Optical and structural investigation of dysprosium doped-Y₂Te₄O₁₁

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In this paper, the optical properties of Y₂Te₄O₁₁ microcrystalline powders doped with Dy³⁺ ions, ranging between 0.01 and 5.0 at%, are reported. The powders were successfully synthesized by the solid state reaction method. Absorption (300 K), excitation (300 K) and fluorescence spectra (at 11.6 and 300 K) as well as fluorescence decay curves recorded at room temperature are presented and analyzed in details. Oscillator strengths, phenomenological Ω₂(λ = 2, 4, 6) Judd-Ofelt parameters, radiative transition probabilities, branching ratios, the radiative lifetime of the ⁴F₉/₂ level as well as the stimulated emission cross-section for the ⁴F₉/₂ → ⁴H₁₃/₂ transition have been determined. The observed non-exponential decay nature and concentration quenching of the ⁴F₉/₂ emitting level of the Dy³⁺ ion, have been attributed to cross-relaxation processes. The high value of the stimulated emission cross-section for the ⁴F₉/₂ → ⁴H₁₃/₂ transition at 576.6 nm, equal to 0.756 × 10⁻²⁰ cm², indicates that Y₂Te₄O₁₁ activated by trivalent dysprosium ions is an attractive candidate for a solid-state laser.

1. Introduction

Materials doped with rare earth ions play an important role in various of scientific and technological fields. Especially promising materials for application in modern optoelectronic technology are those, activated with trivalent dysprosium ions [1–3]. In recent times, more attention was paid on the MIR emission of Dy³⁺ ions. The observed in low phonon materials infrared emissions from Dy³⁺ ions at 1.3 μm (corresponds to the ⁶F₁₁/₂ → ⁶H₅/₂ transition), 2.8–3.2 μm (⁶H₁₃/₂ → ⁶H₁₅/₂ transition), 4.0–4.7 μm (⁶H₁₁/₂ → ⁶H₁₃/₂ transition) and 5.4–6.0 μm (⁶F₁₁/₂ → ⁶H₂₁/₂ → ⁶H₁₃/₂) have found application in optical fiber communication, medicine and for military aims, respectively [4–7]. However, with new possibilities of optical pumping offered by increased availability of different laser sources, investigations on luminescence properties of Dy³⁺-doped materials are currently focusing on the emission in the visible range. In that region the Dy³⁺ ion exhibit three well separated emission bands. The blue emission at 480 nm, the yellow at 580 nm and the weak red at about 660 nm have been attributed to the ⁴F₉/₂ → ⁴H₁₃/₂, the hypersensitive ⁴F₉/₂ → ⁴H₁₃/₂ and the ⁴F₉/₂ → ⁴H₁₅/₂ transition, respectively. Earlier investigation on the unique spectral and emission properties of Dy³⁺ ions in the visible region suggest that Dy³⁺-doped materials can be considered as excellent candidates for application in laser technology in the 560–590 nm region [8,9]. Besides, the hypersensitive transition (ΔL=2, ΔJ=2) is strongly influenced by the local site symmetry of the Dy³⁺ ion. For this reason, the ion will give rise to a white light emission when emitting a suitable yellow to blue intensity ratio. Hence, materials doped with Dy³⁺ or co-doped with other RE³⁺ ions are considered as promising candidates for white LED-s applications [10,11].

The research carried out by Redman, Parada and other authors shows that oxotellurates(IV) of the general formula RE₂Te₄O₁₁(ν) (where ν=n or 5), doped with trivalent lanthanides ions are very attractive host matrices [12,13]. Crystallographic studies on RE₂O₃-(TeO₂)ₙ indicate, that oxotellurates(IV) are isostructural through the entire series of RE=Y, La-Nd, Sm-Lu and crystalize in the monoclinic and triclinic space system for n equal to 4 and 5, respectively [14,15]. One crystallographic site of the RE³⁺ ions RE₂Te₄O₁₁ and a lone pair of electrons in Te(IV) suggest that this type of oxotellurates(IV) possesses interesting properties as luminescent activators. Spectroscopic investigations of oxotellurates(IV) activated Pr³⁺, Nd³⁺ [16], Sm³⁺ [17], Eu³⁺ [18,19] and Tb³⁺ [20] confirm that these compounds are good candidates also for phosphors and laser materials. Additionally, oxotellurates(IV) are characterized by a relatively low temperature of synthesis (below 800 °C), chemical stability and exhibit good mechanical properties.

To the best of our knowledge, the luminescence properties of Dy³⁺-doped Y₂Te₄O₁₁ have not been hitherto studied and reported. In this paper, the spectroscopic properties of microcrystalline powder samples of Dy³⁺ · Y₂Te₄O₁₁ are presented and discussed in details. The luminescence properties of these samples were analyzed by means of optical absorption (300 K), fluorescence (11.6 K and 300 K), photoluminescence excitation (300 K) spectra as well...
as fluorescence decay curves (300 K). The Judd-Ofelt theory has been applied in order to determine the radiative properties arising from the $^{4}F_{9/2}$ level of the $\text{Dy}^{3+}$ ion. The influence of the concentration of $\text{Dy}^{3+}$ ions on the decay time and energy transfer mechanism between the $\text{Dy}^{3+}$-$\text{Dy}^{3+}$ ions is also discussed.

2. Experimental

2.1. Solid-state synthesis

As starting materials, high purity $\text{Y}_2\text{O}_3$ (99.999%, Stanford Materials), Dy$_2$O$_3$ (99.999%, Stanford Materials) and TeO$_2$ (99.95%, Sigma Aldrich) oxides were used. The $\text{Y}_2$-$\text{Y}_3\text{Te}_4\text{O}_{11}$ (where $x=0.01$, 0.02, 0.1, 0.5, 1.0, 2.0 and 5.0 at%) microcrystalline powders were obtained according to the procedure reported for $\text{Y}_2\text{Te}_4\text{O}_{11}$ in Ref. [21]. The starting oxides were mixed in stoichiometric proportions, thoroughly homogenized over 12 h and finally pressed into pellets of 15 mm in diameter at 0.5 GPa. In the next step, the obtained pellets were placed in a platinum-iridium crucibles (20 mm in diameter and 60 mm height) and heated in an electric furnace at 770°C (1043 K) for 24 h in order to obtain a microcrystalline $\text{Dy}^{3+}$-$\text{Y}_2\text{Te}_4\text{O}_{11}$ powder.

2.2. Characterization

X-ray powder diffraction (XRD) measurements were recorded on a Bruker D8 Advance X-ray Diffractometer, using Ni-filtered Cu $K\alpha$ radiation ($\lambda=1.5418$ Å). The measurements were performed in the $2\theta=10$–100° range with the step of $2\theta=0.008°$. The morphology of the $\text{Y}_2\text{Te}_4\text{O}_{11}$ microcrystalline powder was examined by a Hitachi S-3400N scanning electron microscope equipped with an EDS Thermo Scientific Ultra Dry detector. SEM and EDS measurements were carried out using an accelerating voltage of 30 kV. Analyzed samples of $\text{Y}_2\text{Te}_4\text{O}_{11}$, without and with 5.0 at% of an activator, were coated with a ultrathin layer of gold ($\approx20$ nm in thickness).

The concentration of the Dy, Y and Te elements in the $\text{Y}_2\text{Te}_4\text{O}_{11}$ samples with different concentration of dysprosium ions, were determined by inductively coupled plasma (ICP), using an ARL spectrometer, Model 3410 ICP (Fisons Instruments). Approximately 30 mg of the sample was transferred into a Teflon beaker, followed by 30 cm$^3$ 2 M HCl. The mixture was thoroughly stirred until a clear greenish solution has been obtained. The solution was next transferred to a 100 cm$^3$ volumetric flask and brought up to the volume with a 2 M HCl. Single component standards of Dy, Y and Te (each one with the content of 1.000 mg/cm$^3$) were used.

The optical absorption spectra were recorded at 300 K on a Cary 5000 UV–vis-NIR spectrophotometer (Agilent Technologies). High-quality absorption spectra have been obtained from transmittance measurements of a microcrystalline sample of $\text{Dy}^{3+}$-$\text{Y}_2\text{Te}_4\text{O}_{11}$, in the form of a compressed transparent pellet. The diameter (equal to 12.63 mm) and thickness (0.260 mm) of the obtained pellet were measured by using a digital micrometer screw. Before measurements of the absorption spectra the samples have been heated for 1 h at 500°C, in order to remove water from the surface of the pellets.

The fluorescence spectra (at 11.6 and 300 K) were recorded using an Ocean-Optics high-resolution spectrometer (model HR-4000) upon excitation of a 445 nm laser diode. For measurements of the fluorescence spectra at low temperature (11.6 K) a closed cycle helium refrigerator (APD-Crioegenic ARS-2HW) equipped with a temperature controller was used. The fluorescence excitation spectra (300 K) and fluorescence decay curves (300 K) were recorded on a Cary Eclipse Fluorescence Spectrophotometer (Agilent Technologies) equipped with a pulsed xenon lamp as an excitation source.

3. Results and discussion

3.1. X-ray diffraction patterns

$C_{1b}$ In Fig. 1 is shown the X-ray powder diffraction pattern of $\text{Dy}^{3+}$ (5.0 at%) doped-$\text{Y}_2\text{Te}_4\text{O}_{11}$, together with the indexed theoretical simulation pattern (ICSD#418854) [19]. One may notice that the diffraction peaks of the sample may be assigned to the pure $\text{Y}_2\text{Te}_4\text{O}_{11}$ phase. Yttrium oxotellurate(IV) crystallizes in the monoclinic space group C2/c $C_{1b}$ (No. 15) with $Z=4$ and is isostuctural with Ln$_2$Te$_4$O$_{11}$ (Ln=La-Nd, Sm-Lu). The unit-cell parameters are: $a=12.3876$, $b=5.1068$, $c=16.0193$ Å, $\beta=106.154^\circ$ and $V=973.38$ Å$^3$ [19]. No other phase could be detected. It indicates that the $\text{Dy}^{3+}$ ions replace $\text{Y}^{3+}$ ions on the single crystallographic position of the $C_1$ site symmetry, due to a similar ionic radius $r$: $(\text{Y}^{3+})=1.075$ Å, $r:(\text{Dy}^{3+})=1.027$ Å for the coordination number equal to 8 [22].

3.2. SEM and EDS analyses

Fig. 2a–c show the representative SEM images of the un-doped $\text{Y}_2\text{Te}_4\text{O}_{11}$ (Fig. 2a) and $\text{Dy}^{3+}$ (5.0 at.%)-doped $\text{Y}_2\text{Te}_4\text{O}_{11}$ (Fig. 2b–c). The presented SEM images indicate that the grains, of various shapes and sizes (between 10 to 25 μm), are randomly distributed and the morphology is independent of the activator concentration. Fig. 2d presents the EDS spectrum of the $\text{Dy}^{3+}$ (5.0 at%)-$\text{Y}_2\text{Te}_4\text{O}_{11}$ sample, which shows the presence of Te, O, Y and Dy elements. The molar percentage of the elements in the $\text{Dy}^{3+}$ (5.0 at%) doped $\text{Y}_2\text{Te}_4\text{O}_{11}$ sample was calculated on the basis of a quantitative EDS microanalysis. The received similar theoretical (Y=11.47%, Dy=0.30%, Te=23.53% and O=64.70%) and experimental (Y=12.48±0.18%, Dy=0.33±0.03%, Te=22.35±0.18% and O=64.89±0.71%) values indicate that the Y:Dy:Te:O molar percentage ratio of the elements is in good agreement with the structural formula.

3.3. Absorption spectra, Judd-Ofelt analysis and radiative properties

The room-temperature optical absorption spectrum of $\text{Dy}^{3+}$ (2.0 at%)-$\text{Y}_2\text{Te}_4\text{O}_{11}$ (1.53 $\times$ 10$^{17}$ ions per cm$^3$) in the 5450–14000 cm$^{-1}$ spectral range, is shown on Fig. 3. The spectrum was calibrated in absorption cross-section units (in cm$^2$). In the 5430–14280 cm$^{-1}$ (1842–700 nm) range, relatively intense and well

![Fig. 1. Theoretical [19] and experimental XRD pattern of the $\text{Y}_2\text{Te}_4\text{O}_{11}$ powder.](image-url)
separated bands, originating from transitions between the \(^{6}H_{15/2}\) ground state to various excited levels of the \(4f^{9}\) electronic configuration of the \(\text{Dy}^{3+}\) ion, were observed. The absorption bands between 5450 to 12000 cm\(^{-1}\) (NIR region) with maxima at 5951, 7751, 9049 and 11060 cm\(^{-1}\) have been assigned to transitions from the \(^{6}H_{15/2}\) ground state to the \(^{6}H_{11/2}, ^{6}F_{11/2}\) and \(^{6}H_{9/2}, ^{6}F_{9/2}\) excited levels, respectively. The most intensive absorption band, observed between 7130 – 8360 cm\(^{-1}\) with an absorption cross-section of 8.40 \(\times\) \(10^{-20}\) cm\(^2\), has been attributed to a hypersensitive transition of the trivalent dysprosium ion. The last two bands observed in the vis region have been assigned to transitions from the \(^{6}H_{15/2}\) level to the \(^{6}F_{5/2}\) \((12050–12740\) cm\(^{-1}\)) and \(^{6}F_{3/2}\) \((13010–13436\) cm\(^{-1}\)) multiplets. The absorption bands associated with transitions to higher energy levels of \(\text{Dy}^{3+}\) are masked by strong absorption of the \(\text{Y}_2\text{Te}_4\text{O}_{11}\) host (see inset Fig. 3).

According to the Judd-Ofelt theory [23–25], the theoretical oscillator strengths of an electric dipole transition between two energy level can be calculated using the following formula:

\[
f_{\text{calc}} = \frac{8\pi mc\nu}{3(\lambda(2)+1)\Omega_{\lambda}^2} \left( \frac{n^2+2}{9n} \right)^2 \sum_{\lambda=2,4,6} \Omega_{\lambda}^2 \langle \Psi J \parallel U^\dagger \Psi J' \rangle^2,
\]

where \(m\) is the mass of the electron, \(c\) is the velocity of light, \(\nu\) is the energy of the transition, \(n\) is the refractive index of the sample, \(J\) is the total angular momentum for the ground level \((J=15/2\) for \(\text{Dy}^{3+}\)), \(\Omega_{\lambda}\) \((\lambda=2, 4\) and 6\)) are the phenomenological Judd-Ofelt intensity parameters (in cm\(^2\)) and \(U^\dagger\)\(U\) are the doubly reduced matrix elements of the unit tensor operator in the intermediate coupling approximation for \(\Psi J \rightarrow \Psi J'\) transitions. The applied in the calculation doubly reduced matrix elements were taken from Ref. 26, and the value of refractive index was assumed to be equal to 2.17 [17]. The quality of the fits were determined by using the root-mean-square deviation \((r.m.s.)\) between the experimental \((f_{\text{exp}})\) and calculated \((f_{\text{calc}})\) oscillator strengths.

The \(f_{\text{exp}}\) and \(f_{\text{calc}}\) oscillator strengths for \(\text{Dy}^{3+}:\text{Y}_2\text{Te}_4\text{O}_{11}\) have been determined from four well-separated \(^2S_{1/2} + ^4L_J\) levels and two groups of joint multiplets: \(^{6}H_{9/2} + ^{6}F_{11/2}\) and \(^{6}H_{7/2} + ^{6}F_{9/2}\). Since, for these levels the individual band areas could not be separated, the sum of the appropriate reduced matrix elements of the \(^{6}H_J\) \((J=9/2\) and 7/2\)) and \(^{6}F_J\) \((J=11/2\) and 9/2\)) levels have been used for calculation of the oscillator strength value. All recorded absorption bands of the \(\text{Dy}^{3+}\) ions in \(\text{Y}_2\text{Te}_4\text{O}_{11}\) were assumed to be electric dipole in nature. The obtained values of the \(f_{\text{exp}}\) and \(f_{\text{calc}}\) oscillator strengths and the magnitudes of the phenomenological \(\Omega_{\lambda}\) \((\lambda=2, 4, 6)\) Judd-Ofelt parameters are presented in Table 1. The obtained root-mean-square deviation \((r.m.s.)\) value of 1.10 \(\times\) \(10^{-7}\) indicates a good agreement between the experimental and calculated oscillator strengths. The Judd-Ofelt parameters follows the trend \(\Omega_{2} > \Omega_{4} > \Omega_{6}\), which has been observed also for the \(\text{Dy}^{3+}:\text{LiNbO}_{3}\)
and Dy$_3^{3+}$:YVO$_4$ crystals [28] as well as for phosphate [29] and borate glasses [30]. The relatively large $\Omega_2$ value indicates a high degree of coherence of the Dy-O bond and a high asymmetry of the coordination structure surrounding the Dy$^{3+}$ ion [31]. Additionally, the large magnitude of $\Omega_4$ suggests, that in Dy$_3^{3+}$-doped materials the yellow emission should be always more intense than the blue one [32].

The radiative properties of Dy$^{3+}$ ions in the Y$_2$Te$_4$O$_{13}$ microcrystalline powder have been calculated following the procedure reported in Ref 17. The obtained phenomenological $\Omega_4$ Judd-Ofelt parameters values have been applied for estimation of the transition probabilities ($\Omega_4$), the branching ratios ($\beta_4$) and the radiative lifetime ($\tau_4$) of the $^{4}F_{9/2}$ state of the Dy$^{3+}$ ion. The values of the $\Omega_{6\Omega}$, $\Omega_{4\Omega}$, $\Omega_{6\Omega}$, $\beta_4$ and $\tau_4$ parameters are presented in Table 2. The total transition probability ($\Omega_{6\Omega}$) and radiative lifetime ($\tau_4$) of the $^{4}F_{9/2}$ fluorescence level are equal to 3349 s$^{-1}$ and 299 $\mu$s, respectively.

### 3.4. Fluorescence properties

In Fig. 4 is shown the UV–vis excitation spectrum of the Dy$^{3+}$ (5.0 at.%) Y$_2$Te$_4$O$_{13}$ sample, monitored at 576 nm at room temperature and attributed to the $^{4}F_{9/2}$ $\rightarrow$ $^{6}H_{13/2}$ transition. The low-resolution spectrum consists of several excitation lines, which corresponds to f–f transitions from the $^{6}H_{13/2}$ ground state to various excited states of the Dy$^{3+}$ ion. The lines, with a maximum located at 327, 339, 352, 366, 391, 427, 454 and 474 nm, have been assigned to the excited states of the $^6P_{3/2}$, $^6P_{5/2}$, $^6P_{7/2}$, $^6P_{7/2}$, $^4I_{13/2}$, $^4F_{9/2}$ and $^4F_{9/2}$ levels of Dy$^{3+}$, respectively. The relatively intense bands situated in the 300–500 nm spectral range, indicate that the Y$_2$Te$_4$O$_{13}$ microcrystalline powder can be well excited by ultraviolet and visible light.

Fig. 5 presents the 11.6 K (normal) and 300 K (inverted) fluorescence spectra of the Dy$^{3+}$ (1.0 at.%) Y$_2$Te$_4$O$_{13}$, sample, excited by the 445 nm laser line. The spectrum was corrected for the spectral response of the applied monochromator and detector. The 445 nm laser excites the $^4$F$_{9/2}$ electron from the $^6$H$_{15/2}$ ground state to the $^4$I$_{15/2}$ excited level. The $^4$F$_{9/2}$ fluorescence level of the trivalent dysprosium ion is populated via a non-radiative process. The strongest bands occur in the blue and yellow spectral range. The two bands with a maximum at 20506 cm$^{-1}$ (487.66 nm) and 17333 cm$^{-1}$ (576.93 nm) were assigned to transitions from the $^4$F$_{9/2}$ level to the $^6$H$_{15/2}$ ground state and the first excited state $^6$H$_{13/2}$ of Dy$^{3+}$, respectively. It is generally known that the $^4$F$_{9/2}$ $\rightarrow$ $^4$I$_{13/2}$ hypersensitive transition of Dy$^{3+}$ is strongly influenced by the surrounding of the ion. Hence, when the trivalent dysprosium ion occupy a low symmetry (without inversion symmetry) or a high symmetry site (with inversion symmetry), than in the fluorescence spectrum the $^4$F$_{9/2}$ $\rightarrow$ $^4$H$_{13/2}$ or $^4$F$_{9/2}$ $\rightarrow$ $^4$H$_{13/2}$ transition dominates. As one can notice from Fig. 5, in the fluorescence spectrum (at 16 and 300 K) the strong yellow emission with a maximum at 576.93 nm is dominant which indicates that the

![Excitation spectrum (300 K) of the Dy$^{3+}$ (5.0 at.%) Y$_2$Te$_4$O$_{13}$ powder ($\lambda_{em}$=576 nm).](image1)

![Fluorescence spectra (11.6 and 300 K) of the Dy$^{3+}$ (1.0 at.%) Y$_2$Te$_4$O$_{13}$ powder excited by 445 nm laser line.](image2)

### Table 1

Experimental and calculated oscillator strengths of the Dy$^{3+}$ (2.0 at%):Y$_2$Te$_4$O$_{11}$ microcrystalline powder.

<table>
<thead>
<tr>
<th>No.</th>
<th>Level</th>
<th>Barycentre (cm$^{-1}$)</th>
<th>Oscillator strengths ($\times 10^{-6}$)</th>
<th>$f_{exp}$</th>
<th>$f_{calc}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>$^4$H$_{15/2}$</td>
<td>5853</td>
<td>3.28</td>
<td>3.33</td>
<td>0.05</td>
</tr>
<tr>
<td>2</td>
<td>$^4$H$<em>{13/2}$ + $^4$F$</em>{11/2}$</td>
<td>7760</td>
<td>19.52</td>
<td>19.52</td>
<td>0.00</td>
</tr>
<tr>
<td>3</td>
<td>$^4$F$<em>{13/2}$ + $^4$F$</em>{11/2}$</td>
<td>9072</td>
<td>9.95</td>
<td>9.95</td>
<td>0.00</td>
</tr>
<tr>
<td>4</td>
<td>$^4$F$_{7/2}$</td>
<td>10923</td>
<td>6.40</td>
<td>6.40</td>
<td>0.00</td>
</tr>
<tr>
<td>5</td>
<td>$^4$F$_{5/2}$</td>
<td>12419</td>
<td>2.67</td>
<td>2.62</td>
<td>0.05</td>
</tr>
<tr>
<td>6</td>
<td>$^4$F$_{3/2}$</td>
<td>13255</td>
<td>0.48</td>
<td>0.49</td>
<td>0.01</td>
</tr>
</tbody>
</table>

$\Omega_2 = (9.24 \pm 0.79) \times 10^{-20}$

$\Omega_4 = (7.71 \pm 0.87) \times 10^{-20}$

$\Omega_6 = (3.95 \pm 1.12) \times 10^{-20}$

### Table 2

Energy transition (cm$^{-1}$), radiative transitions probabilities ($A_{nm}$, $A_{out}$ and $A_{out, s^{-1}}$), calculated branching ratios ($\beta_4$) and radiative lifetime ($\tau_4$, $\mu$s) for the $^4$F$_{9/2}$ level of the Dy$^{3+}$-doped Y$_2$Te$_4$O$_{11}$ microcrystalline powder.

<table>
<thead>
<tr>
<th>Transition $^4$F$_{9/2}$ $\rightarrow$ $^2S$ or $^2S$ $\leftarrow$ $^2S$</th>
<th>Energy transition (cm$^{-1}$)</th>
<th>$A_{nm}$ (s$^{-1}$)</th>
<th>$A_{out}$ (s$^{-1}$)</th>
<th>$A_{out, s^{-1}}$</th>
<th>$\beta_4$ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^4$H$_{15/2}$</td>
<td>0</td>
<td>641.3</td>
<td>0.0</td>
<td>19.1</td>
<td>$\tau_4 = 3349 \mu$s</td>
</tr>
<tr>
<td>$^4$H$_{13/2}$</td>
<td>3231</td>
<td>2007.5</td>
<td>0.0</td>
<td>59.9</td>
<td>$\tau_4 = 299 \mu$s</td>
</tr>
<tr>
<td>$^4$H$_{11/2}$</td>
<td>5835</td>
<td>177.8</td>
<td>33.9</td>
<td>6.3</td>
<td>$\tau_4 = 299 \mu$s</td>
</tr>
<tr>
<td>$^4$H$_{9/2}$</td>
<td>7372</td>
<td>56.4</td>
<td>8.6</td>
<td>1.9</td>
<td>$\tau_4 = 299 \mu$s</td>
</tr>
<tr>
<td>$^4$F$_{11/2}$</td>
<td>7372</td>
<td>73.3</td>
<td>148.9</td>
<td>6.6</td>
<td>$\tau_4 = 299 \mu$s</td>
</tr>
<tr>
<td>$^4$F$_{9/2}$</td>
<td>9006</td>
<td>36.5</td>
<td>16.3</td>
<td>1.6</td>
<td>$\tau_4 = 299 \mu$s</td>
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<tr>
<td>$^4$F$_{7/2}$</td>
<td>9006</td>
<td>69.6</td>
<td>9.2</td>
<td>2.4</td>
<td>$\tau_4 = 299 \mu$s</td>
</tr>
<tr>
<td>$^4$F$_{5/2}$</td>
<td>10140</td>
<td>16.6</td>
<td>0.0</td>
<td>0.5</td>
<td>$\tau_4 = 299 \mu$s</td>
</tr>
<tr>
<td>$^4$F$_{3/2}$</td>
<td>10900</td>
<td>19.2</td>
<td>16.3</td>
<td>1.1</td>
<td>$\tau_4 = 299 \mu$s</td>
</tr>
<tr>
<td>$^4$F$_{1/2}$</td>
<td>12462</td>
<td>16.8</td>
<td>0.0</td>
<td>0.5</td>
<td>$\tau_4 = 299 \mu$s</td>
</tr>
<tr>
<td>$^4$F$_{1/2}$</td>
<td>13253</td>
<td>0.2</td>
<td>0.0</td>
<td>0.0</td>
<td>$\tau_4 = 299 \mu$s</td>
</tr>
<tr>
<td>$^4$F$_{1/2}$</td>
<td>13650</td>
<td>0.4</td>
<td>0.0</td>
<td>0.0</td>
<td>$\tau_4 = 299 \mu$s</td>
</tr>
</tbody>
</table>

$A_{out} = 3349 \mu$s

$\tau_4 = 299 \mu$s
Dy$^{3+}$ ions in Y$_2$Te$_4$O$_{11}$ occupy the C$_1$ site symmetry. In the red part of spectral range one may observe also significantly weaker emission bands, which correspond to the $^4F_{9/2} \rightarrow ^6H_{13/2}$ (with a maximum at 15030 cm$^{-1}$) and $^4F_{9/2} \rightarrow ^6H_{9/2}$ transitions. The chromaticity coordinates were calculated on the basis of the fluorescence spectrum, excited by the 445 nm laser line at room temperature. The CIE chromaticity coordinates equal to $x=0.436$, $y=0.470$, located in the greenish yellow region, are shown on Fig. 6.

The structure of the $^{25}_5^+ 1L_1$ multiplets of Dy$^{3+}$ has been determined by means of an analysis of the low temperature fluorescence spectrum recorded at 11.6 K. The experimental crystal field components of the $^6H_{15/2}$ ground state and excited levels of Dy$^{3+}$ in the Y$_2$Te$_4$O$_{11}$ microcrystalline powder are given in Table 3. Several relatively well separated additional lines of low intensity, observed in the 17200–16620 cm$^{-1}$ spectral range of the fluorescence spectrum at 11.6 K, have been assigned as vibronic bands of the $^4F_{9/2} \rightarrow ^6H_{13/2}$ transition. The vibronic positions and vibrational data of the host lattice have been reported in Ref. [17] and are presented in Table 4. The recorded lines are due to a coupling with internal vibrations and can be divided into two categories. To the first group has been assigned the symmetric ($v_1$) and antisymmetric ($v_2$) modes of stretching vibrations of the [TeO$_3$] unit (observed above 480 cm$^{-1}$), whereas the second group (below 480 cm$^{-1}$) consists of symmetric and antisymmetric bending vibrations of the [TeO$_3$] unit, which have been denoted by the $v_3$ and $v_4$ modes, respectively. A good agreement between the positions of the vibronic lines and the vibrational data for Y$_2$Te$_4$O$_{11}$ has been observed. The integrated intensity ratio ($R$) for all assigned vibronic lines, originating from transitions from the $^6H_{13/2}$ level to the integrated intensity of the zero phonon line is found to be equal to 0.18, which indicates a low electron–phonon coupling.

The observed in the yellow spectral range $^4F_{9/2} \rightarrow ^4H_{11/2}$ transition of Dy$^{3+}$, is very attractive for laser operation. The stimulated emission cross-section ($\sigma_{em}$), which is the most important parameter influencing a potential laser transition, can be calculated based on the Füchtbauer-Ladenburg formula [33]:

$$\sigma_{em}(\lambda) = \frac{\beta^2 I(\lambda)}{8\pi \tau_{rad} \int I(\lambda) d\lambda}$$  \hspace{1cm} (2)

where $I(\lambda)$ represents the experimental emission intensity as a function of the wavelength, $c$ is the velocity of light, $n$ is the refractive index of the sample and $\beta$ and $\tau_{rad}$ are the branching ratio and radiative lifetime of the $^4F_{9/2}$ level, respectively. The $\tau_{rad}$ and $\beta$ values were obtained on the basis of the presented above Judd-Ofelt analysis. In Fig. 7 is shown the fluorescence spectrum at 300 K for the $^4F_{9/2} \rightarrow ^4H_{11/2}$ transition of Dy$^{3+}$, calibrated in stimulated emission cross-section units (in cm$^2$). The value of $\sigma_{em}$ for the $^4F_{9/2} \rightarrow ^4H_{11/2}$ transition at 576.6 nm is equal to 0.756 x 10$^{-20}$ cm$^2$. In Table 5 are compared the most important emission parameters of the $^4F_{9/2} \rightarrow ^4H_{11/2}$ transition for Dy$^{3+}$-doped laser glasses and crystals. The results presented in the table, indicate a possible application of Dy$^{3+}$-doped Y$_2$Te$_4$O$_{11}$ as a solid-state laser material, operating in the visible spectrum at 576 nm. Nevertheless, the presented results require further verification by laser experiments.

3.5. Decay curve analysis

Experimental decay curves of the $^4F_{9/2}$ level have been measured at room temperature for all Dy$^{3+}$ concentration (0.01, 0.02, 0.1, 0.5, 1.0, 2.0 and 5.0 at.%). For selective excitations the 352 nm excitation was replaced by laser experiments.

$$\tau_m = \frac{\tau_{rad}}{\int_0^\infty t(t) dt}$$  \hspace{1cm} (3)

The lifetime values of the $^4F_{9/2}$ level are shown in Table 6. The calculated decay times of all investigated samples indicate that the concentration quenching of the $^4F_{9/2}$ level is active. Taking into

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**Table 3**

<table>
<thead>
<tr>
<th>Level</th>
<th>Energy (cm$^{-1}$)</th>
<th>Experimental/theoretical</th>
<th>$\Delta E$</th>
<th>Barycentre (cm$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^5H_{15/2}$</td>
<td>0, 47, 156, 207, 247, 286, 325, 487</td>
<td>8/8</td>
<td>487</td>
<td>219</td>
</tr>
<tr>
<td>$^1H_{13/2}$</td>
<td>3528, 3583, 3618, 3660, 3710, 3737, 3809</td>
<td>7/7</td>
<td>281</td>
<td>3664</td>
</tr>
<tr>
<td>$^1H_{15/2}$</td>
<td>5902, 5933, 5964, 5995, 6023, 6054</td>
<td>6/6</td>
<td>152</td>
<td>5979</td>
</tr>
<tr>
<td>$^3H_{13/2} + ^1F_{9/2}$</td>
<td>7694, 7723, 7760, 7815, 7843, 7867, 7887, 7910, 7955, 7987, 8025</td>
<td>11/11</td>
<td>332</td>
<td>7861</td>
</tr>
<tr>
<td>$^1H_{11/2} + ^1F_{9/2}$</td>
<td>8688, 8920, 9053, 9128, 9181, 9291</td>
<td>6/9</td>
<td>603($^*$)</td>
<td>9044</td>
</tr>
<tr>
<td>$^1H_{9/2}$</td>
<td>Not observed</td>
<td>0/3</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>$^5F_{7/2}$</td>
<td>11007, 11093, 11145</td>
<td>3/4</td>
<td>137($^*)$</td>
<td>11082</td>
</tr>
<tr>
<td>$^5F_{9/2}$</td>
<td>12392, 12429</td>
<td>2/3</td>
<td>37($^*)$</td>
<td>12410</td>
</tr>
<tr>
<td>$^5F_{5/2}$</td>
<td>13233, 13272</td>
<td>2/2</td>
<td>38($^*)$</td>
<td>13253</td>
</tr>
</tbody>
</table>

*$^*$ Determined from absorption spectrum at 300 K.
account the large energy gap between the $^4F_{9/2}$ emitting level and the next lower $^4F_{1/2}$ level (about 8000 cm$^{-1}$) as well as the phonon energy of Y$_2$Te$_4$O$_{11}$ equal to 800 cm$^{-1}$ [17], one may assume that multi-phonon relaxation process is negligible. Consequently, the $^4F_{9/2}$ emitting level of Dy$^{3+}$-doped Y$_2$Te$_4$O$_{11}$ may be depopulated via the following two possible cross-relaxation (CR) mechanisms:

1. Resonant CR

\[4F_{9/2} \rightarrow 4F_{5/2}(7254 \text{ cm}^{-1}) = 6H_{15/2} \rightarrow 6H_{9/2} + 4F_{11/2}(7372 \text{ cm}^{-1}) - 118 \text{ cm}^{-1}\]

\[4F_{9/2} \rightarrow 6H_{9/2} + 6F_{11/2}(13135 \text{ cm}^{-1}) = 6H_{15/2} + 6F_{21/2}(13253 \text{ cm}^{-1}) - 118 \text{ cm}^{-1}\]

2. One phonon assisted CR

\[4F_{9/2} \rightarrow 6F_{11/2}(6857 \text{ cm}^{-1}) = 6H_{15/2} \rightarrow 6H_{9/2} + 6F_{11/2}(7372 \text{ cm}^{-1}) - 515 \text{ cm}^{-1}\]

\[4F_{9/2} \rightarrow 6F_{7/2}(8045 \text{ cm}^{-1}) = 6H_{15/2} \rightarrow 6H_{9/2} + 6F_{11/2}(7372 \text{ cm}^{-1}) + 673 \text{ cm}^{-1}\]

\[4F_{9/2} \rightarrow 6F_{7/2}(9607 \text{ cm}^{-1}) = 6H_{15/2} \rightarrow 6H_{7/2} + 6F_{9/2}(9006 \text{ cm}^{-1}) + 601 \text{ cm}^{-1}\]

}\[\text{In order to estimate the ion-ion interaction, the Inokuti-Hirayama model for analysis of the decay curves, has been applied. In this model the experimental decay curve can be expressed as [42]::}\]

\[\Phi(t) = A \exp \left( -t/T_0 \right) \left[ 4\pi \Gamma \left[ 1 - \frac{3}{5} N_A R_0^2 \right] \left( \frac{t}{T_0} \right)^{3/5} \right], \tag{4}\]

where \(l(0)\) is the emission intensity after pulse excitation, \(t\) represents time and \(T_0\) is the intrinsic decay time of the donor ions in the absence of acceptors. \(S\) signifies the energy transfer mechanism, where for dipole–dipole (DD), dipole–quadrupole (DQ) and quadrupole–quadrupole (QQ) interactions, \(S\) is equal to 6, 8 and 10, respectively. \(\Gamma\) is the Euler function \((\Gamma(1.77) = 1.43, 1.30 \text{ for } S = 6, 8, 10, \text{ respectively})\), \(N_A\) is the concentration of Dy$^{3+}$ ions per unit volume in the Y$_2$Te$_4$O$_{11}$ microcrystal and \(R_0\) is the critical transfer distance. The best fit was obtained for \(S = 6\), which indicates that the character of the cross-relaxation is of the dipole-dipole type (see inset of Fig. 8). The calculated lifetime, \(N_A\) concentration and critical transfer distance \(R_0\) are equal to 307 μs, 3.79 × 10$^{10}$ ions per cm$^3$ (5.0 at% Dy$^{3+}$) and 16.8 Å, respectively.

The donor–acceptor parameter \(C_{DA}\) and energy transfer probability \(W_{DA}\) were estimated following the procedure reported in Ref. 17. The \(C_{DA}\) and \(W_{DA}\) values were found to be equal to 7.38 × 10$^{-50}$ m$^6$s and 3257 s$^{-1}$, respectively. The calculated \(C_{DA}\) parameter is higher than those reported for the Dy$^{3+}$:YAl$_3$(BO$_3$)$_4$ and Dy$^{3+}$:Y$_2$Al$_2$O$_3$ crystals [39,41]. Therefore, the Dy$^{3+}$:Y$_2$Te$_4$O$_{11}$ microcrystalline powder exhibit a stronger concentration quenching than other Dy$^{3+}$-doped crystals.

**4. Summary**

Dy$^{3+}$-doped Y$_2$Te$_4$O$_{11}$ microcrystalline powders with various concentration of the Dy$^{3+}$ ions, were successfully synthesized by a solid-state method. The electronic optical absorption (300 K), excitation (300 K) and fluorescence (116 and 300 K) spectra as well as the fluorescence decay curves of the $^4F_{9/2}$ level of the Dy$^{3+}$...
curves have been obtained for $S_{\text{rad}}$ transition. The evaluation of the phenomenological model with different $S$ values of the stimulated emission cross-section for the $^{4}F_{9/2}$ → $^{4}I_{15/2}$ transition equal to $0.756 \times 10^{-20}$ cm$^2$, is favourable for a laser action in the visible range at about 576 nm.

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### References