Thermal Characterization, Crystal Field Analysis and In-Band Pumped Laser Performance of Er Doped NaY(WO4)2 Disordered Laser Crystals

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Abstract

Undoped and Er-doped NaY(WO4)2 disordered single crystals have been grown by the Czochralski technique. The specific heat and thermal conductivity (κ) of these crystals have been characterized from T = 4 K to 700 K and 360 K, respectively. It is shown that κ exhibits anisotropy characteristic of single crystals as well as a κ(T) behavior observed in glasses, with a saturation mean free phonon path of 3.6 Å and 4.5 Å for propagation along a and c crystal axes, respectively. The relative energy positions and irreducible representations of Stark Er17+ levels up to 4G7/2 multiplet have been determined by the combination of experimental low (< 10 K) temperature optical absorption and photoluminescence measurements and simulations with a single-electron Hamiltonian including both free-ion and crystal field interactions. Absorption, emission and gain cross sections of the 115/2 → 13/2 laser related transition have been determined at 77 K. The 115/2 Er17+ lifetime (τ) was measured in the temperature range of 77–300 K, and was found to change from τ(77K) = 4.5 ms to τ(300K) = 3.5 ms. Laser operation is demonstrated at 77 K and 300 K by resonantly pumping the 115/2 multiplet at λ≈1500 nm with a broadband (FWHM = 20 nm) diode laser source perfectly matching the 77 K crystal 115/2 → 113/2 absorption profile. At 77 K as much as 5.5 W of output power were obtained in π-polarized configuration with a slope efficiency versus absorbed pump power of 57%, the free running laser wavelength in air was λ≈1611 nm with the laser output bandwidth of 3.5 nm. The laser emission was tunable over 30.7 nm, from 1590.7 nm to 1621.4 nm, for the same π-polarized configuration.

Introduction

Lanthanide-doped disordered single crystals are receiving increasing attention in connection to their high potential as gain media in solid state lasers. The large optical transition bandwidth inherent to the coexistence of a distribution of Crystal Fields (CF) around the optical active ion has been found useful to better accommodate the emission bandwidth of diode lasers (DLs) presently used for optical pumping. This spectroscopic property is also greatly desired for mode-locked operation of ultrafast (fs) lasers. In comparison with glasses, single crystals usually have better thermo-optic and spectroscopic parameters, such as better thermal conductivity (κ) and higher emission cross sections (σ).

The disordered crystal families so far considered for this purpose include crystals with the hexagonal apatite structure Sr4Y(2- SiO4)2O2 (melting point, m.p. 2173 K, κ = 1.6 Wm-1K-1) [1], tetragonal melilite SrLaGa3O7 (m.p. 2033 K, κ = 1.95 Wm-1K-1) [2], CaGaAlO4 (m.p. 1973 K, κ = 6.9 Wm-1K-1 for 2% Yb-doped) [3], oxoborates Ca4Ga2O7Y2O3 (m.p. 1753 K, κ = 2.1 Wm-1K-1) [4,5,6], Ca3(NbGa2)2Ga3O12 garnet (m.p. 1743 K, κ = 4.7 Wm-1K-1 for 2 wt% Nd-doped) [7,8], and tetragonal double tungstate NaY(WO4)2 (m.p. 1473 K, κ = 1.06 Wm-1K-1) [9,10,11]. All these crystals melt congruently and can be grown by the technologically desired Czochralski method. The advantage of latter double tungstate is its significantly lower melting point which simplify the crystal growth (platinum instead iridium can be used as crucible material and air can be used as growth atmosphere). At room temperature most of these disordered crystals have relatively low thermal conductivity which has been reported to also decrease with doping, therefore active crystal cooling is important for stable high power laser operation.

Cryogenic cooling at 77 K is presently considered a viable means facilitating power scaling to a multi-kW class continuous wave (cw) laser operation [12]. The inconvenience of liquid nitrogen use is counterbalanced by performance improvements due to the increase of the peak absorption and emission cross sections of trivalent lanthanides (Ln3+) with temperature reduction. However, the spectral width of the Ln3+ absorption bands generally narrows with the increase of their peak absorption. This makes the use of disordered crystals more desirable in order to
more fully utilize the optical power delivered by the pumping DLs. From this point of view crystals with medium CF strength are preferred over crystals with strong CF strength because at 77 K a compromise between the band linewidth and absorption intensity is expected to be found more easily.

To further reduce crystal heating during laser operation and relax cooling requirements resonantly (in-band) pumped solid state lasers are being developed. This pumping scheme minimizes the energy difference between the absorbed pump photons and those emitted by stimulated radiation, i.e., the crystals have low "quantum defect". The most representative examples of this laser operation scheme are the \( ^{2}F_{7/2} \leftrightarrow ^{2}F_{5/2} \) operation of Yb\(^{3+} \) (\( \lambda < 1.06 \) \( \mu m \)) [13], and more recently \( ^{5}I_{6} \leftrightarrow ^{5}I_{7} \) operation of Ho\(^{3+} \) (\( \lambda = 2.07 \) \( \mu m \)) [14], \( ^{3}F_{3} \leftrightarrow ^{3}H_{4} \) operation of Pr\(^{3+} \) (\( \lambda = 1.65 \) \( \mu m \)) [15], and \( ^{4}I_{15/2} \leftrightarrow ^{4}I_{13/2} \) operation of Er\(^{3+} \) (\( \lambda = 1.60 \) \( \mu m \)) [16,17], which are receiving increasing attention. The emission range around 1.60 \( \mu m \) is of particular interest for long range propagation in the atmosphere.

Therefore, laser operation of La\(^{3+} \)-doped disordered crystals in-band pumped by DLs at 77 K is perceived as the most optimized approach to scaling the power of solid state lasers. Unfortunately, the growth and characterization of disordered crystals is still underdeveloped and their physical properties below room temperature are either unknown or not well established. In this

**Figure 1.** 1 at% Er-doped NaY(WO\(_4\))\(_2\) crystal. (a) As grown boule. The small squares in the background scale are 1 \( \times \) 1 \( \mu m \)\(^2\). (b) Polished sample used for laser experiments.

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**Table 1.** Erbium concentration, \([Er]\), erbium segregation coefficient, \(K\), and crystal lattice parameters of undoped and Er-doped NaY(WO\(_4\))\(_2\) crystals.

| [Er]\(_{\text{MELT}}\) (at\%) | Region | [Er]\(_{\text{CRYSTAL}}\) (at\%) | \([Er]_{\text{CRYSTAL}}\) \((10^{20} \text{ cm}^{-3})\) | \(K\) | \(a\) \((\text{\AA})\) | \(c\) \((\text{\AA})\) | \(V\) \((\text{\AA}^3)\) |
|----------------|--------|-------------------------------|-----------------------|-----|------------|------------|----------|
| 0              | Top    | 0.030±0.02                    | 0.0197±0.0013         | 1.5 | 5.1992(4)  | 11.272(1)  | 304.70(5) |
| 0.02           | Top    | 1.04                          | 0.683                 | 1.04| 5.1981(5)  | 11.268(1)  | 304.46(6) |
|                | Medium | 1.04                          | 0.683                 | 1.04|            |            |          |
|                | Bottom | 1.02                          | 0.670                 | 1.02|            |            |          |
| 1              | Top    | 3.15                          | 2.067                 | 1.05| 5.1964(8)  | 11.263(2)  | 304.13(9) |
|                | Bottom | 3.06                          | 2.012                 | 1.02|            |            |          |
| 15             | Medium | 14.7±0.7                      | 9.68±0.46             | 0.98| 5.1937(9)  | 11.261(2)  | 303.8(1)  |

\(^a\) REF 18.
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work we studied the temperature evolution of the thermal parameters and spectroscopic characteristics of Er-doped NaY(WO4)2 single crystals below 300 K. We also demonstrated and characterized Er3+ laser operation in NaY(WO4)2 directly in-band pumped by InGaAsP/InP DLS at room and liquid nitrogen temperatures.

Materials and Methods

1. Crystal Growth

Er-doped NaY(WO4)2 crystals were grown by the Czochralski method in air. The compound was previously synthesized by solid state reaction from Na2CO3 (99.5%), Y2O3 (99.9%), Er2O3 (99.9%) and WO3 (99.5%) starting materials. The starting compounds were annealed to eliminate moisture before weighting and later mixed in the appropriate composition. For synthesis, the mixture was first annealed to 1023 K for 18 h and cooled to room temperature, this product was ground and further annealed to 1123 K for 24 h. The phase of the resulting compound was monitored by powder X-ray diffraction. Afterwards, 1.5 wt% of Na2WO4 was mixed with the synthesized Er-doped NaY(WO4)2 compound in order to decrease the melting temperature, to facilitate the crystal seeding and to compensate for possible evaporative loss of Na and W during the growth process. Overall, this provided a significant improvement in the optical crystal transparency.

For crystal growth, this mixture was melted in a Pt crucible using a vertical resistive furnace. Undoped NaY(WO4)2 crystal oriented in the [100] direction was used as a seed. During the growth, the crucible temperature was related to the mass loss of the crucible to maintain constant crystal diameter. The seed rotation speed during the growth process was 10 r.p.m. and the growth, the crucible temperature was related to the mass loss of the crucible to maintain constant crystal diameter. The seed rotation speed during the growth process was 10 r.p.m. and the crystal pulling rate was 1.6 mm/h. The grown crystal was cooled to room temperature at 10 K/h. Table 1 summarizes the growth parameters and spectroscopic characteristics of Er-doped NaY(WO4)2 crystals below 300 K. We also demonstrated and characterized Er3+ laser operation in NaY(WO4)2 directly in-band pumped by InGaAsP/InP DLS at room and liquid nitrogen temperatures.

Figure 3. Temperature evolution of the specific heat (c_p) of a 1 at% Er-doped NaY(WO4)2 crystal upon cooling from 700 K to 4 K. c_p for T>298 K, black solid squares; c_p for T<298 K, red open circles.

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2. Thermophysical Measurements

Specific heat at a constant pressure (c_p) was measured below room temperature with a Quantum Design Physical Property Measurement system and above room temperature with a TA Instruments DSC Q-100 equipment. In the second case the isotherm operation mode was used, sapphire was taken as a
3. Optical Spectroscopic Measurements

Optical absorption (OA) and photoluminescence (PL) measurements have been performed in the 7–300 K temperature range by using a closed-cycle He cryostat. OA was measured by a Varian spectrophotometer, model Cary 5E, whose light beam was filtered by using a Glan-Taylor calcite polarizer. For λ≈1.5 μm PL measurements the emission was dispersed in a SPEX 340E (f'=34 cm) spectrometer and detected with a Hamamatsu photomultiplier, model H9170-75, connected to a lock-in amplifier.

Further OA and PL measurements were made specifically at 77 K. In this case an Oxford flux cryostat operated with liquid nitrogen was used to assure temperature during OA experiments. The 77 K PL spectrum was obtained by illuminating a 0.02 at% Er-doped NaY(WO4)2 crystal with 970 nm DL emission and collecting the emission with a Yokogawa optical spectrum analyzer, model AQ6370. A polarization beam splitter was inserted between the sample and the collecting optics to separate π- and σ-polarized emissions.

According to the tetragonal character of the crystal the experimental spectra can be labeled as σ (E and B∥c-axis), σ (E∥//a-axis and B//c-axis) or π (E∥//a-axis and B//σ-axis), where E and B are the electric and magnetic fields of the light, respectively.

4. Laser Measurements

Laser experiments were performed with a 1 at% Er-doped NaY(WO4)2 crystal with dimensions 2.8×7×10 mm, see Figure 1b. The 7×10 mm faces were anti-reflection (AR) coated for the spectral range of 1480–1620 nm. For measurements at cryogenic temperatures, crystals were mounted on the copper cold finger inside a boil-off liquid nitrogen cryostat and cooled down to ∼79 K. For room temperature measurements, the crystals were placed on a water-cooled copper mount and were conductively cooled to 291 K.

The crystals were longitudinally pumped by a DL module which puts out a collimated beam delivering up to 17 W of CW π-polarized pump power with the output spectrum centered at 1501 nm. The non-narrowed output bandwidth of this InGaAsP/InP DL module used in our laser experiments was measured to be ∼20 nm FWHM. The module consists of 10 single emitters space-combined into a single polarized beam with the divergence of ∼7 mrad in both vertical and horizontal directions. Each InGaAsP/InP single emitter emits with the output spectral bandwidth of 10–12 nm FWHM, typical of this material, but multiple emitters for this module were not pre-selected to have the same peak wavelength position at the same temperature. So the integral spectral bandwidth of the module is ∼20 nm FWHM due to the dispersion in a single diode emitter peak positions. More details of the experimental laser methods are given later.

Results and Discussion

1. Thermophysical Properties

Figure 3 shows the results of the cp measurements obtained for the 1 at% Er-doped NaY(WO4)2 crystal. The specific heat shows typical behavior of a dielectric crystal, both in terms of the dependence on temperature (T) and of its value.

Figure 4 shows the results of the k(T) measurements. The k(T) shape and value are very much different than those observed for a typical dielectric single crystal of relatively good quality. The k change of the tested NaY(WO4)2 crystals does not exceed 100% over the entire investigated temperature range while typically k changes by some orders of magnitude of the value. From low temperature k increases with temperature and displays a maximum at T ≈ 8 K. Such a maximum is a typical feature of thermal conductivity of a crystal and it is due to the interplay between the increasing (with temperature) energy of phonons and increasing intensity of the three-phonon scatterings, also known as U-processes, in which the momentum of the created phonon is opposite to the sum of the momenta of the two interacting phonons, leading to a strong thermal resistivity [21]. For a dielectric crystal at temperatures well above the maximum the U-processes also dominate in the thermal conductivity and cause it to change as T−η, where η=1. However, in the NaY(WO4)2 crystals here investigated after the initial drop following the maximum, the thermal conductivity attains its minimum at around 70 K and
then starts to increase again with temperature. This increase cannot be explained by typical lattice thermal transport mechanisms.

For further analysis of the experimental results we will utilize an expression originating from the kinetic theory of gases which allows us to write the thermal conductivity $k$ as

$$ k \approx \frac{1}{3} \rho c_p v \ell $$

where $\rho = 6.616$ Mg/m$^3$ is the NaY(WO$_4$)$_2$ crystal density, $v$ is the sound velocity (for NaY(WO$_4$)$_2$, $v/a = 4700$ m/s and $v/c = 4190$ m/s) [22] and $\ell$ is the phonon mean free path. From the expression given above one can find that with increasing temperature $\ell$ decreases down to a saturation constant value inducing a $k$ minimum near 70 K (for 1 at% Er-doped NaY(WO$_4$)$_2$, $k/a = 1.20$ Wm$^{-1}$K$^{-1}$ and $k/c = 1.27$ Wm$^{-1}$K$^{-1}$) and for higher temperatures the $k(T)$ evolution depends on $c_p(T)$. Taking into account the room temperature values of the thermal conductivity (for 1 at% Er-doped NaY(WO$_4$)$_2$, $k/a = 1.47$ Wm$^{-1}$K$^{-1}$ and $k/c = 1.62$ Wm$^{-1}$K$^{-1}$) and $c_p(300 K) = 0.3868$ Jg$^{-1}$K$^{-1}$, the phonon mean free path saturation values result $\ell/a = 3.6$ Å and $\ell/c = 4.5$ Å. The independence of the phonon mean free path of temperature in high temperature region is a glassy structure feature [23] (in crystals the phonon mean free path varies at these temperatures approximately as $T^{-\frac{1}{2}}$). Therefore, despite that from the macroscopic point of view the studied crystals exhibit the typical features of single crystals, like a marked anisotropy of the physical constants and well defined X-ray diffraction peaks, in terms of thermal properties NaY(WO$_4$)$_2$ is rather a glass-like structure than a crystal. At the lowest investigated temperatures, where one observes in glasses a plateau of the thermal conductivity of a small value of the coefficient $k < 0.1$ Wm$^{-1}$K$^{-1}$ some

Figure 5. Low temperature (7 K) optical absorption coefficient ($\alpha$) and photoluminescence (PL) of Er-doped NaY(WO$_4$)$_2$ crystal. $\sigma$-polarization, red dashed line; $\pi$-polarization, black solid line.

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Table 2. Observed ($E_o$) and calculated ($E_c$) energy levels (cm$^{-1}$) of Er$^{3+}$ in NaY(WO$_4$)$_2$ crystal, in an average $S_4$ symmetry.

| $^{2S+1}L_J$ | $^a$ | IR$^b$ | $E_o$ (cm$^{-1}$) | $E_c$ (cm$^{-1}$) | $^{2S+1}L_J$ | $^a$ | IR$^b$ | $E_o$ (cm$^{-1}$) | $E_c$ (cm$^{-1}$) |
|-------------|------|--------|----------------|----------------|-------------|------|--------|----------------|----------------|
| $^4I_{15/2}$ | $\sigma$ | $\Gamma_{5,6}$ | 0 | $^4I_{15/2}$ | $\sigma$ | $\Gamma_{5,6}$ | 0 | $^4I_{15/2}$ | $\sigma$ | $\Gamma_{5,6}$ | 0 |
| $^4I_{13/2}$ | $\sigma$ | $\Gamma_{7,8}$ | 30 | 36 | $^4I_{13/2}$ | $\sigma$ | $\Gamma_{7,8}$ | 30 | 36 |
| $^4I_{11/2}$ | $\pi$ | $\Gamma_{7,8}$ | 254 | 246 | $^4I_{11/2}$ | $\pi$ | $\Gamma_{7,8}$ | 254 | 246 |
| $^4I_{9/2}$ | $\sigma$ | $\Gamma_{7,8}$ | 294 | 291 | $^4I_{9/2}$ | $\sigma$ | $\Gamma_{7,8}$ | 294 | 291 |
| $^4I_{7/2}$ | $\sigma$ | $\Gamma_{7,8}$ | 216 | 214 | $^4I_{7/2}$ | $\sigma$ | $\Gamma_{7,8}$ | 216 | 214 |
| $^4I_{5/2}$ | $\pi$ | $\Gamma_{7,8}$ | 2671 | 2658 | $^4I_{5/2}$ | $\pi$ | $\Gamma_{7,8}$ | 2671 | 2658 |
| $^4I_{3/2}$ | $\sigma$ | $\Gamma_{7,8}$ | 6531 | 6540 | $^4I_{3/2}$ | $\sigma$ | $\Gamma_{7,8}$ | 6531 | 6540 |
| $^4I_{1/2}$ | $\pi$ | $\Gamma_{7,8}$ | 10204 | 10197$^c$ | $^4I_{1/2}$ | $\pi$ | $\Gamma_{7,8}$ | 10204 | 10197$^c$ |

$^a$OA observed polarization character ($\parallel$).
$^b$Irreducible representation (IR).
$^c$Levels with heavily mixed wavefunctions.

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“crystalline” characteristics of the investigated samples such as the little maximum discussed above appear. The dominant glassy character of the investigated crystals also explains the very little effect of Erbium doping on thermal conductivity. In view of small changes observed as Er concentration increases, the origin of the phonon scattering must be related to the presence of multiple local ionic arrangements due to the near to random distribution of Na and Y over the 2d and 2b sites of the NaY(WO4)2 crystalline structure. [18].

At room temperature the anisotropy of κ shown in Figure 4b (κ//a<κ//c) qualitatively agree with previous results obtained using the laser flash method for 5 at% Yb-doped NaY(WO4)2 [11] and Yb-doped NaGeO3 [24] however the absolute κ values obtained by the heat-flow method are slightly larger. This anisotropy becomes smaller with sample temperature reduction and eventually its sign changes, i.e., below certain temperature κ//a>κ//c. This low temperature anisotropy behavior can be attributed to the distinct arrangement of the (Na/Y)O8 and WO4 polyhedra building the crystallographic structure of NaY(WO4)2. Along the [100] direction the more rigid WO4 polyhedra with short (~1.8 Å) strong covalent W-O bonds alternate with (Na/Y)O8 polyhedra with considerably larger bond distance (~2.4 Å), in contrast, the [001] direction is characterized by the presence of dimeric 2(Na/Y)O8 units sharing edges.

2. Er3+ Energy Levels

The Er3+ Stark energy level sequence has been deduced from the analysis of 7–300 K OA and PL spectra. Stark levels of the 2S1/2,1LJ excited multiplets were determined by their ground state 4I13/2,1LJ(n) transition is summarized in Table 3. The partition functions (Z) of the 4I15/2 and 4I13/2 multiplets involved in the 1.5 µm emission can be obtained from the level energies summarized in Table 2, as

$$Z = \sum_k d_k e^{-E_k/k_BT}$$

(2)

where dk = 2 because of the double degeneracy of the Kramers doublets, Ek is the energy of a given Stark level with respect to the minimum energy of its multiplet, kB is the Boltzmann constant and T is the temperature. The Z values obtained for the 4I13/2 and 4I15/2 multiplets are 9.38 and 9.20, respectively.

Properties of Er:NaY(WO4)2 Laser Crystals
Table 3. Irreducible representations (IR) observed for $S_4$ symmetry.

| J  | IR         |
|----|------------|
| 1/2| $\Gamma_{1/2}$ |
| 3/2| $\Gamma_{3/2} + \Gamma_{1/2}$ |
| 5/2| 2 $\Gamma_{3/2} + \Gamma_{1/2}$ |
| 7/2| 2 $\Gamma_{3/2} + 2 \Gamma_{1/2}$ |
| 9/2| 2 $\Gamma_{3/2} + 3 \Gamma_{1/2}$ |
| 11/2| 3 $\Gamma_{3/2} + 3 \Gamma_{1/2}$ |
| 13/2| 4 $\Gamma_{3/2} + 3 \Gamma_{1/2}$ |
| 15/2| 4 $\Gamma_{3/2} + 4 \Gamma_{1/2}$ |
| 17/2| 4 $\Gamma_{3/2} + 5 \Gamma_{1/2}$ |

Table 4. Selection rules for induced electric dipole ED and magnetic dipole MD transitions for the $S_4$ symmetry.

| IR | ED | MD |
|----|----|----|
| $\Gamma_{5,6}$ | $\Gamma_{7,8}$ | $\Gamma_{5,6}$ | $\Gamma_{7,8}$ |
| $\sigma_\alpha$ | $\alpha$ | $\sigma_\alpha$ |
| $\sigma_\beta$ | $\beta$ |

3. Spectroscopic Properties Related to Resonantly Pumped ~1.6 µm Laser

$T \approx 77$ K is a convenient cryogenic cooling temperature because of the wide availability of liquid nitrogen that can be distilled from air. The purpose of this section is to evaluate the spectroscopic parameters of Er$^{3+}$ in NaY(WO$_4$)$_2$ at this temperature. Figure 7 shows the 77 K $4I_{13/2}$ absorption cross section, $\sigma_{\text{ABS}} = 2/\text{[Er]}$, for $\sigma_\alpha$ and $\sigma_\beta$-polarization. The largest absorption, $\sigma_{\text{ABS}} = 5.3 \pm 0.2 \times 10^{-20}$ cm$^2$, is obtained at $\lambda = 1501$ nm for $\sigma_\alpha$-polarization with a full width at half maximum (FWHM) for the convolution of the several overlapping peaks of 17.5 nm.

The reduction of the sample temperature from room temperature (300 K) to liquid nitrogen temperature (77 K) induces significant increase of the peak absorption cross section of the $4I_{11/2} \rightarrow 4I_{13/2}$ transition, and a nearly structureless broad absorption band is observed at 1501 nm, see Figure 7a. The absorption at 77 K is composed by overlapping of several peaks and it shows a nearly perfect matching with the emission spectrum of our spectrally non-narrowed InGaAsP/InP DL module with the spectral bandwidth of FWHM ~ 20 nm, used for pumping the Er$^{3+}$:NaY(WO$_4$)$_2$ laser.

Larger peak cross sections can be obtained by further sample cooling up to the liquid He temperature, but this develops two well resolved bands and a central minimum with an absorption efficiency half of that corresponding to the nearby maxima, therefore the emission of the DL cannot be absorbed so efficiently for a given sample thickness. At the $\lambda = 1501$ nm fixed wavelength the sample absorption follows an exponential function related to the Boltzmann distribution of the electronic population of the $4I_{11/2}$ multiplet, see inset of Figure 7a.

The emission cross-section on the $4I_{3/2} \rightarrow 4I_{13/2}$ transitions were obtained by stitching up the results of the reciprocity [20] (1470–1531.8 nm)

$$\sigma_{\text{EMI}} = \sigma_{\text{ABS}} \frac{Z_{\text{d}}}{n} \frac{(E_{\text{d}} - \hbar \omega)}{h^2 B^2}$$

($E_{\text{d}}$ is the energy of the $0 \rightarrow 0'$ transition and Fuchtbauer-Landenburg [29] (1511.8–1640 nm) methods using the measured PL and lifetime (see below) of the $4I_{13/2}$ manifold:

$$\sigma_{\text{EMI}} = \frac{\beta}{8 \pi c h^2 \tau_{\text{em}}} \sum \frac{I(\lambda) \lambda^4}{\lambda d\lambda}$$

where $\tau_{\text{rad}}$ is the radiative lifetime of the $4I_{13/2}$ state of Er$^{3+}$, $n$ is the refractive index [30] of the crystal, $I(\lambda)$ is the fluorescence intensity in arbitrary units, $\lambda$ is the average emission wavelength, $c$ is the speed of light and $\beta$ is the branching ratio corresponding to the transition $4I_{13/2} \rightarrow 4I_{13/2}$ ($\beta = 1$).

Figure 8 shows the polarization resolved $4I_{13/2} \rightarrow 4I_{13/2}$ emission cross sections of Er-doped NaY(WO$_4$)$_2$ crystal in the wavelength range of 1470–1640 nm at 77 K and 300 K. The peak emission cross-section of Er-doped NaY(WO$_4$)$_2$ crystal at 77 K in the 1560–1630 nm wavelength region for $\pi$-polarization (0.8 $\times 10^{-20}$ cm$^2$) is slightly higher than that for $\sigma$-polarized ones ($\sim 0.65 \times 10^{-20}$ cm$^2$) and it is shifted to long-wavelength region compared with $\sigma$-polarized emission spectrum.

The gain cross section $\sigma_{\text{GAIN}} = 4\pi\sigma_{\text{EMI}}$ $\frac{1 - \eta\sigma_{\text{ABS}}}{\eta}$, $\eta$ being the ratio between Er$^{3+}$ ions in the excited state versus the total Er$^{3+}$ concentration, provides first information about the lasing capability of resonantly pumped laser systems. Figure 9 shows the polarization resolved $\sigma_{\text{GAIN}}$ results obtained from data of Figures 7 and 8. Two lasing regions can be distinguished, the first one around 1540 nm is characterized by narrow bands and it requires high inversion ratios, $\eta > 0.3$. The second one, extending from 1560 nm to 1625 nm for both $\pi$-polarized and $\sigma$-polarized configurations, occurs even for low $\eta$ values and it is characterized by broad bands, indicating of significant laser tunability potential (and femtosecond laser operation) in this wavelength range.

Figure 10 shows the lifetime dependence on temperature of the upper laser level ($4I_{13/2}$) of the 0.02 at% Er-doped NaY(WO$_4$)$_2$ crystal. The lifetime measurements were done on a pulverized sample with low concentration of Er$^{3+}$ ions ($\approx 1.9 \times 10^{10}$ cm$^{-3}$) in order to avoid effects of radiation trapping and fluorescence reabsorption on measurement results.

4. Resonantly Pumped Laser Experiments

Figure 11 shows a schematic representation of experimental setup and optical cavity used for laser characterizations. The quasi-CW performance of the 1 at% Er-doped NaY(WO$_4$)$_2$ laser resonantly pumped into the 1501 nm absorption band (corresponding to $4I_{15/2}(0) \rightarrow 4I_{15/2}(4)$ transition, see Table 2) at 77 K is shown in Figure 12a for three different OC reflections. Without a wavelength selective element in the cavity the laser operated in $\pi$-polarization. The Er-doped NaY(WO$_4$)$_2$ laser power in this case is presented versus absorbed pump power since the fraction of the absorbed pump power was observed to significantly vary with pump power due to saturation effects (averaging from 0.83 to ~0.7 depending on the output coupler reflectivity and the pump density).

The best output of 5.5 W and a slope efficiency $\eta = 57\%$ versus absorbed pump power have been achieved with the cavity length of 12 cm, RoC of the OC ~230 mm and OC reflectance of 85%. The TEM$_{00}$ mode size in this case was about 500 µm along the entire crystal length and provided the best fit with the pumped volume. The measured laser beam divergence was about
3.3 mrad, which is close to a calculated value of the TEM\textsubscript{00} mode divergence for the used laser cavity configuration. The $p$-polarized output spectrum of the Er-doped NaY(WO\textsubscript{4})\textsubscript{2} laser (taken with an optical spectrum analyzer) was centered at $\lambda = 1611$ nm (air) and had a bandwidth of $\Delta \lambda = 3.5$ nm, thus the laser operates with the quantum defect of $\eta = 7\%$. The measured composite passive loss in the cavity, including cryostat windows, was found to be $L = 4\%$ for a single-pass at $\lambda = 1610$ nm and was mainly introduced by the AR coatings on the crystal.

The evidence of the laser efficiency improvement upon cryo-cooling comes from comparison of Figures 12a and 12b. The output of the laser in Fig. 12b is also represented versus the absorbed pump power (both Q-CW with the same duty factor of 0.1). The best laser performance was achieved with the cavity length of $L = 8$ cm and RoC of the concave OC of 100 mm. The pump beam was focused into the crystal by the lens with the focal length of $f = 75$ mm. The diameter of the TEM\textsubscript{00} laser mode along the crystal in this resonator was $d = 340$ mm, i.e. slightly smaller than the diameter of the pumped volume. The maximum obtained laser slope efficiency at room temperature with respect to absorbed pump power was 32.7\% with the output coupler reflectivity of $R = 98\%$. This value of the slope efficiency at room temperature is nearly twice higher than that reported recently by Huang, et al., for Er:Yb:Ce:NaY(WO\textsubscript{4})\textsubscript{2} laser [31]. The fraction of the pump power absorbed in the crystal with respect to incident pump power at room temperature was measured to be $\eta = 0.65$–0.55, depending on the output coupler reflectivity and the pump density. It is noticeably lower than that at 77 K, however, not as low as one could expect from comparison of the absorption spectra at cryogenic and room temperatures, see Figure 7. We believe that the reason for this is much smaller influence of the saturation effects on laser performance at room temperature.

Maximum laser output power obtained at room temperature was $P = 1$ W. The laser output spectrum at room temperature was centered at $\lambda = 1609.6$ nm (air) with the bandwidth of $\Delta \lambda = 4$ nm.

To assess the tunability potential of the Er-doped NaY(WO\textsubscript{4})\textsubscript{2} laser, we performed tuning experiments with cryogenically cooled (77 K) Er-doped NaY(WO\textsubscript{4})\textsubscript{2} laser by inserting a three-stage birefringent tuner in the cavity between the laser crystal and the output coupler. The wavelength tuning was measured separately for two laser polarizations. For the $p$-polarized laser output, the tuning range was measured to be $\Delta \lambda = 22$ nm, from 1588 nm to 1610.2 nm, with the maximum at $\lambda = 1595$ nm. For the $s$-polarized laser output, the tuning range was measured to be $\Delta \lambda = 22$ nm, from 1588 nm to 1610.2 nm, with the maximum at $\lambda = 1595$ nm. For the $s$-polarized laser output, the tuning range was measured to be $\Delta \lambda = 22$ nm, from 1588 nm to 1610.2 nm, with the maximum at $\lambda = 1595$ nm.

![Figure 7. 77 K $^4\text{I}_{13/2}$ absorption cross section of Er-doped NaY(WO\textsubscript{4})\textsubscript{2} single crystal (lines) for $\pi$ (a) and $\sigma$ (b) polarizations.](doi:10.1371/journal.pone.0059381.g007)
polarization the tuning curve was wider, around 30.7 nm, from 1590.7 nm to 1621.4 nm, with the maximum at 1610 nm. Both tuning curves correspond well with the calculated gain cross section profiles of Er-doped NaY(WO₄)₂ crystal for σ- and π-polarizations, see Figure 9. The measured tuning range was obviously limited by the coating of the cavity optics preventing lasing in the λ<1540 nm region. This wide wavelength tuning range of Er-doped NaY(WO₄)₂ laser is very beneficial and will potentially support generation of ultra-short laser pulses with pulse durations down to ~100 fs.

Conclusions

The thermal conductivity of disordered NaY(WO₄)₂ crystal has a behavior resembling that observed in glasses, i.e., after the mean free path of phonons saturates to a constant value the recovery of the thermal conductivity is related to the increase of the specific heat with temperature. Despite this fact, the thermal conductivity retains the characteristic anisotropy of single crystals and is little affected by doping with Er ions, which is indicative of the principal phonon scattering processes association with the near to random distribution of Na and Y(or Er) in two possible crystal lattice sites, 2b and 2d. Therefore this behavior is expected to be also found in lasers doped with other lanthanides. Although it is well known that dopants (Er and other laser lanthanides) reduce the thermal conductivity of the laser crystals, the present results suggest that a further reduction of the thermal conductivity could be expected in disordered crystals based on the coexistence of several sites for the laser dopants. The extension of similar thermal measurements to disordered laser crystals mentioned in the Introduction section seems very necessary to quantify the relative magnitude of both possible thermal conductivity reduction mechanisms.

Figure 8. Polarization resolved emission cross sections of the 4I_{13/2} → 4I_{15/2} transition of Er³⁺ in NaY(WO₄)₂ single crystal measured at 77 K (red continuous line) and 300 K (black dashed line); (a) π-polarized spectra, (b) σ-polarized spectra.

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Figure 9. Gain cross sections of Er-doped NaY(WO₄)₂ crystals at 77 K for different inversion ratios, Y: (a) π-polarization, (b) σ-polarization.

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Figure 10. The lifetime of the 4I_{13/2} manifold versus temperature for the pulverized 0.02 at% Er-doped NaY(WO₄)₂ crystal.

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From low temperature (<10 K) polarized optical absorption and photoluminescence measurements assisted by the assessment with an energy simulation including the erbium free ion and crystal field interactions the relative energy sequence of the Er³⁺ Stark levels and their irreducible representations have been
determined up to the $^{4}G_{7/2}$ multiplet. Further, the 77 K absorption, emission and gain cross sections have been determined. It was shown that at 77 K the main absorption at $\lambda = 1501$ nm (p-polarized) perfectly fits the spectral distribution of the non-narrowed diode laser module used for resonant optical pumping of Er-doped NaY(WO$_4$)$_2$ laser. The lifetime of the upper $^{4}I_{15/2}$ multiplet of Er$^{3+}$ ions is $\approx 4.5$ ms at 77 K and gets reduced to $\approx 3.7$ ms at room temperature.

Erbium lasing may occur in narrow bands around 1550 nm or continuously between 1560 nm and 1625 nm. It was shown that by cooling the crystal to 77 K the maximum output power can be increased by a factor of five and the slope efficiency (versus absorbed power) by a factor of two with respect to laser operation at room temperature. The best resonantly pumped laser efficiency was obtained at 77 K by using a near to constant TEM$_{00}$ cavity mode and pump mode size of about 300 $\mu$m of diameter along the entire crystal length. In this case the maximum achieved output power was 5.5 W with a slope efficiency (versus absorbed power) of $\eta = 57\%$. The laser output was p-polarized and centered at $\lambda=1611$ nm with a FWHM of $\approx 3.5$ nm. Laser tuning of over 30.7 nm (from 1590.7 nm to 1621.4 nm) has been demonstrated at 77 K for p-polarization. The tuning range for s-polarization was slightly narrower and limited by the coatings of the cavity optics.

**Author Contributions**

Conceived and designed the experiments: CZ AJ MD. Performed the experiments: MS CC XH CZ PS NT VF. Analyzed the data: MS CC XH CZ AJ PS NT VF MD. Contributed reagents/materials/analysis tools: MS CC XH. Wrote the paper: CZ AJ MD.

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**Figure 11.** Simplified optical layout of the cryogenically cooled Er-doped NaY(WO$_4$)$_2$ laser. doi:10.1371/journal.pone.0059381.g011

**Figure 12.** Laser output power vs. absorbed pump power (both quasi-CW) for the resonantly pumped 1 at% Er-doped NaY(WO$_4$)$_2$ laser (points). Quasi-CW regime: pulse duration 10 ms, pulse repetition frequency 10 Hz. (a) Cooled to 77 K. (b) Cooled at room temperature. The legend shows the reflectance of the used output coupler, $R_{\text{out}}$, and the slope efficiency, $\eta$, obtained from the linear fits (lines). doi:10.1371/journal.pone.0059381.g012
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