## INTRODUCTION

The optical spectra of rare-earth ions are sensitive to the state of the host crystal lattice. A change in temperature alters the amplitude of lattice vibrations and the number of phonons, which affects the width, position and intensity of spectral lines. External pressure, in turn, reduces interionic distances and thereby modifies the crystal-field strength and the covalent bonding of the 4f electrons with the ligands [1, 2]. Both factors make it possible either to "tune" the spectra or, conversely, to use them as sensors.

The effect of temperature is of great practical importance. In high-power lasers and amplifiers, the active element is heated by the pump by up to hundreds of kelvin, which changes the gain coefficient, the lasing threshold and the spectral properties [3]. Conversely, cooling the active element to liquid-nitrogen temperature effectively converts quasi-three-level lasers (e.g. Yb:YAG) into a four-level scheme and sharply increases their efficiency [4]. On the other hand, the temperature dependence of luminescent properties underlies non-contact optical thermometry [5].

The study of pressure effects provides important information for fundamental physics. By generating pressures of tens of gigapascals in diamond anvil cells, the dependence of the crystal-field parameters on interionic distance can be measured directly [6, 7]. In addition, the narrow luminescence lines of some rare-earth ions are widely used as optical gauges for measuring high pressures. In particular, the 685 nm line of the $Sm^{2+}$:$SrB_4O_7$ crystal is almost temperature-independent and therefore provides reliable pressure measurement even in high-temperature experiments [8].

The mechanisms by which temperature and pressure affect the spectra of rare-earth ions are described within the theory of electron–phonon interaction. This theory shows that the simultaneous absorption and emission of phonons (the two-phonon Raman process) leads to line broadening and shift, whereas one-phonon processes give rise to transitions between closely spaced Stark levels [9].

An analysis of the available literature shows that, whereas studies of temperature effects have been carried out mainly for laser crystals and phosphors, data on pressure effects are relatively scarce and are largely limited to the $Pr^{3+}$, $Nd^{3+}$, $Eu^{3+}$ and $Sm^{2+}$ ions [6, 7]. In many practical situations – for example, in high-power laser elements – temperature and mechanical stress act simultaneously, and separating their effects on the spectrum is a complex problem. It is therefore a topical task to systematise the main regularities of both effects within a unified approach and to provide simple, verifiable quantitative estimates.

The aim of this work is to analyse the main mechanisms by which temperature and hydrostatic pressure affect the optical spectra of rare-earth ions, to estimate these effects quantitatively for Yb:YAG and $Sm^{2+}$:$SrB_4O_7$, and to demonstrate the practical significance of the results obtained.

## MATERIALS AND METHODS

### *Thermal population of levels*

In thermodynamic equilibrium, the relative population of the i-th Stark level within a multiplet is given by the Boltzmann distribution:

$$f_i(T) = g_i \exp(-E_i/kT) / \Sigma_j g_j \exp(-E_j/kT) \quad (1)$$

where $E_i$ is the level energy and $g_i$ is its degeneracy ($g_i = 2$ for all Kramers doublets). The calculations used the Stark levels of Yb:YAG reported in the literature: the $^2F_{7/2}$ multiplet – 0, 565, 612, 785 $cm^{-1}$; the $^2F_{5/2}$ multiplet – 10327, 10624, 10679 $cm^{-1}$ [4, 10]. The 1030 nm laser transition occurs from the 10327 $cm^{-1}$ level to the 612 $cm^{-1}$ level.

***Linewidth model***

The homogeneous width of the spectral lines of rare-earth ions is determined mainly by residual mechanisms at low temperatures and by the two-phonon Raman process at high temperatures. According to the McCumber–Sturge model [9]:

$$\Gamma(T) = \Gamma_0 + \bar{\alpha}\,(T/T_D)^7 \int_0^{T_D/T} x^6 e^x/(e^x - 1)^2\,dx \qquad (2)$$

where $\Gamma_0$ is the temperature-independent width (inhomogeneous broadening and one-phonon transitions between Stark levels), $\bar{\alpha}$ is the electron–phonon coupling parameter and $T_D$ is the effective Debye temperature. The line shift is described by a similar expression:

$$\delta E(T) = \alpha'\,(T/T_D)^4 \int_0^{T_D/T} x^3/(e^x - 1)\,dx \qquad (3)$$

In the calculations, $T_D = 750$ K was adopted for YAG, and the results were normalised to the value at 300 K. The integrals were evaluated numerically (SciPy library).

***Effect of pressure***

Under hydrostatic pressure, the change in the optical transition energy at low pressures is described in the linear approximation:

$$\lambda(P) = \lambda_0 + (d\lambda/dP)\cdot P \qquad (4)$$

For $Sm^{2+}$:$SrB_4O_7$, the wavelength of the $^5D_0 \rightarrow {}^7F_0$ line at ambient pressure was taken as $\lambda_0 = 685.41$ nm and the pressure

coefficient as $d\lambda/dP \approx 0.2556$ nm/GPa [8]. At higher pressures (above 20 GPa), non-linear corrections are introduced.

### *Experimental procedure*

The following procedure is recommended for the experimental verification of the calculated results. Temperature-dependent spectra are measured in a closed-cycle helium cryostat over 4–300 K and in an optical furnace with temperature control to ±0.1 K over 300–700 K. The spectra are recorded with a high-resolution monochromator (0.01–0.05 nm); the linewidth and position are determined by fitting with Lorentzian or Voigt functions. Hydrostatic pressure is generated in a diamond anvil cell, with a methanol–ethanol mixture (hydrostatic up to 10 GPa) or condensed inert gases used as the pressure-transmitting medium. The pressure is determined from the luminescence of small ruby or $Sm^{2+}$:$SrB_4O_7$ crystals placed next to the sample [7, 8]. From the data obtained, the parameters $\bar{\alpha}$, $\alpha'$ and $T_D$ are found using formulas (2) and (3), and the coefficients $d\lambda/dP$ are derived from the pressure dependence.

## RESULTS

### *Effect of temperature*

The populations of the Yb:YAG Stark levels calculated using formula (1) are given in Table 1.

**Table 1.** Thermal population of the lower laser level (612 $cm^{-1}$) and the upper laser level (10327 $cm^{-1}$) within their multiplets in the Yb:YAG crystal

| T, K | kT, $cm^{-1}$ | Lower laser level population $f_l$, % | Fraction of the upper level within $^2F_{5/2}$ $f_u$, % | Relative phonon width $\Gamma_{ph}(T)/\Gamma_{ph}(300\ K)$ |
|---|---|---|---|---|
| 77 | 53.5 | ~0.00 | 99.5 | 0.003 |
| 150 | 104.3 | 0.28 | 91.6 | 0.104 |
| 200 | 139.0 | 1.19 | 83.5 | 0.300 |
| 300 | 208.5 | 4.65 | 70.2 | 1.000 |
| 400 | 278.0 | 8.50 | 61.5 | 2.065 |

The table shows that at room temperature 4.65% of the $Yb^{3+}$ ions reside in the lower laser level. Although this value appears small, it is what makes Yb:YAG a quasi-three-level laser: to reach inversion, these ions must first be "emptied", i.e. additional pump power must be spent. At 400 K this fraction increases to 8.5%, and the lasing threshold roughly doubles. At 77 K, by contrast, the lower level is practically empty ($f_l < 10^{-4}$ %), and the laser operates in a fully four-level scheme [4].

The distribution within the upper multiplet is also temperature-dependent: at room temperature 70.2% of the excited ions are in the upper laser level (10327 $cm^{-1}$), and at 400 K this fraction decreases to 61.5%. This leads to a reduction of the effective emission cross-section on heating. Both aspects of the temperature effect are shown in Fig. 1.

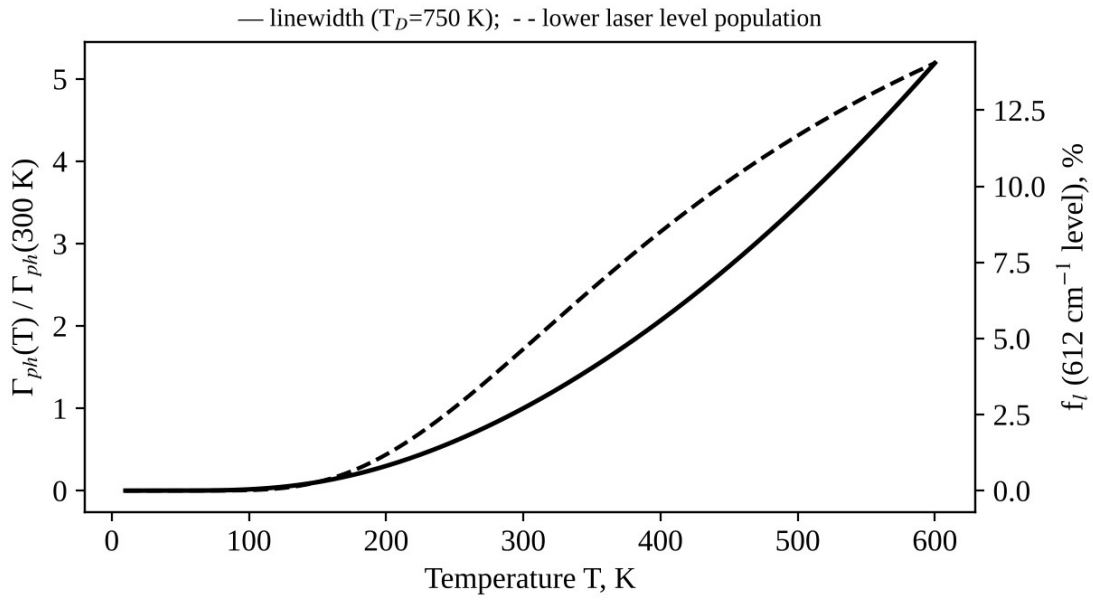



*Fig. 1. Temperature dependence of the phonon broadening (solid line) and of the lower laser level population (dashed line) for Yb:YAG*

The phonon broadening calculated using formula (2) grows rapidly, following approximately a $T^7$ law: at 77 K it is about 330 times, and at 150 K about 10 times, smaller than at room

temperature. At high temperatures ($T > T_D/2$) the growth slows down and approaches a $T^2$ dependence. Hence, at low temperatures the width of spectral lines is determined mainly by inhomogeneous broadening, whereas at room temperature phonon broadening makes the dominant contribution. This result confirms once again the necessity of studying the spectra of rare-earth ions at low temperatures.

### *Estimate for optical thermometry*

To estimate the sensitivity of the intensity-ratio method that follows from the Boltzmann distribution, the relative sensitivity $S_r = \Delta E/kT^2$ was calculated for various values of ΔE between thermally coupled levels. At T = 300 K, for ΔE = 500, 750 and 1000 $cm^{-1}$, $S_r$ amounts to 0.80, 1.20 and 1.60 %/K, respectively. At 400 K these values decrease to 0.45, 0.67 and 0.90 %/K, since the sensitivity is inversely proportional to $T^2$. At the same time, if ΔE is very large, the population of the upper level decreases, the signal weakens and the measurement error increases. From a practical standpoint, the optimal range is $200 < \Delta E < 2000$ $cm^{-1}$ [5]. The 612 $cm^{-1}$ level in the ground multiplet of Yb:YAG also falls within this range, i.e. the population values in Table 1 can be used directly as a thermometric calibration curve.

### *Effect of pressure*

The wavelengths of the $Sm^{2+}$:$SrB_4O_7$ optical gauge line calculated using formula (4) are given in Table 2.

**Table 2.** Dependence of the $Sm^{2+}$:$SrB_4O_7$ $^5D_0 \rightarrow {}^7F_0$ line on hydrostatic pressure

| P, GPa | λ, nm | Δλ, nm | ΔE, $cm^{-1}$ |
|---|---|---|---|
| 0 | 685.41 | 0 | 0 |
| 2 | 685.92 | 0.51 | −10.9 |
| 5 | 686.69 | 1.28 | −27.2 |

| P, GPa | λ, nm | Δλ, nm | ΔE, $cm^{-1}$ |
|---|---|---|---|
| 10 | 687.97 | 2.56 | −54.3 |
| 15 | 689.24 | 3.83 | −81.2 |
| 20 | 690.52 | 5.11 | −108.0 |

With increasing pressure the line shifts to the red; at 20 GPa the shift amounts to 5.11 nm, or approximately −108 $cm^{-1}$. The average energy coefficient is −5.4 $cm^{-1}$/GPa. This value lies within the range of −1 to −10 $cm^{-1}$/GPa characteristic of the 4f–4f transitions of rare-earth ions [2, 7].

## DISCUSSION

The effect of temperature on the spectra of rare-earth ions manifests itself through three main mechanisms. The first is the change in the thermal population of the Stark levels, which alters the relative intensities of the lines and gives rise to hot lines. This mechanism is purely statistical in nature and is described exactly by formula (1). The second is the broadening and shift of lines due to electron–phonon interaction. The third is the enhancement of multiphonon relaxation and thermally activated quenching, which leads to a decrease in luminescence intensity and lifetime [1, 9].

The results obtained for Yb:YAG clearly explain the advantages of cryogenically cooled lasers. At 77 K, the empty lower laser level, together with a several-fold increase in the thermal conductivity of YAG and a reduction of its thermo-optic coefficients, makes it possible to build lasers with average powers at the kilowatt level and high beam quality [4]. At the same time, the absorption bands narrow at low temperature, which requires more precise matching of the pump-source spectrum.

The temperature dependence of the population ratio of thermally coupled levels is also used in optical thermometry. For a

two-level system, the luminescence intensity ratio varies as $R = B \cdot \exp(-\Delta E/kT)$, and the relative sensitivity equals $S_r = \Delta E/kT^2$ [5]. For example, for the $^2H_{11/2}$ and $^4S_{3/2}$ levels of the $Er^{3+}$ ion with $\Delta E \approx 700–800$ $cm^{-1}$, $S_r \approx 1.1–1.3$ %/K at room temperature. This method is immune to electromagnetic interference and enables remote temperature measurement in biological tissues and microelectronic devices.

The effect of pressure is associated mainly with the enhancement of the nephelauxetic effect. Under compression, the ligands approach the rare-earth ion, the overlap of the 4f orbitals with the ligand orbitals increases and the interelectronic repulsion (the Slater integrals) decreases. As a result, the separation between multiplets shrinks and the optical transitions shift to the red [6, 7]. At the same time, the crystal-field parameters $B^k_q$ increase and the Stark splitting becomes larger. The ratio of these two effects is analysed through the power law of the dependence on interionic distance ($B^k \sim R^{-t_{k}}$), which allows the parameters of the superposition model to be determined [11].

The main advantage of the $Sm^{2+}$:$SrB_4O_7$ gauge is that its $^5D_0 \rightarrow {}^7F_0$ line is not split by the crystal field, since both states are non-degenerate (J = 0). This line is single, narrow and does not overlap with other lines. Its temperature coefficient is very small ($\sim 10^{-4}$ nm/K), so that, unlike the ruby gauge, the pressure can be determined without separate temperature measurement even in samples heated to several hundred degrees [8]. As our calculations show, a spectral accuracy of 0.05 nm allows the pressure to be measured with an accuracy of about 0.2 GPa.

The combined effect of temperature and pressure must also be taken into account. When the crystal is heated, thermal expansion increases the interionic distances, which is similar to the action of a

"negative pressure" and shifts the lines to the blue. At the same time, the electron–phonon contribution in formula (3) usually produces a red shift. The observed total shift is the sum of these two contributions, and separating them requires combined temperature- and pressure-dependent measurements [7]. Such comprehensive studies are the most reliable way of determining the electron–phonon coupling parameters in new host materials.

The results obtained can be used in the design of high-power laser devices. For example, taking into account that the central part of the active element of a Yb:YAG laser can heat up to 350–400 K, Table 1 shows that the lower laser level population in this region reaches 6–8.5%. This changes the radial gain distribution and affects the beam quality. Therefore, when choosing the geometry of the active element (thin disk, fibre, cooled rod), the temperature distribution should be modelled together with the spectral properties.

## CONCLUSIONS

1. The effect of temperature on the optical spectra of rare-earth ions has been analysed in terms of the Boltzmann population of the Stark levels, line broadening due to electron–phonon interaction, and thermally activated quenching mechanisms.

2. For the Yb:YAG crystal, it has been calculated that the population of the lower laser level (612 $cm^{-1}$) is practically zero at 77 K, 4.65% at 300 K and 8.5% at 400 K, while the fraction of the upper laser level amounts to 99.5%, 70.2% and 61.5%, respectively.

3. It has been shown, using the McCumber–Sturge model, that the phonon broadening at 77 K is about 330 times smaller than at room temperature and follows a $T^7$ law at low temperatures.

4. It has been established that the line of the $Sm^{2+}$:$SrB_4O_7$ optical pressure gauge shifts to the red by 5.11 nm (−108 $cm^{-1}$) over the range 0–20 GPa; this shift has been attributed to the enhancement of the nephelauxetic effect under pressure. The results can be applied in optical thermometry, high-pressure physics and the design of laser devices.

5. The relative sensitivity of an optical thermometer based on thermally coupled levels has been estimated: $S_r$ = 0.8–1.6 %/K for ΔE = 500–1000 $cm^{-1}$ at 300 K and 0.45–0.9 %/K at 400 K. It has been shown that the population of the 612 $cm^{-1}$ level of Yb:YAG can be used directly as a thermometric calibration.

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