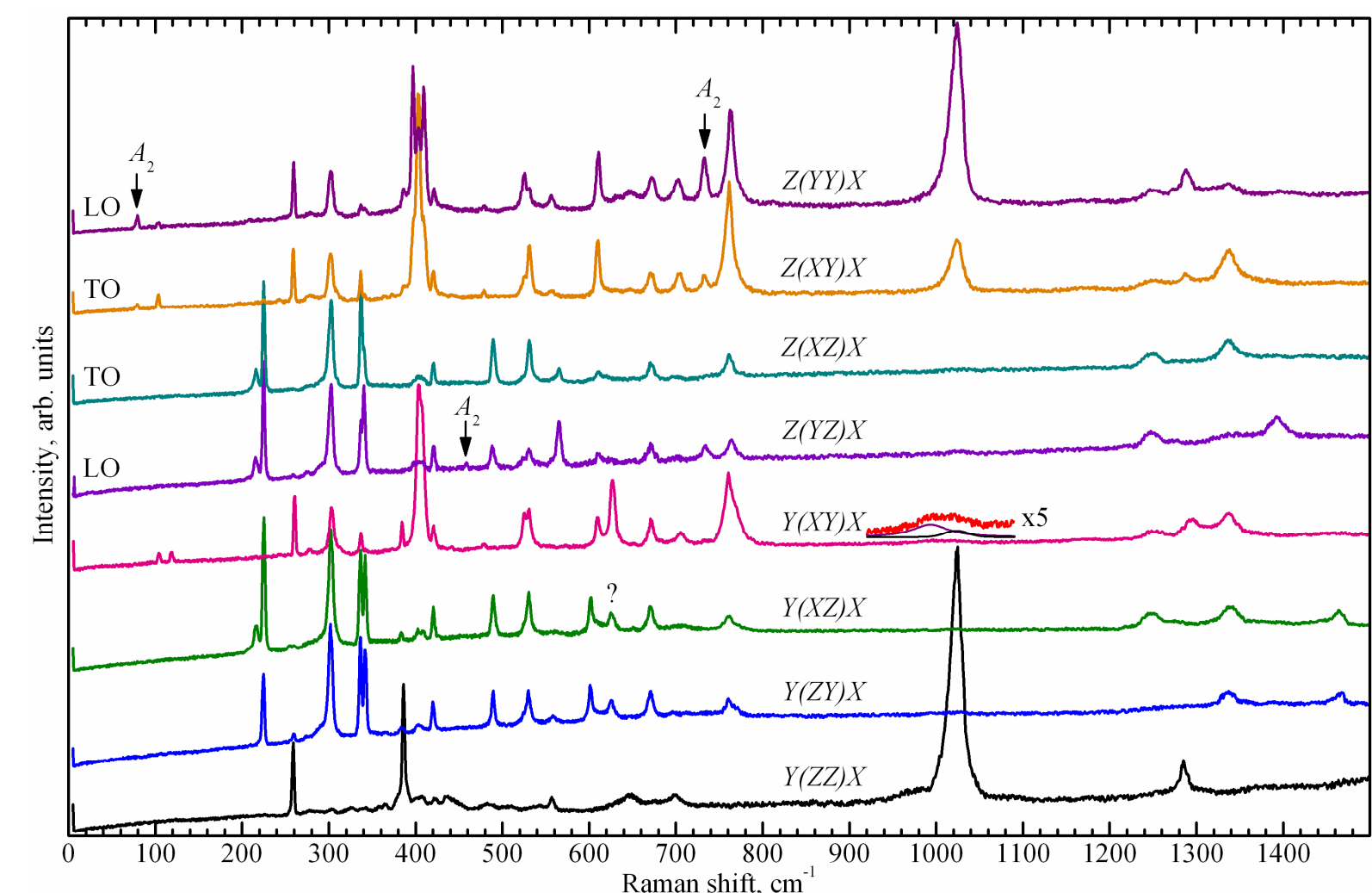

Fig. 1. Crystal structure of $TbAl_3(BO_3)_4$.

Fig. 2. Raman spectra of the $TbAl_3(BO_3)_4$ single crystal at 5 K in the different polarization geometries; λ_{exc} = 532 nm (36 mW); the spectral resolution of 3.0 cm⁻¹.

The Raman spectra in the $TbAl_3(BO_3)_4$ single crystal were investigated in the frequency range of 3 – 1600 cm⁻¹ and luminescence spectra were measured in the frequency range of 11800 – 21000 cm⁻¹ in the temperature range of 5 – 300 K. The spectra were taken with Nd:YAG (neodymium-doped yttrium aluminum garnet) solid-state laser (λ_{exc} = 532 nm) and He-Ne laser (λ_{exc} = 632.8 nm). The using of the different excitation wavelengths made it possible to unambiguously separate Raman and luminescence spectra.

The lattice vibrations are described with $\Gamma_{vibr} = 7A_1 + 13A_2 + 20E$ symmetry types, including the acoustic ones - $\Gamma_{ac} = A_2 + E$. It follows that $7A_1$ and doubly degenerate polar $19E$ modes are Raman-active and $12A_2 + 19E$ modes are IR-active. The non-zero components of the scattering tensor for the above setting have the form: $A_1 – XX, YY, ZZ; E – XX, YY, YZ, ZY, XY, YX, XZ, ZX$. The vibrational modes can be divided into the external - $\Gamma_{ext} = 3A_1 + 8A_2 + 11E$ and internal vibrations of the BO_3 group - $\Gamma_{int} = 4A_1 + 4A_2 + 8E$.
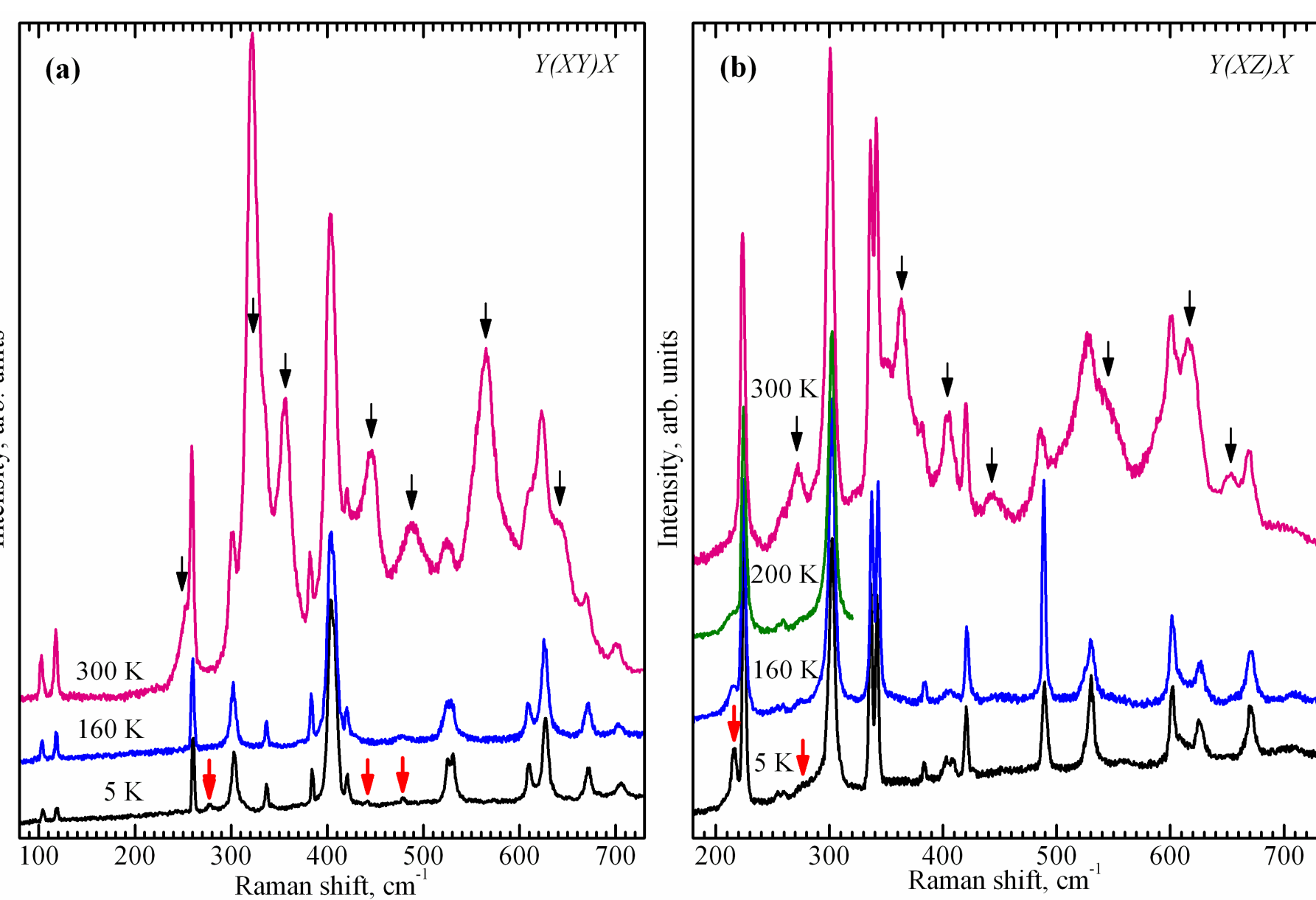
TbAl₃(BO₃)₄, present work, 5 K		TbFe₃(BO₃)₄ [1], 300 K		ν_TbAl/ν_TbFe	IR [2], 300 K
A_1		A_1			
259.1		180.6		1.434	
385.7		308.2		1.251	
557.2		476.0		1.171	
$A_2\ (\theta = 45°)$		$A_2\ (\theta = 45°)$			
79.0		60.5		1.306	80
458.5		372.6		1.231	462
E_{TO}	E_{LO}	E_{TO}	E_{LO}		
103.3	118.2	84.2	93.6	1.246	108
224.7		159.9		1.405	223
259.2	260.5	197.1	198.3	1.315	258
302.2		230.4		1.311	302
336.7	341.8	269.4		1.259	338
384.4	396.8	273.5	289.0	1.389	376?
403.1	409.7	315.4	330.4	1.259	401
420.5		350.7	355.8	1.191	
489.0		394.2		1.240	492
525.0		445.0		1.180	511?
530.0	601.5		489.0	1.230	546

TbAl₃(BO₃)₄, present work, 5 K		TbFe₃(BO₃)₄ [1], 300 K		ν_TbAl/ν_TbFe	IR [2], 300 K
A_1		A_1			
-		637.5			
-		959			
1023.3		989		1.037	
1285.3		1234.5		1.041	
$A_2\ (\theta = 45°)$		$A_2\ (\theta = 45°)$			
732.7		709.5		1.033	731
E_{TO}	E_{LO}	E_{TO}	E_{LO}		
612.5		580.0		1.055	612
671.5		631.6		1.063	
703.0		670.5	674.5	1.045	704
761.2	763.2	733.5		1.039	765
993.5		966.5		1.028	993
1250		1201.5	1216.5	1.034	1245
1295		1233.0		1.050	1280
1337	1465	1278.0	1414.5	1.041	1360

Table 1,2. Comparative analysis of the energy values (cm⁻¹) of the observed A_1, A_2, and E external and internal vibrational modes in $TbAl_3(BO_3)_4$ single crystal at 5 K and the literature data.

Fig. 3. The temperature evolution of Raman spectra of the $TbAl_3(BO_3)_4$ single crystal in the different polarization geometries: a – $Y(XY)X$ and b – $Y(XZ)X$; λ_{exc} = 532 nm (36 mW); the spectral resolution of 3.0 cm⁻¹.

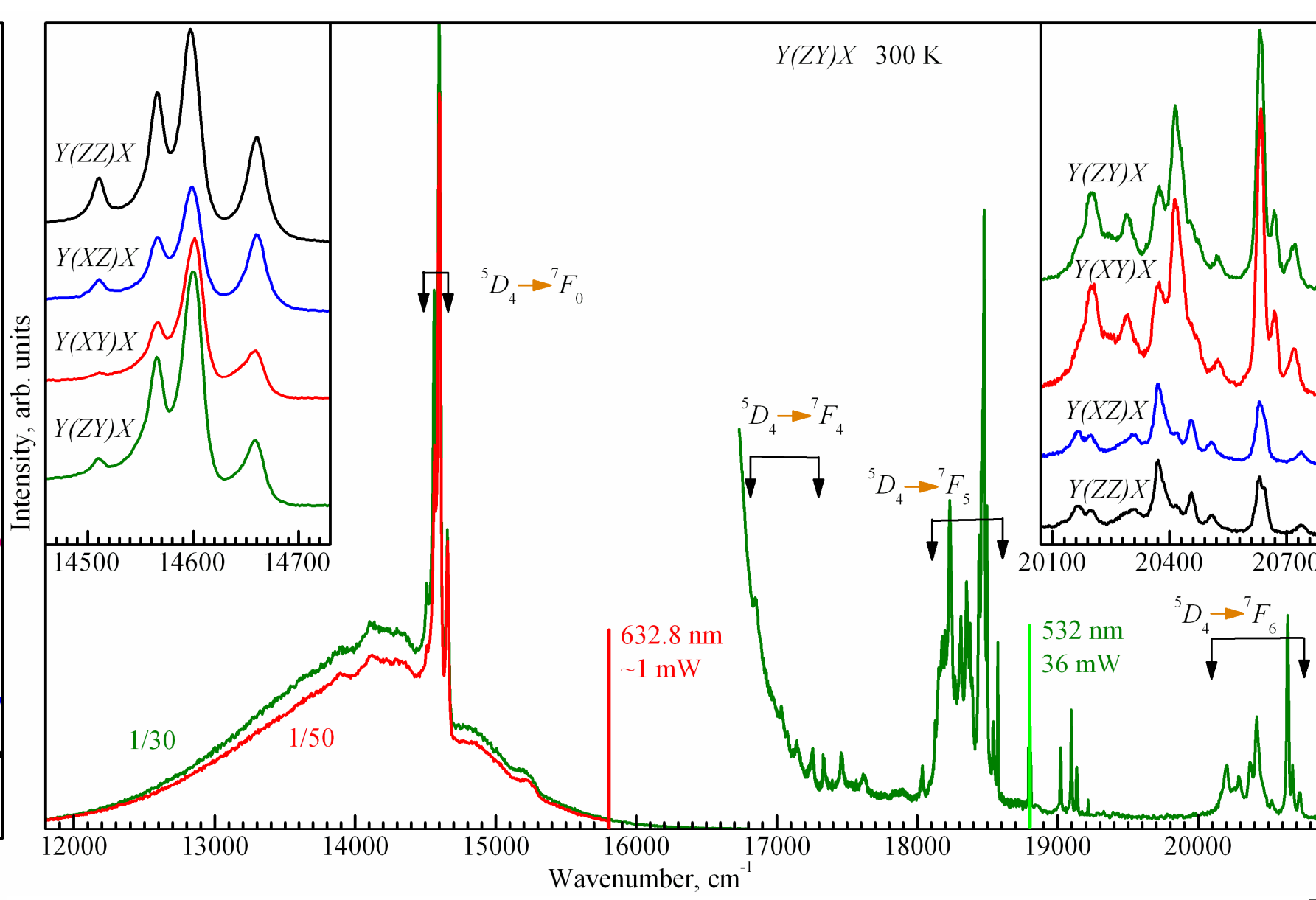**Fig. 4. Raman spectra and luminescence of the $TbAl_3(BO_3)_4$ single crystal at 300 K; λ_{exc} = 532 nm (36 mW, ~1.2 mW (11800–16800 cm⁻¹) and λ_{exc} = 632.8 nm (~1 mW); the spectral resolution of 3.0 cm⁻¹.**

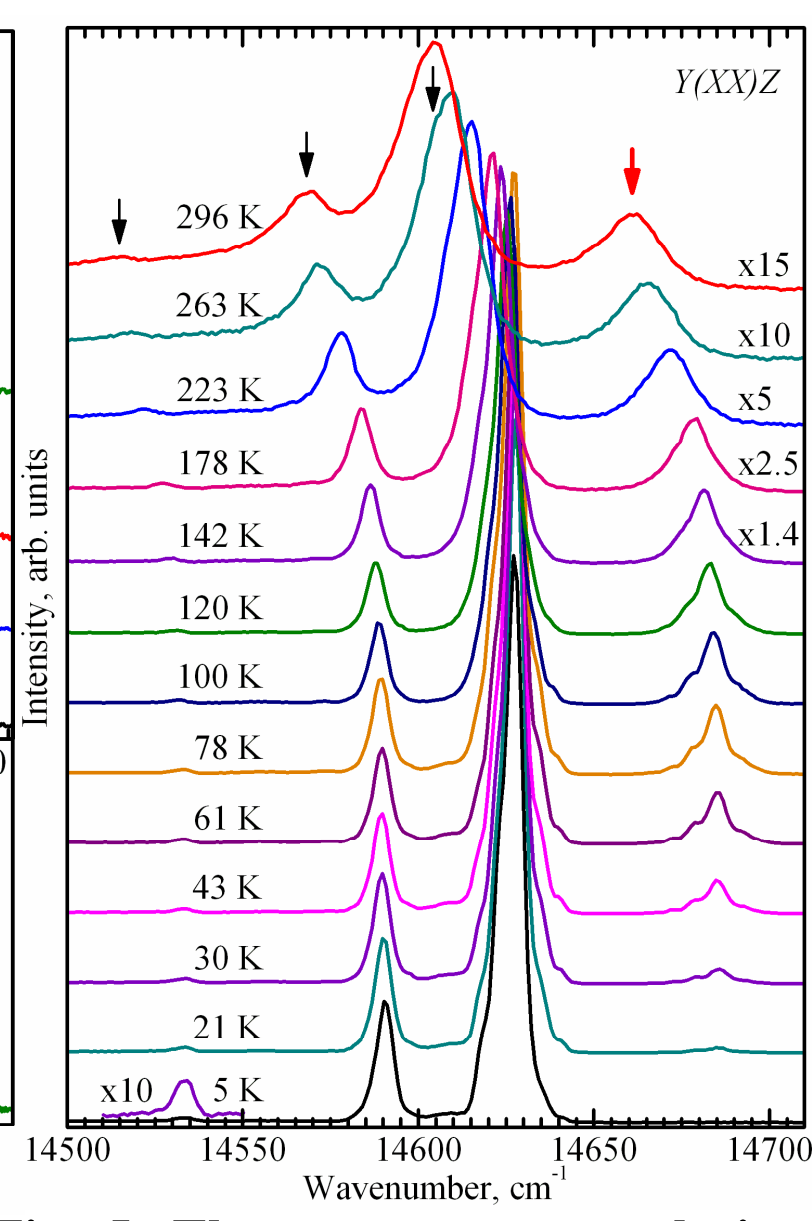**Fig. 5. The temperature evolution of the luminescence spectra of the $TbAl_3(BO_3)_4$ single crystal; λ_{exc} = 632.8 nm (~ 0.03 mW) ; the spectral resolution of 3.0 cm⁻¹.**
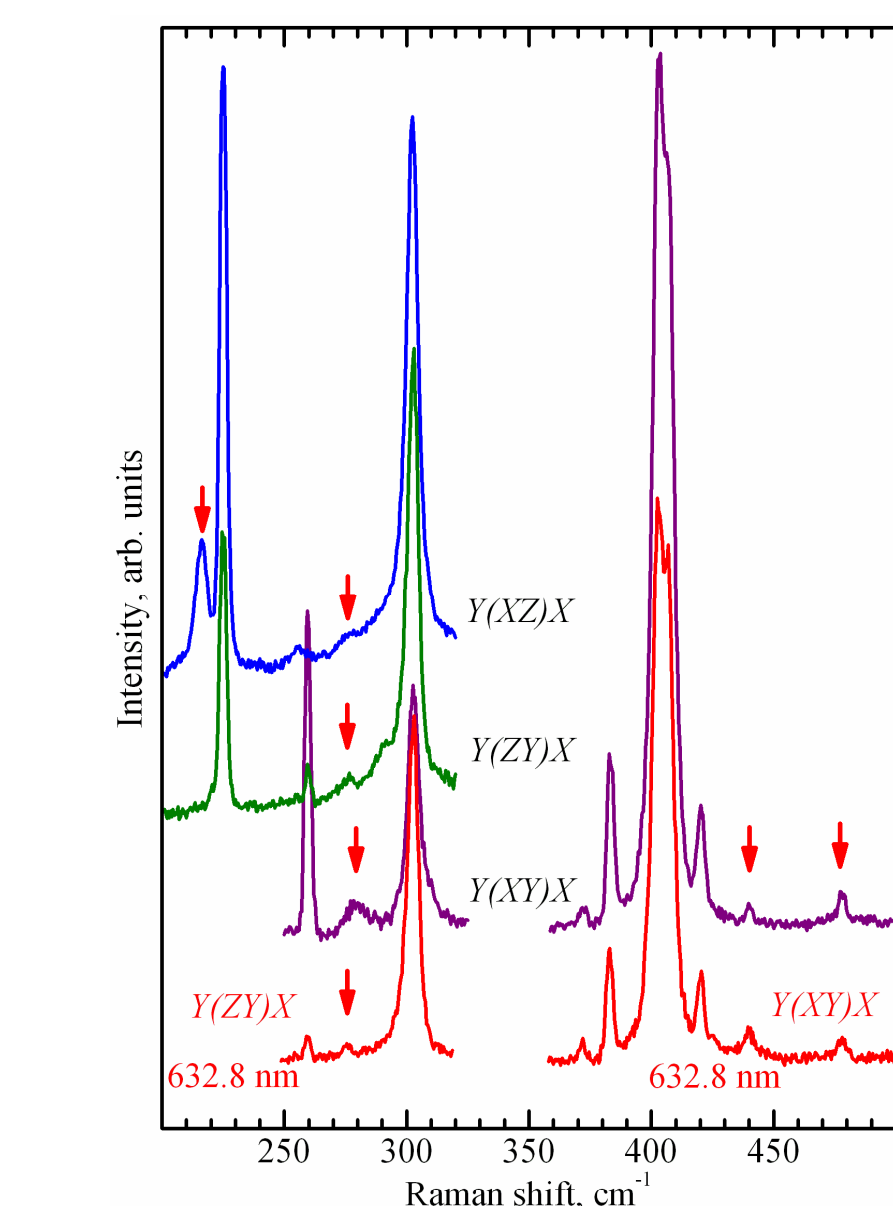

Fig. 6. Raman spectra of $TbAl_3(BO_3)_4$ taken in the different polarization configurations within main multiplet $^7F_6$ at 5 K; λ_{exc} = 532 nm and 632.8 nm (bottom red spectra); the spectral resolution of 5.0 cm⁻¹.

Present work		[3]	[4]
5 K	300 K	77 K	77 K
216.5	213	210	217
276.0	271	272	271
279.5	280	275	275
440.1	429	434	436
478.0	469	472	472

Table 3. The comparative analysis of the energy values (cm⁻¹) of the observed electronic transitions of Tb^{3+} in the $TbAl_3(BO_3)_4$ single crystal taken at 5 and 300 K and the literature data.

Conclusions

The analysis of Raman spectra of the single crystal has revealed 5 of 7 A_1 and all E phonon modes predicted by group-theory analysis. The splitting energy between the LO and TO components of polar E phonons was determined. Analysis of the phonon spectrum and its comparison with the isomorphic $TbFe_3(BO_3)_4$ compound were carried out.

A group of intense bands associated with the $^5D_4 \rightarrow {}^7F_0$ electronic transition was observed in the energy range of 14520–14680 cm⁻¹ in the luminescence spectra (Fig. 4). The intensity of these bands decreases upon heating. At the same time, the bands which can be assigned with the $^5D_4 \rightarrow {}^7F_6$, $^5D_4 \rightarrow {}^7F_5$, and $^5D_4 \rightarrow {}^7F_4$ transitions were revealed in the luminescence spectra at room temperature (Fig. 4). The intensity of these bands is comparable to the intensity of Raman spectrum of $TbAl_3(BO_3)_4$. The observation of luminescence from the $^5D_4$ level (20600–20750 cm⁻¹) upon excitation with λ_{exc}=632.8 nm (15803 cm⁻¹) and λ_{exc}=532 nm (18797 cm⁻¹) indicates strong nonlinear properties of the studied crystal.

The structure of the main $^7F_6$ multiplet of the Tb^{+3} ion in the $TbAl_3(BO_3)_4$ single crystal has been studied by Raman spectroscopy at 5 K. The energies of the electronic levels of the $^7F_6$ and $^5D_4$ multiplets were determined by analyzing the luminescence spectra measured at 300 K.

References:

1. A.V. Peschanskii, A.V. Yeremenko, V.I. Fomin, L.N. Bezmaternykh, I.A. Gudim, Low Temp. Phys. 40, 171 (2014).

2. E.A. Dobretsova, E.Yu. Borovikova, K.N. Boldyrev, et al, Optics and Spectroscopy 116, 77 (2014)

3. C. Gorller-Walrand, P. Vandevelde, I. Hendrickx, P. Porcher, and J.C. Krupa, Inorg. Chim. Acta 139, 277 (1987).

4. I. Couwenberg, K.Binnemans, H. De Leebeeck, C. Gorller-Walrand, Journal of Alloys and Compounds 274, 157 (1998).