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STUDIES OF LUMINESCENCE AND ABSORPTION SPECTRA OF CRYSTALS

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Abstract. When carrying out optical, magneto-optical and magnetic measurements of rare earth orthoaluminates and garnets, a number of experimental measuring installations were used:

a) Installation for measuring the spectra of the degree of MCPL and luminescence.

b) Modified single-beam spectrophotometer with continuous recording of the optical absorption signal.

Keywords. crystal, spectrum, luminescence, absorption, transitions, wavelength, frequency, polarization, degree of polarization, radiation, research, ultrasound, infrared.

INTRODUCTION

All of the above measuring devices made it possible to carry out reliable experimental studies of the optical, magnetic and magneto-optical characteristics of rare earth orthoaluminates and garnets in a wide temperature range of 78÷300 K with good hardware resolution.

Various methods for measuring the degree of polarization (in particular, circular) are based on modulation of the state of polarization with its subsequent conversion into modulation of the intensity of the light flux.

ANALYSIS OF SCIENTIFIC SOURCES

The basic principles of using the modulated polarization method in precision optical experiments are described in detail in [1-2], which also concluded that there are significant advantages of using a method based on modulation of the ellipticity of the light beam, which occurs at high frequencies (20÷100 kHz), in polarization measurements. modulation of birefringence of a homogeneous block of isotropic material. Undoubtedly, the strength of such a technique is the possibility of using light

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radiation with almost ~100% modulation depth of the polarization state, which turns out to be very important when studying strongly absorbing (or poorly reflecting) or weakly luminous media, since traditional polarimetric techniques in this case have a rather low signal-to-noise ratio [1].

Currently, fused silica is commonly used as a polarization modulator. Polarization modulation in this case is produced by a change in the optical anisotropy of fused quartz, which is caused by its periodic deformation, and the degree of optical anisotropy of quartz is proportional to its mechanical deformation [2]. The optical anisotropy of quartz is proportional to its deformation, therefore, when longitudinal vibrations with frequency Ω are excited in quartz, the phase shift between the orthogonal components of the electric vector of the light wave is equal to:

$$\delta = \frac{2\pi}{\lambda} l \cdot \Delta n \cdot \sin \Omega t = A \cdot \sin \Omega t \tag{1}$$

where l-is the thickness of the quartz sample, Δn is the maximum difference in refractive index, proportional to the amplitude of quartz deformation, A-is the amplitude of the phase shift, λ-is the wavelength of light (in vacuum). Let partially polarized light fall on a circular polarization analyzer consisting of a quartz photoelastic modulator and a linear polarizer placed behind it, the transmission plane of which is oriented at an angle of 45° to the quartz axes induced as a result of periodically changing deformation.

Since partially polarized light can be represented as a superposition of two unequal in amplitude incoherent left- and right-circular intensity components, the light intensity at the output of the "circular analyzer" will contain a variable and a constant component and can be represented as [1]:

$$I' = \left(\frac{I_+ + I_-}{2}\right) + \left(\frac{I_+ - I_-}{2}\right) \cdot \sin\left(A \sin \Omega t\right) = \left(\frac{I_+ + I_-}{2}\right) + \left(\frac{I_+ - I_-}{2}\right) \cdot \left[2J_1(A) \sin \Omega t + ...\right] \tag{2}$$

where $J_1(A)$ - is the 1st order Bessel function, the maximum value of which is 0.586 when the value of the argument A≈108^0.

If the registration of light radiation at the output of a circular polarization analyzer is carried out in the phase shift modulation mode with frequency Ω, then to determine the degree of circular polarization - $P = \frac{I_+ - I_-}{I_+ + I_-}$, it is enough to measure the ratio of two signals, proportional to the ratio of the components of light intensity:

$$\frac{U^{\approx}(\Omega)}{U^{=}(0)} = K \cdot \frac{I'(\Omega)}{I'(0)} = 2J_1(A) \cdot K \cdot \left(\frac{I_+ - I_-}{I_+ + I_-}\right) \cdot \sin \Omega t \tag{3}$$

where $I'(\Omega)$ is the intensity component at the modulation frequency; $I'(0)$ is a constant signal determined by the average (over the period) value of the sum of two orthogonal $(I_+ + I_-)/2$ circular intensity components; the constant K is determined by the ratio of the gain factors of the recording circuit for alternating - $U^{\approx}(\Omega)$ and constant - $U^{=}(0)$ electronic signals.

ANALYSIS AND RESULTS

Studies of the spectral dependences of the MCPL in a wide temperature range were carried out on an experimental setup, the block diagram of which is shown in Fig.1. The photoluminescence excitation source is a high-pressure mercury lamp DRSh-250.

The light flux generated by a condenser (L), consisting of two quartz lenses L1 and L2, is focused by it onto a sample placed in the gap of an electromagnet (EM).

To isolate the required spectral region in the exciting radiation, light filters of the UFS-1 and UFS-5 types were used, located between the condenser (L) and the sample.

Secondary radiation is collected by the output glass lens L3 and focused on the entrance slit of the monochromator (M) through a photoelastic modulator (PM) and analyzer (P).

After the monochromator, the luminescence radiation enters the photodetector (photomultiplier), after which the photocurrent is amplified and detected by an electronic recording circuit, which makes it possible to determine the value of the ratio $P = \dfrac{I_+ - I_-}{I_+ + I_-}$ in relative units.

Obviously, in this experimental geometry, measuring the degree of MCPL is reduced to determining the degree of circularity of the secondary (partially polarized) glow, caused by the magnetization of the sample under study in a longitudinal magnetic field H using a phase-controlled “circular analyzer” [1], and the magnitude (and sign) the ratio of the alternating $U^{\approx}$ and constant $U^{=}(0)$ signals (see also formula (2.) completely determines the magnitude (and sign) of the degree MCPL - R.

Thus, measuring the MCPL comes down to determining the degree of circularity of partially polarized radiation caused by the magnetization of the sample under study in a longitudinal magnetic field H using a phase-controlled “circular analyzer”. As can be seen from formula (3), the value of the 1st order Bessel function directly affects the experimentally determined value of P.

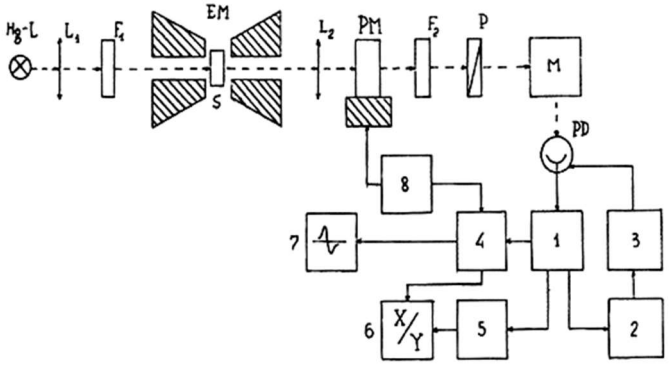

Fig.1. Schematic diagram of the measuring setup for studying the degree of MCPL:

Hg-L – mercury lamp; L1 – condenser, L2 – glass lens; F1 – UF filter; EM – electromagnet; S – sample; PM – photoelastic polarization modulator; F2 – light filter; P – polarizer (analyzer); M – monochromator; PD – photomultiplier; 1 – preamplifier (RUP); 2 – unit for stabilizing the average current of the photomultiplier; 3 – high-voltage rectifier; 4 – synchronous amplifier (selective amplifier with synchronous detector); 5 – DC amplifier; 6 – block for measuring the ratio of two signals; 7 – recorder; 8 – self-generator.

We have already noted above that with the value of the argument of the Bessel function ($\approx 108^0$), the Bessel function J_1 has a maximum value of 0,586. Consequently, the value $\frac{U^{\approx}(\Omega)}{U^{=}(0)}$ also becomes maximum (at a given wavelength), which can be experimentally established by the maximum of the alternating signal $U^{\approx}(\Omega)$ in formula (3).

Calibration of the installation for studying the degree of polarization was carried out in order to determine the value of the proportionality coefficient $B = 2J_1(A) \cdot K$ that arises when measuring the ratio $I_+ - I_- / I_+ + I_-$. To do this, an incandescent microlamp was placed in the gap of the electromagnet (EM), the radiation of which, after passing through the polarizer, the "λ/4" plate, the modulator and the analyzer, was focused on the entrance slit of the monochromator.

Since the light radiation emerging from the polarizer-plate "λ/4" system is circularly polarized (with a degree of ellipticity equal to unity), the ratio of the light intensity components in expression (3) becomes equal to the coefficient B (or the installation constant) for of a given wavelength, which can then be taken into account when calculating the true value of the MCPL value. During calibration, the axes of the "λ/4" plates were installed parallel to the induced axes of the photoelastic modulator, while the transmission plane of the analyzer was set parallel (or perpendicular) to the transmission plane of the input polarizer.

Thus, the ratio of the alternating $-U^{\approx}$ and constant – $U^{=}$ signals completely determines the magnitude (and sign) of the degree of the MCPL, and for reliable registration of the alternating signal, the synchronous detection technique is used.

Let us now dwell on some design features of the measuring setup. The sources of polarized exciting UV radiation were (as noted above) high-pressure mercury lamps of the type DRSh-250 (or 500), with a power of 250 W (500 W), respectively, operating in direct current mode. To monochromatize the light radiation, a high-aperture diffraction monochromator MDR-23 was used.

The spectral width of the monochromator slit when measuring the MCPL did not exceed ~0,15÷0,1 nm. The polarization modulator is a photoelastic light modulator with optical feedback, proposed in [3]. Magnetic fields with a strength of up to 10 kOe were created by an electromagnet with a closed Ш-shaped core, the winding of which was connected to the output of the VSA-5K rectifier. Photomultiplier tubes FEU-71 and FEU-100 were used as light radiation receivers in the wavelength range 400÷650 nm.

When registering the MCPL at the load resistance of the PMT, two signals arise: alternating with a frequency of 120 kHz and constant, after which they are separately amplified by a selective amplifier (≈120 kHz) and a direct current amplifier, respectively.

When registering the MCPL at the load resistance of the PMT, two signals arise: alternating $U^{\approx}(\Omega)$ with a frequency of 120 kHz and constant $U^{=}(0)$, after which they are separately amplified by a selective amplifier (≈120 kHz) and a direct current amplifier, respectively.

To eliminate the influence of the wave impedance of the connecting cables on the alternating signal $U^{\approx}$ taken from the PMT load, a broadband isolating amplifier-repeater (RUA) with a gain equal to ~2.0 was used. A constant signal $U^{=}(0)$ from the output of the RUP is fed to the input of a direct current amplifier (DCA) with a gain close to ~10 and made on the K544UD1 microcircuit.

From the output of the UPT, it is then fed to the denominator input of the block for measuring the value of the ratio (IO) of two signals of the digital voltmeter V2-22.

The alternating signal $U^{\approx}$, after amplification by a selective amplifier SU (100 times), is supplied to the input of a synchronous detector (SD), the function of which is performed by the base amplifier UPI-1 (see Fig.1). A selective amplifier with a frequency of 120 kHz is made on the basis of the K140UD1 microcircuit and an oscillating circuit. The output of UPI-1 is connected to the numerator input of the IO block of the V2-22 voltmeter and as a result, the value of the ratio $U^{\approx}(\Omega)/U^{=}(0)$ is recorded (in relative units) at the output of the V2-22 voltmeter. A reference signal of ~1 V, required

for synchronous detection of an alternating signal $U^{\approx}$, is output from the load resistance of the source follower in the optical feedback circuit of the photoelastic modulator (PM). Note that the azimuths of the natural axes of the optical polarization elements (polarizer, plate "λ/4") used in the optical feedback circuit of the photoelastic modulator are similar to the azimuths of the optical elements used in calibrating the measuring setup (see above).

The MCPL signal was recorded both using the digital display of a V7-22 voltmeter and by recording it on an NS-307 recorder (in the "x–t" scan mode) connected to the output of the UPI-1 synchrodetector. In this case, scanning of the MCD spectrum (by wavelength) was carried out with a smooth rotation of the diffraction grating (~1200) performed by the scanning unit of the MDR-23 monochromator. When continuously recording the value $U^{\approx}(\Omega)/U^{=}(0)$, the method of measuring the ratio of two signals ($U^{\approx}$ и $U^{=}(0)$) was equivalently replaced by the method of stabilizing the average current of the photomultiplier [60], as a result of which the output signal of the LED determined (in relative units) the value of the measured ratio of two signals-alternating $U^{\approx}(\Omega)$ and permanent $U^{=}(0)$. To stabilize the average PMT current, a stabilization unit (BS) was used, consisting of a direct current differential amplifier - UPT (made on the basis of operational amplifiers K140UD8, K544UD1, etc.) and a comparison amplifier of a high-voltage rectifier (VS-22, BNVN-0,5), at the input of which this UPT is switched on.

The operating principle of the BS stabilization unit is such that it maintains the average PMT current at the same level with an accuracy of ~1÷2% when the illumination of the PMT photocathode changes by more than 100 times. The amplitude of the stabilized signal is controlled by a DC voltmeter and can vary from 100 mV to 1 V.

The relative error in determining the P value was ~2÷3% in the center of the absorption band, and up to ~10% at the edges of the band. It was due to the following reasons: the accuracy of determining the installation constant K ~1÷2%, which depended on the error in determining the azimuths of the axes of the optical elements (approximately $0{,}5^0$), as well as errors due to inaccurate setting of the maximum of the alternating signal (during calibration of the installation) ~1÷2% and noise of the electronic amplification circuit ~1%.

Errors arising when measuring the magnitude of the magnetic field were estimated by us to be within ~1÷2%.

Particular attention was paid to taking into account the systematic error arising from the nonlinearity of the electronic amplification circuit and the choice of the PMT operating mode when determining the value of the ratio $U^{\approx}(\Omega)/U^{=}(0)$. According to our estimates, in the operating modes used, it did not exceed ~5%.

In addition, a significant source of errors in determining the value of $U^{\approx}(\Omega)/U^{=}(0)$ is the shot noise of the photomultiplier, especially when working at the edges of the luminescence band, due to which the error in determining the degree of MCPL - P increased to ~7÷10% at the edges of the luminescence band. Since the stability of the exciting UV radiation plays a large role in the MCPL technique, especially when using high-pressure mercury lamps (type DRSH-250, 500), this possible source of uncontrolled errors was minimized by using an electronic circuit for stabilizing the intensity of the light flux, as a result fluctuations in the intensity of the exciting radiation did not exceed ~1÷2% [4].

When carrying out optical and magneto-optical studies at low temperatures, a small-sized “filled” cryostat made of stainless steel was usually used, the design and principle of operation of which are described in detail in [5, 6]. This cryostat of the original design made it possible to cool the samples under study down to 85÷90 K. In addition, after complete evaporation of liquid nitrogen in the process of natural heating of the sample to room temperature (the heating rate is ~0,2 K/s), studies were also carried out on the temperature dependence of the optical and magneto-optical effects.

The optical absorption and luminescence spectra of paramagnetic TbGaG garnet were studied in the spectral range 483÷493 nm (20300÷20750 sm^{-1}) at a temperature T=78 K with a resolution no worse than ≈1,0÷1,5 sm^{-1} in the region of ~20400 sm^{-1}.

Figure 2 shows the spectrum of the absorption band at the 4f÷4f transition $^7F_6 \div ^5D_4$ of the Tb^{3+} ion in TbGaG, recorded in the absence of an external field at T=78 K, and the corresponding spectrum of the luminescence band. Characteristic features of the absorption and luminescence bands (coinciding in energy) are indicated by vertical arrows. It is clearly seen from the figure that absorption lines 1, 4, 5, 6 and 7 are singlets, and apparently originate from the ground state of the $^7F_6$ rare earth multiplet -Tb^{3+} ion. In addition, absorption lines at energies ~20550 sm^{-1} (~486,6 nm) and ~20428 sm^{-1} (~489,5 nm) are doublet lines 2, 3 and 8, 9, respectively, and lines 2, 3 are also due to optical transitions from the ground state, while, lines 8, 9 are associated with optical transitions occurring from excited Stark sublevels of the main multiplet $^7F_6$ RE - Tb^{3+} ion in the structure of terbium gallium garnet.

Figure 4 shows the spectral dependences of the $^7F_6 \div ^5D_4$ absorption band, recorded in the right σ_+ and left σ_- circular polarizations at T=90 K in isomorphic TbAG garnets with an external field H=7 kOe oriented along the crystallographic directions [110] and [001], respectively. It is interesting to note that, although significant Zeeman shifts of the resonant frequencies of lines 1 and 3 of the $^7F_6 \div ^5D_4$ absorption band in TbAG have different signs, the nature of the change in their intensities in polarizations σ_+ and σ_- is completely similar to the behavior of the intensities of lines 5 and 6 in the absorption spectrum of TbGaG (from literature data).

Figure 5 shows the luminescence spectrum of TbGaG at a temperature of 78 K at the radiative 4f-4f transition. The sufficiently high optical resolution of the used spectrofluorimeter made it possible to register the fine structure of a number of emission lines (especially for the radiative 4f-4f transitions

$^5D_4 \div ^7F_6$ and $^5D_4 \div ^7F_5$) of the rare earth ion Tb^{3+} in the structure of terbium-gallium garnet in the [111] direction on the radiative 4f-4f transition $^5D_4 \div ^7F_5$. The figure shows the numbers of the corresponding luminescence lines.

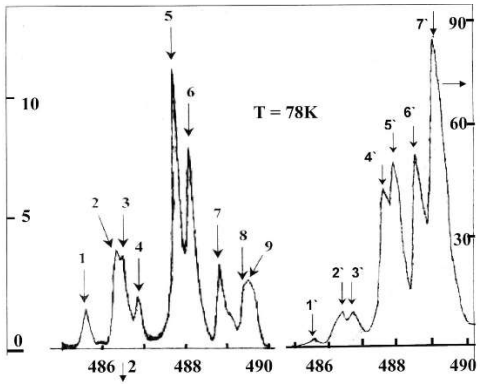

Fig.2. Spectrum of the $^7F_6 \div ^5D_4$ absorption band (left) and the spectrum of the $^5D_4 \div ^7F_6$ luminescence band (right) in TbGaG, recorded at T=78 K.

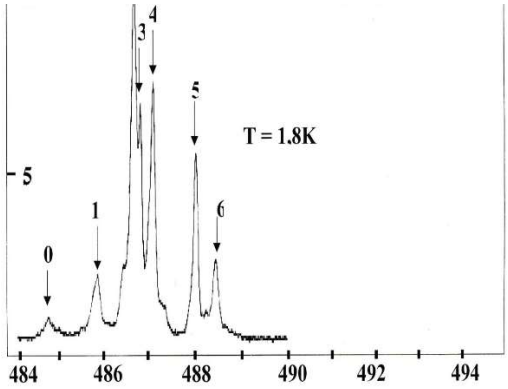

Fig.3. Absorption bands $^7F_6 \div ^5D_4$ at T=1,8. TbGaG. Characteristic features of absorption and luminescence bands are indicated by numbered vertical arrows (literature data).

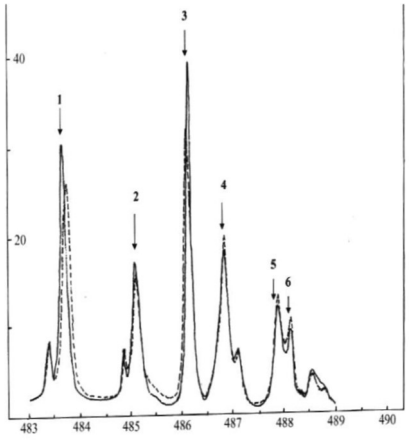

Fig.4. Spectrum of the absorption band $^7F_6 \div ^5D_4$ in TbAlG, recorded in the right σ_+ (solid lines) and left σ_- (dotted line) polarizations at T=90K in an external magnetic field H=7 kOe, parallel to the crystallographic axis [001]. Inset: field dependence of Zeeman splitting of absorption line 1 at T=90K.

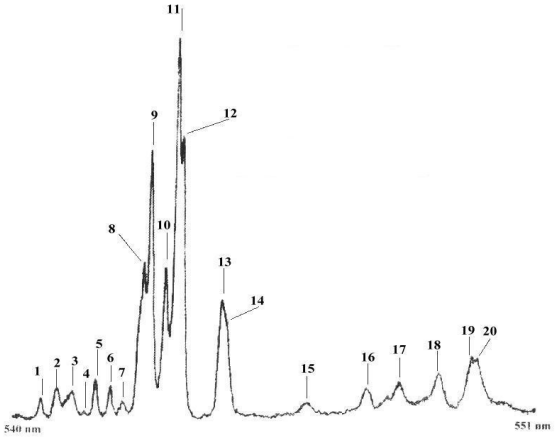

Fig.5. Luminescence spectrum of paramagnetic garnet $Tb_3Ga_5O_{12}$, recorded at T=78K.

Based on the measured absorption spectra of $DyAlO_3$, a strong anisotropy of the polarization spectra of optical absorption $4f$-$4f$ transitions $^6H1_{5/2} \div {}^6F_{3/2}$ and $^6H1_{5/2} \div {}^6F_{5/2}$ in $DyAlO_3$ at a temperature T=78K in the infrared region of the spectrum was detected when light propagated along crystallographic direction [001] – crystal axis.

CONCLUSIONS AND OFFERS

Experimental installations for measuring luminescence spectra and absorption spectra have been mastered. The spectra of the $^7F_6 \div {}^5D_4$ absorption band and the spectrum of the $^5D_4 \div {}^7F_6$ luminescence band in TbGaG, recorded at T=78 K, were measured. Spectrum of the absorption band $^7F_6 \div {}^5D_4$ in TbAlG, recorded in the right σ_+ and left σ_- polarizations at T=90K in an external magnetic field H=7 kOe, parallel to the crystallographic axis [001].

References

1. Altshuller S.A., Kozyrev B.M. Electron paramagnetic resonance of compounds of intermediate group elements. 2nd ed. - M.: Nauka, 1972. - 462 p.

2. J.B.Gruber, B. Zandi, U.V. Valiev, and Sh. A. Rakhimov, Crystal Field Splitting of Some Quintet States of Tb^{3+} in Aluminum Garnets.// Phys. Rev. B 69, 115103 (2004).

3. Buckmaster H.A. Tables of angular momentum transformation matrix elements $d^{(j)}_{mm'}(\beta)$ (j = 2,4,6) Can. J. Phys. - 1964. - v. 42**. –** p**.** 386-391.

4. Valiev U.V., Gruber J.B., Rustamov U.R., K.S. Saidov, Sokolov V.Yu. Magneto-optical study of the odd component of the crystal field in terbium-yttrium aluminum garnet // Technical Physics Letters. - 2003. - T.29.- issue 21. - p.7-16.

5. Joshi B. D. and Page A. G. Fluorescence and absorption spectra of Tb^{3+} ions in iyttrium-gallium garnet // Journ. of Lumines. – 1977. - Vol.15. - p. 29-34.

6. Gruber J.B., Seltzer M.D., Richardson F.S., Pugh V.J. Electronic energy-level structure of trivalent holmium in yttrium aluminum garnet // Journ. Appl. Phys. -1995. - Vol.77. - No11. - p. 5882-5901.

7. A. M. Madaliev, U. V. Valiev, Sh. I. Mukhamedkhanova. Studies of spectra and absorption of crystals. Physics fanining bugungi rivozhida istedodli yoshlarning ўrni. “Yosh olimlar va iktidorli talabalar anzhumani.” NUUz. 2011. pp. – 71.

8. A. M. Madaliev. Studies of luminescence and absorption spectra of crystals. NUUz. T. 2011.