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Spectroscopic study of GdVO₄: Yb + Er crystals

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Abstract. GdVO₄ crystals doped with different erbium and ytterbium concentrations have been grown in order to study their spectroscopic and kinetic properties and identify the nature of active centres in them. Their polarised transmission and luminescence spectra have been used to construct energy level diagrams of the Er³⁺ ion. The lifetime of the lower level of the ⁴I_{11/2} excited-state multiplet has been shown to decrease markedly with increasing ytterbium concentration. Inequivalent erbium centres have been observed to form in the crystals with increasing ytterbium concentration.

Keywords: GdVO₄:Yb + Er, Stark levels, luminescence, lifetime, inequivalent centres.

1. Introduction

Yb³⁺ and Er³⁺ ions are widely used as a pair in photonics in multilayer film light sources [1], microchip lasers [2], novel compact ‘eye-safe’ fibre lasers [3], efficient up-conversion sources [4, 5], optical memory [6], etc. The Yb³⁺ and Er³⁺ trivalent ions, a sensitiser and an activator, respectively, serve different functions: owing to its rich system of energy levels, erbium allows one to obtain emission in different spectral ranges, whereas ytterbium ensures strong pump absorption and efficient energy transfer to erbium (Fig. 1). RVO₄ (R = Gd, Y) vanadate crystals (zircon structure) doped with erbium and ytterbium optically active ions have excellent optical characteristics [7 – 14]. They are commonly known to be promising and widely used laser materials owing to their unique properties: good chemical stability, excellent thermal conductivity and large absorption and emission cross sections [15 – 19].

Gadolinium vanadate has the zircon (ZrSiO₄ mineral) structure. It has the form of colourless crystals with tetragonal symmetry: space group I4_{1/amd} (*Z* = 4), unit-cell parameters *a* = 0.7212 nm and *c* = 0.6346 nm [20]. Its crystal structure is schematised in Fig. 2. Each gadolinium atom is coordinated by eight O²⁻ oxygen ions. The gadolinium site has point symmetry D_{2d}. The GdO₈ polyhedra form a three-dimensional network. Each polyhedron shares one edge with each of the four adjacent GdO₈ polyhedra. In addition, the GdO₈ polyhedra are linked through VO₄ tetrahedra isolated from each other. The Er³⁺ ion has a rich set of optical transitions, among which the 4I_{13/2} → 4I_{15/2} transition falls in the very important spectral range around *λ* = 1.5 μm.

This spectral range is of great interest for telecommunications because here silica fibre has a minimum absorption. Besides, the spectral range 1.5 - 1.6 μm is known to be eye-safe and is used in telemetry. The ability to improve the performance of emitters operating in this range, including laser sources, has been the subject of extensive studies (see e.g. Refs [21 - 24]). In the Er - Yb codoped samples, process 1 (Fig. 1: relaxation from the $4I_{11/2}$ multiplet to $4I_{13/2}$, followed by emission at $\lambda = 1.55 \mu\text{m}$) competes with process 2 - up-conversion through energy transfer from ytterbium to excited erbium, which is thus brought to the $^4F_{7/2}$ state, following which visible emission channels appear. In practice, processes 1 [3, 12] and 2 [7, 8, 10, 11, 14, 16] occur simultaneously. Despite the extensive studies of the optical properties of erbium- and/or ytterbium-doped GdVO_4 crystals and nanopowders, information about the energy level structure of Er^{3+} and Yb^{3+} ions in this host is still limited. In this paper, we report a systematic study of the energy level structure of optically active erbium and ytterbium ions in GdVO_4 crystals. GdVO_4 single crystals doped with different erbium and ytterbium concentrations were grown by the Czochralski technique. Their spectroscopic properties were studied by optical absorption and luminescence spectroscopies. We determined the lifetime of the $\text{Er}^{3+} 4I_{11/2}$ level in different crystals and examined how it was influenced by the sensitizer concentration.

2. Experimental

We grew $\text{GdVO}_4 : \text{Er}$ (1 at %), $\text{GdVO}_4 : \text{Yb}$ (2 at %), $\text{GdVO}_4 : \text{Yb}$ (10 at %) + Er (0.5 at %) and $\text{GdVO}_4 : \text{Yb}$ (37 at %) + Er (0.5 at %) single crystals. For measurements, we prepared plane-parallel plates whose faces were parallel to the c axis. Transmission spectra were obtained at temperatures from 4.5 to 300 K and frequencies from 5 000 to 22 500 cm^{-1} on a Bruker IFS 125HR high-resolution Fourier transform spectrometer. To gain information about the symmetry of levels, spectra were measured for two light polarisations: σ ($\mathbf{k} \perp c$, $\mathbf{E} \perp c$, $\mathbf{H} \parallel c$) and π ($\mathbf{k} \perp c$, $\mathbf{E} \parallel c$, $\mathbf{H} \perp c$). Luminescence spectra were excited by the radiation from an argon laser (Coherent Innova 90) pumped Ti:sapphire laser (Coherent Ring Model 899) and synchronously detected using a monochromator fitted with a PbS detector. In lifetime measurements, excitation was provided by a parametric oscillator at the absorption wavelength of the Yb^{3+} ion. The oscillator was pumped by the BM:In:YAG third harmonic. The excitation pulse duration was 10 ns. The emission from the sample was detected at the monochromator output using an InGaAs detector and 150-MHz digital oscilloscope. The signal was averaged over 256 measurements.

3. Results and discussion

In the crystal structure of GdVO_4 , the Gd^{3+} trivalent ions and rare-earth (RE) substituents occupy sites of tetragonal symmetry (point group D_{2d}). The wave functions of an RE ion having an odd number of electrons (as in Er^{3+} and Yb^{3+}) transform according to the Γ_6 and Γ_7 irreducible representations of point group D_{2d} . Table 1 presents nonzero components of the electric and magnetic dipole moments for optical transitions in this symmetry group. It is seen that the $\Gamma_7 \leftrightarrow \Gamma_6$ electric dipole (ED) transitions are allowed for both the σ - and π -polarisations. At the same time, the $\Gamma_7 \rightarrow \Gamma_7$ and $\Gamma_6 \rightarrow \Gamma_6$ ED transitions can only be observed in the case of σ -polarisation. Figure 3 shows transmission spectra of the $\text{GdVO}_4 : \text{Er}$ (1 at %) crystal in the spectral range of the $\text{Er}^{3+} 4I_{15/2} \rightarrow 4I_{11/2}$ intermultiplet transition for both σ - and π -polarisations. This multiplet consists of six doublets, three of each symmetry: $3\Gamma_6 + 3\Gamma_7$. We assume the ground state of the Er^{3+} ion to have Γ_7 symmetry, as in $\text{YVO}_4 : \text{Er}$ [25] and the isostructural compound $\text{YPO}_4 : \text{Er}$ [26]. Since the energy of the first excited state of the Er^{3+} ion in the crystal under study is 39 cm^{-1} , as evaluated from spectra, only the ground state is populated at a

temperature of 4.5 K, so just six lines, corresponding to transitions from the ground state (of Γ_7 symmetry) to the six levels of the $4I_{15/2} \rightarrow 4I_{11/2}$ multiplet, should be seen in the spectrum of the $4I_{11/2}$ transition. According to selection rules, three lines of $\Gamma_7 \rightarrow \Gamma_6$ ED transitions are allowed for π -polarisation, which we observe as strong lines in Fig. 3b. The $\Gamma_7 \rightarrow \Gamma_7$ transitions for π -polarisation can show up only as MD transitions. In the case of σ -polarisation, all transitions are allowed in the ED approximation. Thus, we were able to determine not only the energy but also the symmetry of the Stark levels of the $4I_{11/2}$ multiplet (Table 2). Also indicated in Table 2 are the present data for the $4I_{13/2}$ multiplet. The energies of the $4I_{13/2}$ multiplet levels determined in this study agree well with those reported by Ter-Gabrielyan et al. [12].

Figure 4 shows absorption spectra of the $\text{GdVO}_4 : \text{Er}$ (1 at %), $\text{GdVO}_4 : \text{Yb}$ (2 at %) and $\text{GdVO}_4 : \text{Yb}$ (10 at %) + Er (0.5 at %) crystals. It is seen that the Er^{3+} and Yb^{3+} ions in the GdVO_4 host have identical lower level energies of the $4I_{11/2}$ (Er) and $2F_{5/2}$ (Yb) multiplets, which is a critical condition for efficient energy transfer. The lines at 10155 cm^{-1} in spectra 1 and 2 are seen to have weak satellites, which are probably due to RE pair centres [27, 28].

Figure 5a shows luminescence spectra in the region of the $4I_{13/2} \rightarrow 4I_{15/2}$ transition at liquid-nitrogen and room temperatures. At the higher temperature, the emission lines are broad. Cooling markedly reduces their width and leads to an intensity redistribution due to changes in level populations in the upper multiplet, which are determined by the Boltzmann distribution. Analysis of the spectra with the use of the data in Table 2 makes it possible to identify all spectral lines with certainty and reliably determine the energies of the upper Stark levels 6, 7 and 8 of the $4I_{15/2}$ multiplet in Fig. 5b: 245, 265 and 300 cm^{-1} , respectively. The measured lifetime of the lower level of the $4I_{11/2}$ multiplet in the $\text{GdVO}_4 : \text{Er}$ (1 at %) crystal is 230 ms. In the codoped Yb - Er samples, the fluorescence around 1 μm originates from the thermalised $2F_{5/2}$ (Yb) and $4I_{11/2}$ (Er) multiples and the measured lifetime decreases to 195 ms in the case of $\text{GdVO}_4 : \text{Yb}$ (10 at %) + Er (0.5 at %) and is even shorter (79 ms) in the $\text{GdVO}_4 : \text{Yb}$ (37 at %) + Er (0.5 at %) crystal. At the same time, the lifetime of the $4I_{13/2}$ state is essentially independent of the ytterbium concentration in the crystals: ~ 2.76 ms. The decrease in the lifetime of the $4I_{11/2}$ state with increasing ytterbium concentration is likely due to the increase in up-conversion probability (Fig. 1, process 2).

Figure 6 shows the line shapes in the low-temperature transmission spectra for the same transitions in two GdVO_4 crystals: one singly doped with erbium and the other co-doped with erbium and ytterbium. In the former case, the lines are rather narrow and their width is determined by inhomogeneous broadening. In the latter, each line has a complex shape and is a combination of a few lines. A similar line shape in spectra of RE ions was observed by us previously for other compounds co-doped with RE ions [29 - 31]. It occurs when the nearest neighbour environment of an RE ion contains another RE ion having a different ionic radius. As shown in Fig. 2, each gadolinium ion in GdVO_4 has four gadolinium ions as nearest neighbours. The $\text{GdVO}_4 : \text{Yb}$ (10 at %) + Er (0.5 at %) crystal can contain different erbium centres: a usual centre, surrounded by four gadolinium ions; a centre in which one nearest neighbour site is occupied by ytterbium instead of gadolinium; etc. Thus, there are inequivalent centres. Since the Gd^{3+} and Yb^{3+} ions differ in ionic radius, the GdO_8 and YbO_8 polyhedra are distorted because they share one edge, or in other words two oxygens. The crystal field distortion for such a centre entails corrections to its Hamiltonian and, accordingly, corrections to its Stark level energies. As shown earlier [30, 31], the integrated intensities of envelopes constituting a composite line are proportional to the probabilities (P) of formation of inequivalent centres. Such probability can be found as

$$P = C_n^4 x^4 (1 - x)^{4-n}, \quad (1)$$

where x is the fraction of an impurity ion producing defects and n is the number of nearest neighbour impurity atoms. The situation can also be described in terms of clusters. The main cluster has the form of ErGd_4 ; a centre with one defect is an ErYbGd_3 cluster. Using relation (1), it is easy to obtain that, in the case of $\text{GdVO}_4:\text{Yb}$ (10 at %) + Er (0.5 at %), the probability of formation of the main cluster is ~ 0.65 and that of the first defect cluster is 0.29. At first glance, such relations qualitatively describe the complex line shapes in the spectra in Fig. 6.

4. Conclusions

Polarised transmission spectra of erbium- and ytterbium doped GdVO_4 crystals have been measured for the first time, and information about the energies and symmetries of the Stark levels of the $4I_{11/2}$ and $4I_{13/2}$ multiplets has been obtained. Varying the ytterbium doping level (ytterbium concentration) changes the probabilities of phonon relaxation and up-conversion from the $4I_{11/2}$ multiplet. The formation of inequivalent erbium centres with increasing ytterbium concentration leads to complex, multicomponent shapes of the spectral lines corresponding to Er^{3+} intermultiplet transitions.

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D_{2d}	Γ_6	Γ_7
	d_x, d_y	d_z, d_x, d_y
Γ_6	μ_z, μ_x, μ_y ($\sigma_{e,m}, \pi_m$)	μ_x, μ_y ($\sigma_e, \pi_{e,m}$)
	d_z, d_x, d_y	d_x, d_y
Γ_7	μ_x, μ_y ($\sigma_e, \pi_{e,m}$)	μ_z, μ_x, μ_y ($\sigma_{e,m}, \pi_m$)

Table 1. Nonzero components of the electric and magnetic dipole moments, d_i and μ_i ($i = x, y, z$), respectively, of transitions for point group D_{2d} and ions having an odd number of electrons. The subscripts e (electric dipole, ED) and m (magnetic dipole, MD) indicate allowed transitions for the corresponding polarisation.

${}^4I_{13/2}$		${}^4I_{11/2}$	
E/cm^{-1}	Symmetry	E/cm^{-1}	Symmetry
6536.9 (6539)	7	10155	6
6537.9 (6549)	6	10200	7
6578.9 (6581)	7	10218	6
6588.9 (6591)	7	10233	7
6628.2 (6630)	6	10256	6
6679.3 (6681)	6	10267	7
6697.4 (6698)	7		

Note. The numbers in brackets are data from Ref. [12].

Table 2. Energies (E) and symmetries of the Stark levels of the ${}^4I_{13/2}$ and ${}^4I_{11/2}$ multiplets.

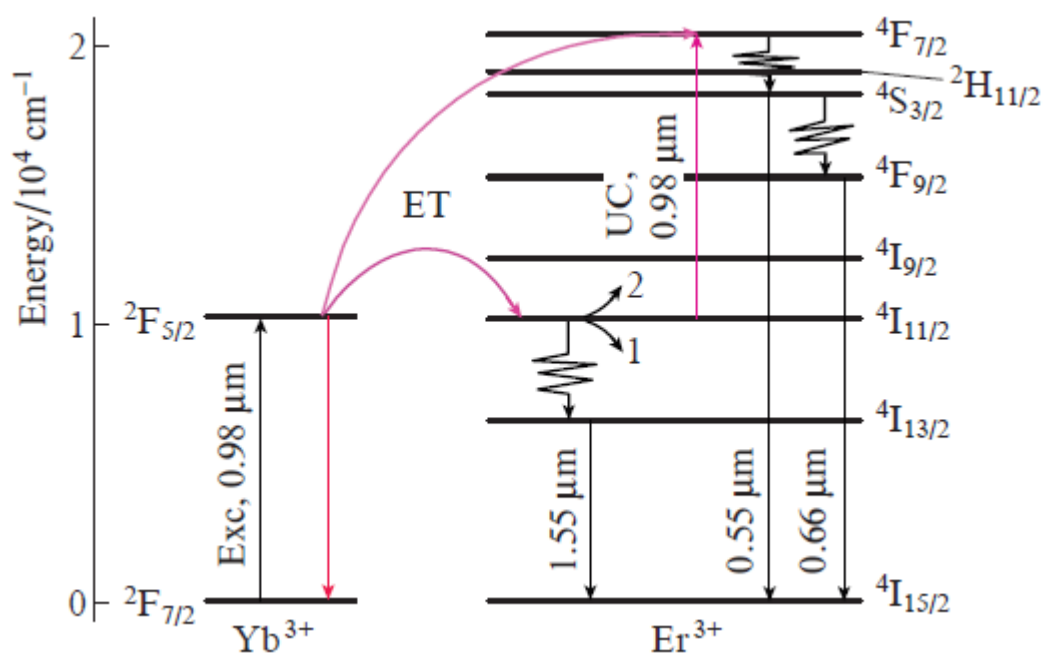


Figure 1. Energy level diagram of the Yb^{3+} and Er^{3+} ions, showing multiplets and the wavelengths of some transitions; Exc, excitation; ET, energy transfer; process 1: nonradiative relaxation and emission; process 2: up-conversion (UC).

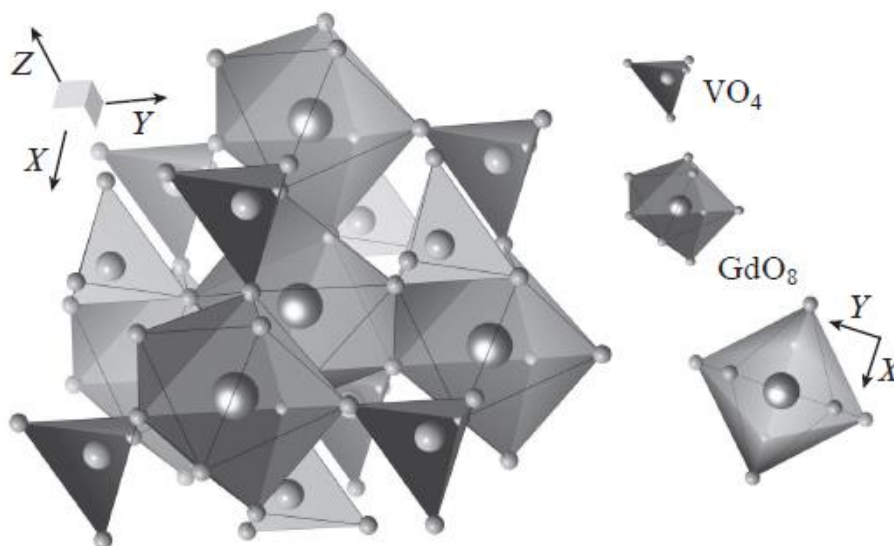


Figure 2. Partial crystal structure of GdVO_4 . Right side: GdO_8 polyhedron projected along the twofold rotation axis parallel to the crystallographic axis Z .

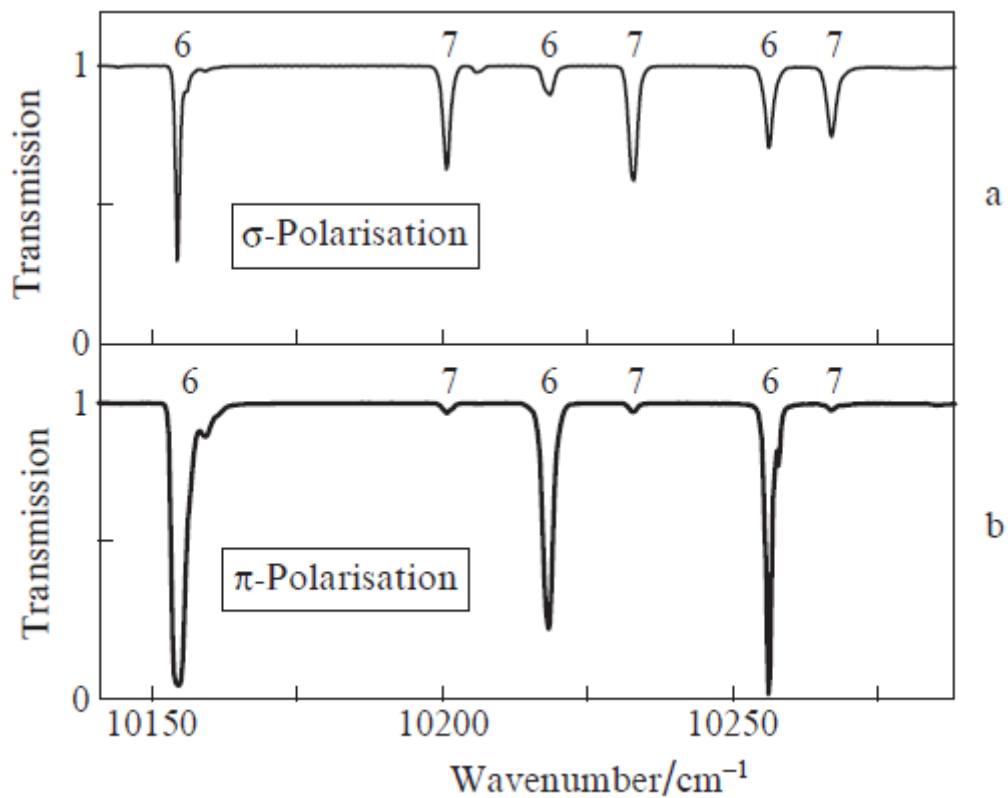


Figure 3. Transmission spectra of the $\text{GdVO}_4 : \text{Er}$ (1 at %) sample for the $\text{Er}^{3+} 4\text{I}_{15/2} \rightarrow 4\text{I}_{11/2}$ transition at a temperature of 4.5 K in polarised light for (a) σ - and (b) π -polarisations. Also indicated are representations of the symmetry group D_{2d} : 6 (Γ_6) and 7 (Γ_7) of the $4\text{I}_{11/2}$ multiplet levels.

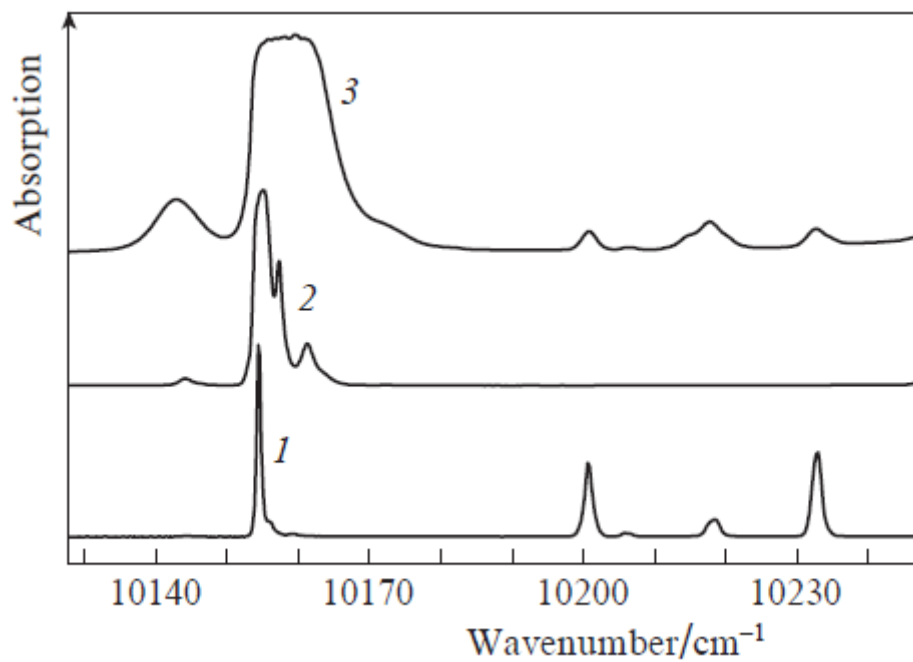


Figure 4. Absorption spectra of the (1) $\text{GdVO}_4 : \text{Er}$ (1 at %), (2) $\text{GdVO}_4 : \text{Yb}$ (2 at %) and (3) $\text{GdVO}_4 : \text{Yb}$ (10 at %) + Er (0.5 at %) samples in the region of the $\text{Yb}^{3+} 0 - 0$ transition at a temperature of 4.5

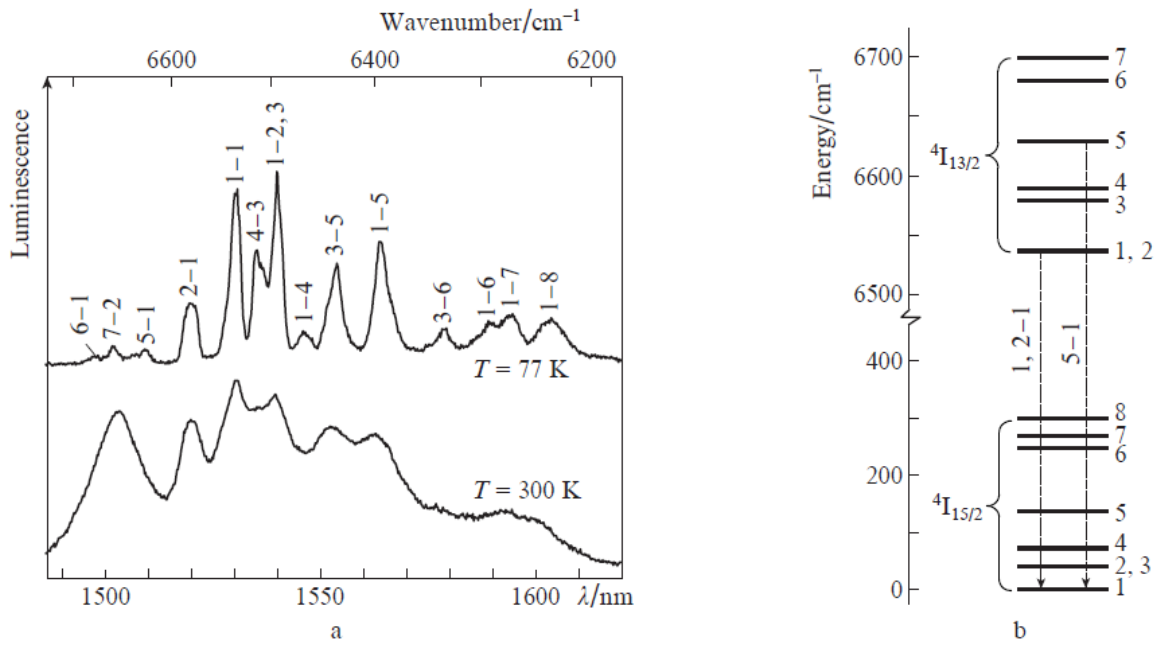


Figure 5. (a) Luminescence spectra of the $\text{GdVO}_4 : \text{Yb}$ (37 at %) + Er (0.5 at %) crystals at temperatures of 77 and 300 K; (b) energy level diagram of the $4I_{15/2}$ ground-state and $4I_{13/2}$ excited-state multiplets, with some spectral transitions indicated.

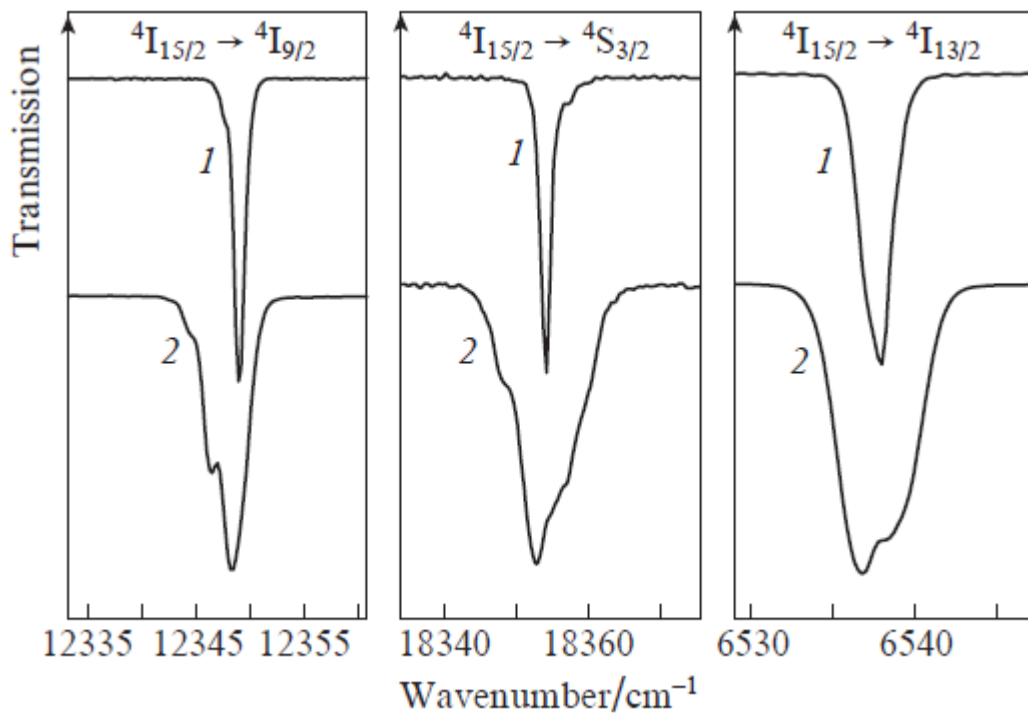


Figure 6. Spectral lines of the $4I_{15/2} \rightarrow 4I_{9/2}$, $4I_{15/2} \rightarrow 4S_{3/2}$ and $4I_{15/2} \rightarrow 4I_{13/2}$ transitions for the (1) $\text{GdVO}_4 : \text{Er}$ (1 at %) and (2) $\text{GdVO}_4 : \text{Yb}$ (10 at %) + Er (0.5 at %) samples at a temperature of 4.5 K, demonstrating the presence of inequivalent centres in the ytterbium-rich sample.