Stokes and anti-Stokes luminescence from cubic elpasolite Cs$_2$NaYF$_6$ crystals doped with Er$^{3+}$ and Yb$^{3+}$ ions

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Er$^{3+}$ and Yb$^{3+}$ doped cubic elpasolite Cs$_2$NaYF$_6$ crystals including stoichiometric compositions Cs$_5$Na$_2$ErF$_{16}$ and Cs$_5$Na$_2$YbF$_{16}$ have been synthesized under hydrothermal conditions. Absorption, stimulated-emission and gain cross-sections spectra have been determined for the $^{2}F_{5/2}$, $^{2}F_{7/2}$ (Yb$^{3+}$) and $^{4}I_{13/2}$, $^{4}I_{15/2}$ (Er$^{3+}$) transitions at room-temperature. The maximum $\sigma_{\text{se}}$ values are $1.8 \times 10^{-21}$ cm$^2$ at 993 nm (Yb$^{3+}$) and $3.8 \times 10^{-21}$ cm$^2$ at 1535 nm (Er$^{3+}$). Elpasolite crystals provide exceptionally long radiative lifetimes of the excited-states for both ions, namely $\tau(2F_{5/2}) = 6.3$ ms and $\tau(4I_{13/2}) = 32$ ms for 10 at% Yb$^{3+}$:Cs$_2$NaYF$_6$ and 10 at% Er$^{3+}$:Cs$_2$NaYF$_6$, which can be used in high pulse energy Q-switched lasers. Up-conversion luminescence has been studied for Er$^{3+}$ doped and Er$^{3+}$, Yb$^{3+}$ codoped Cs$_2$NaYF$_6$ crystals.

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1. Introduction

Halide compounds having the elpasolite structure can be described by a general formula A$_2$BMX$_6$, where A and B are monovalent alkali ions provided that the ionic radius of A is greater than that of B, M stands for trivalent metal ions, which can be Al, Sc, transition elements and rare earth elements, and X is a halogen [1]. The elpasolite compounds crystallize in the face-centered cubic space group Fm3m [2] and can be described as double perovskites. In the structure the A alkali cations are located in the cuboctahedral sites whereas the B alkali cations and the M trivalent metal ions regularly alternate along the unit cell axes in octahedral sites. Accordingly, the MX$_6$ octahedra are perfectly cubic with O$_h$ site symmetry for trivalent metal ions, while the MX$_6$ octahedra do not share halide ions with each other, i.e. the elpasolite structure is characterized by the isolated MX$_6$ octahedra. In addition, as all the halide compounds, elpasolites are materials with low-photon energy.

The above mentioned peculiarities of elpasolite hosts lead to a significant reduction of the multiphonon relaxation rates for optically active rare earth (RE) ion dopants, which allows for an increased lifetime of some excited levels that can relax radiatively or can store energy for further up-conversion and cross-relaxation as well as provide relatively low concentration quenching of luminescence, which allows obtaining efficient luminescence in A$_2$BMX$_6$ containing high trivalent RE ion concentrations up to 100 at%.

To date, some spectroscopy data for several RE ions (Er$^{3+}$, Yb$^{3+}$, Tm$^{3+}$, Eu$^{3+}$) doped into the Cs$_2$NaYF$_6$ compound have been published; however, characterization of these materials is far from completeness mainly due to the difficulty of synthesizing optical quality crystals of elpasolites in general and Cs$_2$NaYF$_6$ in particular. For example, VUV 5d–4f luminescence of Er$^{3+}$ ions, including a stoichiometric Cs$_5$Na$_2$ErF$_{16}$ compound, has been studied followed by crystal field calculations for Er$^{3+}$ ions [3,4]. Near-IR (~2.7 μm) emission of Er$^{3+}$ ions in Cs$_2$NaYF$_6$ has been also investigated and the lifetime of the $^{4}I_{15/2}$ excited-state has been detected to be as long as ~1 ms at room-temperature for highly-doped (> 10 at%) samples [5]. Absorption and emission as well as crystal field analysis for Yb$^{3+}$ ions in Cs$_2$NaYbF$_6$ has been reported [6–8]. In particular, very long lifetime of the Yb$^{3+}$ excited-state, $\tau(2F_{5/2}) = 5.83$ ms, at room-temperature is observed for Cs$_5$Na$_2$YbF$_{16}$. Some spectroscopic peculiarities of Tm$^{3+}$ ions in Cs$_5$Na$_2$YF$_{16}$ have been also studied [3,6,9] and crystal field calculations for a Tm:Cs$_5$Na$_2$YF$_{16}$ crystal have been performed [10]. The spectroscopic properties of Eu$^{3+}$ and Tb$^{3+}$ ions doped into Cs$_5$Na$_2$YF$_{16}$ have been investigated as well [11–13].

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The fluoride cubic elpasolite Cs2NaYF6 is isostructural with the chloride elpasolite Cs2NaYCl6, that has been extensively studied as an low phonon energy host for optically active ions of 3d, 4f and 5f elements, for example Er3+ [14,15]. In particular, Cs2NaYCl6 crystals doubly doped with Er3+ and Yb3+ have been studied as the near-IR-to-visible frequency converters [16,17] based on photon upconversion processes [18]. As a result of upconversion mechanisms, Er3+-Yb3+ ion pairs can convert near-IR (~1 μm) emission of InGaAs laser diodes to green and red light. On the other hand, Cs2NaYF6 is harder and less moisture-sensitive than Cs2NaYCl6. Thus, the study of visible emissions in Er3+ and Yb3+ ions doped Cs2NaYF6 crystals is of practical interest for developing photon upconverters. High efficiency of up-conversion in the cubic elpasolite Cs2NaYF6 can be achieved due to the low value of the maximum phonon frequency which is 468 cm−1 [11]. This value is higher than that for Cs2NaYCl6 (285 cm−1) [19] but it is acceptable for energy storage on excited levels. In addition, long lifetimes of the first excited-states of Er3+ and Yb3+ ions observed for highly-doped Cs2NaYF6 crystals indicate their potential for generation of high pulse energies in passively Q-switched near-IR lasers.

In the present paper, the data on optical absorption, near-IR and visible f–f emissions of Cs2NaYF6 crystals doped with Er3+ and Yb3+ ions as well as Cs2NaErF6 and Cs2NaYbF6 are reported.

2. Experimental

Crystals of cubic elpasolite Cs2NaYF6 doped with Er3+ and Yb3+ ions as well as Cs2NaErF6 and Cs2NaYbF6 were grown under hydrothermal conditions. For hydrothermal experiments, copper-insert lined autoclaves with a volume of 40 cm3 were utilized, the reaction of the aqueous solutions containing 35 mol% CsF and 8–10 mol% NaF with oxide mixtures (1–x)Y2O3–xLn2O3 (Ln=Er and Yb) at a temperature of ~750 K in the synthesis zone, a temperature gradient along the reactor body of up to 3 K/cm, and a pressure of ~100 MPa. Under these conditions, spontaneously nucleated crystals of up to 0.5 cm3 were grown in the upper crystallization zone of the autoclave for 200 h. The purities of the utilized rare earth oxides were 99.99%.

The structure type and phase purity of synthesized samples were characterized with conventional powder X-ray diffraction (XRD) technique and powder XRD patterns were obtained by using a Bruker D8 Advance X-Ray powder diffractometer with Cu Kα radiation. Absorption spectrum was measured for 10 at% Er3+ and 10 at% Yb3+ doped Cs2NaYF6 crystals with a Varian CARY 5000 spectrophotometer (the spectral bandwidth, SBW, was 0.1 nm). Thin polished platelets (~1 mm) of crystals were used. Luminescence spectra were measured with a lock-in amplifier, a monochromator MDR-23 (SBW ~0.1 nm) and Hamamatsu G5851 and C5460-01 photodetectors. The spectral sensitivity of the set-up was accurately determined with a halogen lamp with calibrated spectral power density. Near-IR luminescence and upconversion luminescence (UCL) of Er3+ and Yb3+ ions was excited by InGaAs laser diode emitting at ~960 nm (excitation to the 4I13/2 state or Yb3+ 2F5/2 state). Excitation light was focused on a sample in a ~100 μm spot; the maximum power density was ~40 kW/cm2. Luminescence was also excited at ~355 and ~520 nm (excitation to the 2G7/2 and 2H11/2 states of Er3+, respectively) and a ns optical parametric oscillator (OPO) Lotis TII LT-2214 was used. CIE chromaticity coordinates of phosphors were calculated by using the photoluminescence data.

For the studies of luminescence decay of Yb3+ ions, OPO with the pulse duration of ~20 ns was tuned to 960 nm. Luminescence was collected by a wide-aperture lens and re-imaged to the input slit of a monochromator MDR-12 (tuned to 1020 nm, SBW ~1 nm); then it was detected with a fast Hamamatsu G5851 photodetector (response time, < 100 ns) and a 500 MHz Tektronix TDS-3052B digital oscilloscope. To avoid the reabsorption loss, studied crystals were finely powdered and immersed in glycerin (~5 wt% powder content).

All spectroscopic studies were performed at room temperature.

3. Results and discussion

The X-ray phase analysis has confirmed that all the synthesized compounds are single-phase samples containing only the cubic elpasolite phases, space group Fm3m, Z=4 (ICDD PDF Cards: 00-0201214; 00-0210221; 00-0210224) [1]. X-ray diffraction patterns of Cs2NaYF6, Cs2NaErF6 and Cs2NaYbF6 are showed in Fig. 1 and they can be indexed with a cubic cell with the lattice parameter, a=9.057 Å, 9.045 Å and 9.016 Å, respectively. Lattice parameter (a), volume of the unit cell (V), density (ρ) and concentration (N) of the Y3+, Er3+ and Yb3+ ions which have been obtained from the X-ray diffraction studies for these compounds are summarized in Table 1. One can see that there is a marginal change in cell parameters due to differences in rare earth ionic radii and it should be also noted that the unit cell parameters determined in this study are notably less than those tabulated in [1].

An absorption spectrum measured for a 10 at% Er3+:Cs2NaYF6 crystal is shown in Fig. 2. For the 4I15/2 → 4I11/2 transition, the peak absorption cross-section is σabs=0.07 × 10−21 cm2 at 963 nm. The full width at half maximum (FWHM) for this band is ~24 nm. Such low absorption determines low efficiency for the excitation of Er3+ ions by using InGaAs diodes. Indeed, for the stoichiometric Cs2NaErF6 crystal, the corresponding peak absorption coefficient is α ~0.37 cm−1, which means that the absorption of diode emission is not complete even for a few mm-thick crystal. For the 4I15/2 → 4I13/2 transition that is typically used for the in-band excitation of

![Diagram](image)

**Table 1**

<table>
<thead>
<tr>
<th>Composition</th>
<th>a, Å</th>
<th>V, Å³</th>
<th>ρ, g/cm³</th>
<th>N, at/cm³</th>
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<td>732.9</td>
<td>5.24</td>
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Er$^{3+}$ ions, the absorption is much stronger, $\sigma_{\text{abs}} = 4.6 \times 10^{-21} \text{cm}^2$ at 1532.2 nm. The FWHM of this band is 5.4 nm.

Near-IR emissions of Er$^{3+}$ ions have been studied under 960 nm excitation by using a stoichiometric Cs$_2$NaErF$_6$ crystal. The luminescence band related to the Er$^{3+}$ $^4\text{I}_{13/2}$ - $^4\text{I}_{15/2}$ transition spans from $24.1$ to $24.65 \mu$m, see Fig. 3(a). The band in the 920–1060 nm spectral range is attributed to the $^4\text{I}_{11/2}$ - $^4\text{I}_{15/2}$ transition of Er$^{3+}$ ions.

Emission of Er$^{3+}$ ions at $\sim 1.5 \mu$m is eye-safe and interesting for laser operation. To calculate the corresponding stimulated-emission cross-sections $\sigma_{\text{SE}}$, two methods can be used. The first one is the reciprocity method [20]:

$$\sigma_{\text{SE}}(\lambda) = \sigma_{\text{abs}}(\lambda) \frac{Z_1}{Z_2} \exp \left( -\frac{hc}{\lambda c} - \frac{E_{\text{ZL}}}{kT} \right).$$

where $Z_1$ and $Z_2$ are the lower and upper manifold partition functions, respectively, $E_{\text{ZL}}$ is the energy corresponding to the zero phonon line, $h$ is the Planck constant, $c$ is the speed of light, $\lambda$ is the light wavelength, $k$ is the Boltzmann constant and $T$ is the crystal temperature (room-temperature). Partition functions are determined as:

$$Z_m = \sum_k g^m_k \exp \left( -\frac{E^m_k}{kT} \right),$$

where $m = 1, 2$; $g^m_k$ is the degeneration of the sublevel having the number $k$ and the energy $E^m_k$ measured from the lower sublevel of the corresponding multiplet. The set of $E^m_k$ values for the $^4\text{I}_{13/2}$ and $^4\text{I}_{15/2}$ states of Er$^{3+}$ ions in the Cs$_2$NaYF$_6$ crystal [4] is listed in Table 2.

Calculation of $\sigma_{\text{SE}}$ with the reciprocity method is beneficial as it does not require the information about the radiative lifetime $\tau_{\text{rad}}$ of the emitting state as well as direct measurement of the emission spectrum which can be changed as a result of the reabsorption loss. The obtained results are shown in Fig. 4(a). The maximum $\sigma_{\text{SE}}$ value is $3.8 \times 10^{-21} \text{cm}^2$ at 1532.2 nm. This value is lower than the typical peak $\sigma_{\text{SE}}$ values for the Er$^{3+}$ $^4\text{I}_{13/2}$ - $^4\text{I}_{15/2}$ transition in widespread oxide and fluoride laser hosts, $0.5$–$1 \times 10^{-20} \text{cm}^2$ [21]. In the spectral range where laser operation is expected, the maximum $\sigma_{\text{SE}}$ value is $1.5 \times 10^{-21} \text{cm}^2$ at 1574.1 nm. Radiative lifetime of the Er$^{3+}$ emitting state ($^4\text{I}_{13/2}$) can be calculated with the reciprocity and F-L methods [21].

$$\beta = \frac{N_2}{N}$$

where $\beta$ is the inversion ratio.

Table 2

<table>
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<tr>
<th>Multiplet (Yb$^{3+}$)</th>
<th>Sub-levels, cm$^{-1}$</th>
<th>Multiplet (Er$^{3+}$)</th>
<th>Sub-levels, cm$^{-1}$</th>
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<td>$^4\text{I}_{13/2}$</td>
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<td></td>
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<td>287</td>
</tr>
<tr>
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<td>$^4\text{I}_{15/2}$</td>
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<tr>
<td></td>
<td>11,109</td>
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<td>6686</td>
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</tbody>
</table>

Fig. 2. Absorption cross-section spectra for a 10 at% Er$^{3+}$:Cs$_2$NaYF$_6$ crystal.

Fig. 3. Near-IR emission spectra of Cs$_2$NaErF$_6$ (a) and Cs$_2$NaYbF$_6$ (b) crystals; excitation wavelength is denoted by arrow (960 nm).

Fig. 4. (a) Stimulated-emission cross-section spectra calculated with the reciprocity and F-L methods for a 10 at% Er$^{3+}$:Cs$_2$NaYF$_6$ crystal, (b) gain cross-sections $\sigma_{\text{g}} = \beta \sigma_{\text{SE}} - (1 - \beta) \sigma_{\text{abs}}$ spectra, $\beta = N_2/N$ is the inversion ratio.
For $\text{Er}^{3+}$:Cs$_2$NaYF$_6$ crystal, $\tau_{\text{rad}}(4\text{I}_{13/2})$ has been determined to be $\sim 32 \pm 2$ ms. Previously, lifetime of this state was measured for 1 at% $\text{Er}^{3+}$:Cs$_2$NaYF$_6$ crystal only at cryogenic temperature (4 K), $\tau(4\text{I}_{13/2}) \sim 100$ ms [5] and this value can be considered as a radiative one at low temperatures, as the reabsorption for such crystal doping is nearly vanishing. Such long values are inherent for all the elpasolite crystals [14]. In particular, $\tau(4\text{I}_{13/2}) = 22$ ms for a cubic Cs$_2$NaErCl$_6$ crystal [23]. Independent estimation of the $\tau_{\text{rad}}$ for $\text{Er}^{3+}$:Cs$_2$NaYF$_6$ crystal can be done with the Judd–Ofelt modeling that will be performed in a separate study.

Using the measured emission spectrum $W(\lambda)$, Fig. 3(a), and the determined radiative lifetime $\tau_{\text{rad}}(4\text{I}_{13/2})$, it is possible to calculate a stimulated-emission cross-sections spectrum for the $4\text{I}_{11/2} - 4\text{I}_{15/2}$ transition with the Füchtbauer–Ladenburg (F–L) equation [24]:

$$\sigma_{\text{SE}}(\lambda) = \frac{4}{3\pi c} \frac{\lambda^3}{\tau_{\text{rad}}} \int \frac{W(\lambda)}{\lambda} d\lambda$$

(4)

The obtained results are shown in Fig. 4(a) and they are in good agreement with the ones from the reciprocity method, considering strong reabsorption at short wavelengths.

For assessing the prospects of elpasolite crystals to lasers, a useful parameter is the gain cross-section, $\sigma_{g}$:

$$\sigma_{g}(\lambda) = \beta \sigma_{\text{SE}}(\lambda) - (1 - \beta) \sigma_{\text{abs}}(\lambda)$$

(5)

where $\beta$ is the inversion ratio, $\beta = N_2/N_0$ where $N_2$ and $N_0$ are the numbers of ions in the upper laser level and the overall number of ions, respectively. Gain spectra for a 10 at% $\text{Er}^{3+}$:Cs$_2$NaYF$_6$ crystal are shown in Fig. 4(b). For these calculations, we used stimulated-emission cross-sections spectra obtained with the reciprocity method. For low inversion ratios ($\beta < 0.4$), laser operation is expected at several wavelengths, $\sim 1624, 1658$ or 1694 nm. For high inversion ratios, the peak centered at 1574 nm dominates in the spectrum.

An absorption spectrum measured for a 10 at% $\text{Yb}^{3+}$:Cs$_2$NaYF$_6$ crystal is shown in Fig. 5(a) representing the $4\text{F}_{5/2} - 4\text{F}_{7/2}$ transition of $\text{Yb}^{3+}$ ions. The peak absorption cross-section is $\sigma_{\text{abs}} = 1.3 \times 10^{-21}$ cm$^2$ at 962.0 nm. Thus, Cs$_2$NaYF$_6$ crystals containing both $\text{Er}^{3+}$ and $\text{Yb}^{3+}$ ions provide significant improvement of the excitation efficiency under using InGaAs laser diodes. In particular, the peak absorption coefficient for the stoichiometric Cs$_2$NaYbF$_6$ crystal, $\alpha = 6.9$ cm$^{-1}$ and FWHM for this band is 5.2 nm.

The stimulated-emission cross-sections spectrum for a 10 at% $\text{Yb}^{3+}$:Cs$_2$NaYF$_6$ crystal has been calculated with the reciprocity method, Eq. (1). The spectrum is shown in Fig. 5(a) and the energies of Stark sub-levels for the $4\text{I}_{13/2}$ and $4\text{I}_{15/2}$ states of $\text{Yb}^{3+}$ ions used for calculations are listed in Table 2 [8]. The maximum $\sigma_{\text{SE}}$ value is $\sim 1.8 \times 10^{-21}$ cm$^2$ at 992.4 nm. Emission of $\text{Yb}^{3+}$ ions spans from $\sim 920$ to 1080 nm. Thus, the tuning range wider than 100 nm is expected under using this crystal as a laser gain medium. This is in agreement with the near-IR emission spectrum of the Cs$_2$NaYbF$_6$ crystal measured directly under 960 nm excitation and shown in Fig. 3(b).

The radiative lifetime of the $4\text{I}_{13/2}$ state of $\text{Yb}^{3+}$ ions in the Cs$_2$NaYF$_6$ crystal determined from the modified reciprocity method, Eq. (3), is $\tau_{\text{rad}}(4\text{I}_{13/2}) = 6.4$ ms. This value is in close agreement with the decay time of $\text{Yb}^{3+}$ emission measured directly for a powdered 10 at% $\text{Yb}^{3+}$:Cs$_2$NaYF$_6$ composition, $\tau = 6.3$ ms. The corresponding decay curve is shown in Fig. 6 and it is clearly single-exponential. For a stoichiometric Cs$_2$NaYbF$_6$ crystal, similar measurement yields $\tau = 5.7$ ms, which is close to the previously reported value [6], $\tau = 5.63$ ms. Thus, the anomalously weak concentration quenching is observed for $\text{Yb}^{3+}$:Cs$_2$NaYF$_6$ crystals. Determined lifetimes are at least two times longer than those for typical $\text{Yb}^{3+}$-doped fluoride laser hosts with $\tau$ ranging typically from 1.5 to 3 ms. This indicates the potential of highly-doped $\text{Yb}^{3+}$:Cs$_2$NaYF$_6$ crystals (up to 100 at%) for generation of high pulse energies in the Q-switched operation mode.

Gain cross-sections spectra for a 10 at% $\text{Yb}^{3+}$:Cs$_2$NaYF$_6$ crystal are shown in Fig. 5(b). For low inversion ratios ($\beta < 0.1$), the gain spectrum is flat and it spans from 1000 to 1080 nm, so the multi-peak spectral behavior is expected. For high inversion, two intense local peaks centered at $\sim 992$ nm and 1009 nm are observed. This indicates the possibility of dual-wavelength laser operation for this crystal.

The lifetimes of the $4\text{F}_{5/2}$ excited-state and the $4\text{I}_{11/2}$ and $4\text{I}_{13/2}$ excited-states for $\text{Er}^{3+}$ ions are presented in Table 3. In this context, it is worth mentioning that even for a stoichiometric Cs$_2$NaErF$_6$ crystal, the value of $\tau(4\text{I}_{11/2})$ is as long as 0.7 ms at room-temperature [5], which indicates that it can be promising medium for $\sim 3 \mu$m laser operation on the $4\text{I}_{11/2} - 4\text{I}_{13/2}$ transition [25].

UCL spectra of $\text{Er}^{3+}$:Cs$_2$NaYF$_6$ crystals under the excitation at 960 nm to the $4\text{I}_{13/2} - 4\text{I}_{11/2}$ state are shown in Fig. 7(a). For a 10 at% $\text{Er}^{3+}$ doped crystal, the green emission band spanning from 510 to 580 nm and related to the transitions from the closely located and thermalized state $2\text{H}_{11/2}$ and $2\text{S}_{3/2}$ to the ground state $4\text{I}_{15/2}$.
Emission from the Cs$_2$NaYbF$_6$ crystal (c): measured UCL spectrum, calculated cooperative emission from the Cs$_2$NaYbF$_6$ crystal is much weaker than the green one. The ratio for integrated emission in the range 630–566 nm are observed within this emission band. The red dominates in the spectrum. Four intense peaks at 540, 551, 557 and 566 nm are observed within this emission band. The red emission in the range 630–700 nm related to the transition $^4$F$_{9/2} \rightarrow ^{4}I_{15/2}$ is much weaker than the green one. The ratio for integrated intensities of these bands (R/G ratio) is 0.27 which is referred to the domination of the excited-state absorption (ESA) over the cross-relaxation (CR) mechanism in generation of UCL, however, further time-resolved studies of UCL are required to support this [26]. In the blue region there is a weak emission band which is due to the transition from the higher-lying excited state $^{1}G_{4}$ to the $^{4}I_{15/2}$ ground-state.

These features determine the yellow-green color of UCL from Cs$_2$NaYF$_6$ with $x = 0.385$ and $y = 0.603$ in the 1931 CIE chromaticity coordinates as well as high color purity, $p > 98\%$, caused by the dominant wavelength at 562 nm. Color purity $p$ was calculated from the CIE 1931 chromaticity diagram with respect to the CIE-E Illuminant (uniform white, $x = 0.333$ and $y = 0.333$). It is defined as $p = a/b$ where $a$ is the distance from the white point to the sample color point and $b$ is the distance from the white point to the point on the spectral locus corresponding to the dominant wavelength. The color purity is a quantitative measure of the saturation of a particular color. For a stoichiometric Cs$_2$NaErF$_6$ crystal and a 1 at% Er$^{3+}$, 10 at% Yb$^{3+}$:Cs$_2$NaYbF$_6$ crystals, very similar UCL spectra are observed, see Fig. 7. Color characteristics for UCL from the studied crystals are summarized in Table 4.

In addition, UCL from a stoichiometric Cs$_2$NaYbF$_6$ crystal has been studied under the excitation at 960 nm to the Yb$^{3+}$ to impurity Tm$^{3+}$ and Er$^{3+}$ ions and UCL from Tm$^{3+}$ dominates. Both Tm and Er are presented as trace impurities in ytterbium oxide, Yb$_2$O$_3$, reagent and thus their amount in stoichiometric crystal is enough to provide detectable UCL. The bands at 450–505, 640–680 and 750–820 nm are related to the transitions $^1G_{4} \rightarrow ^3H_{6}$, $^1G_{4} \rightarrow ^{2}F_{4}$ and $^3H_{4} \rightarrow ^{2}H_{6}$ for Tm$^{3+}$, respectively, whereas weak green Er$^{3+}$ emission from the $^4H_{11/2}$ and $^4S_{3/2}$ states to the $^4I_{15/2}$ ground state is detected at ~ 550 nm. The red Er$^{3+}$ emission from the $^4I_{15/2}$ state at ~ 650 nm can overlap with the red Tm$^{3+}$ one, so it is not discovered. Accordingly, UCL from the Cs$_2$NaYbF$_6$ crystal is blue–violet.

In the previous study of a Cs$_2$NaYbF$_6$ crystal [6], the strong emission band at ~ 480 nm is at least partially attributed to cooperative emission from Yb$^{3+}$–Yb$^{3+}$ ion pairs [27]. This effect is known for materials with the strong clustering of Yb$^{3+}$ ions [28]. In this case, a pair of closely located ions can form a virtual excited state with the energy $2E(^{2}F_{5/2}) \sim 20,000$ cm$^{-1}$. The emission from this state can be observed in the region 480–500 nm [29]. The emission spectrum can be calculated as the convolution of the near-IR emission spectrum of Yb$^{3+}$ ions related to the $^4F_{5/2} \rightarrow ^2F_{7/2}$ transition [27]:

$$F_{\text{coop}}(E) = \int F_{\text{Ef}}(E')F_{\text{IF}}(E-E')dE'.$$

The result of this calculation is presented in the inset of Fig. 7(c). The cooperative emission should occur in the spectral range 475–510 nm with a maximum at ~ 484 nm that is very close to the maximum of the $^1G_{4} \rightarrow ^3H_{6}$ Tm$^{3+}$ emission in the Cs$_2$NaYbF$_6$ crystal [3]. Thus, it is difficult to distinguish these effects spectrally. In [6] it has been found that the decay time of blue emission from a Cs$_2$NaYbF$_6$ crystal is 2.73 ms, which is almost exactly half of $\tau$$_{0.7}$ $10$ at% Er$^{3+}$:Cs$_2$NaYbF$_6$ crystals, $\tau$$_{0.7}$ $10$ at% 6.3; 6.4 rec

### Table 3

<table>
<thead>
<tr>
<th>Ion concentration</th>
<th>Yb$^{3+}$ ion $\tau$($^{4}F_{9/2}$), ms</th>
<th>Er$^{3+}$ ion $\tau$($^{4}I_{13/2}$), ms</th>
<th>Er$^{3+}$ ion $\tau$($^{4}I_{11/2}$), ms</th>
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</thead>
<tbody>
<tr>
<td>This work/ [6]/RT</td>
<td>This work/ [5]/4 K</td>
<td>This work/ [5]/4 K</td>
<td>This work/ [5]/4 K</td>
</tr>
<tr>
<td>1 at%</td>
<td>6.3; 6.4 rec</td>
<td>100</td>
<td>12</td>
</tr>
<tr>
<td>10 at%</td>
<td>5.7</td>
<td>5.63</td>
<td>0.7</td>
</tr>
</tbody>
</table>

* RT - room temperature, REC - estimated with the reciprocity method.

### Table 4

<table>
<thead>
<tr>
<th>Crystal</th>
<th>$x$</th>
<th>$y$</th>
<th>$\lambda_d$ nm</th>
<th>$p$</th>
<th>Color</th>
</tr>
</thead>
<tbody>
<tr>
<td>Exc. 960 nm</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>10 at% Er$^{3+}$:Cs$_2$NaYbF$_6$</td>
<td>0.385</td>
<td>0.603</td>
<td>562</td>
<td>98%</td>
<td>Yellow–green</td>
</tr>
<tr>
<td>Cs$_2$NaErF$_6$</td>
<td>0.343</td>
<td>0.656</td>
<td>556</td>
<td>99%</td>
<td>Yellow–green</td>
</tr>
<tr>
<td>1 at% Er$^{3+}$, 10 at% Yb$^{3+}$:Cs$_2$NaYbF$_6$</td>
<td>0.340</td>
<td>0.660</td>
<td>555</td>
<td>99%</td>
<td>Yellow–green</td>
</tr>
<tr>
<td>Cs$_2$NaYbF$_6$</td>
<td>0.325</td>
<td>0.586</td>
<td>553</td>
<td>75%</td>
<td>Yellow–green</td>
</tr>
<tr>
<td>Exc. 355 nm</td>
<td></td>
<td></td>
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<td></td>
<td></td>
</tr>
</tbody>
</table>
There is the same situation for red emission from the $^4F_{9/2}$ state at 660 nm where $n=2.1$ Normally, excitation of Er$^{3+}$ ions to the higher lying excited states is achieved in two steps, for example ground-state absorption (GSA) $^4I_{15/2}$ followed by excited-state absorption (ESA) from the $^4I_{11/2}$ or the $^4I_{13/2}$ states. For Cs$_2$NaErF$_6$, cross-relaxation (CR) between the adjacent Er$^{3+}$ ions, which can participate as an additional mechanism for the population of the $^4F_{9/2}$ state, seems to be very weak. Indeed, the R/G ratio for UCL is not enhanced when the Er$^{3+}$ concentration in Cs$_2$NaYF$_6$ increases from 10 to 100 at%, Fig. 7(a). This well correlates with the large distance between the isolated Y$^{3+}$ sites in the Er$^{3+}$-Cs$_2$NaYF$_6$ crystal, so the probability of CR is not varied with the increase of the Er$^{3+}$ concentration in the elpasolite hosts. No significant dependence of R/G ratio on the excitation power was detected.

In Fig. 8(a), log–log plots for the UCL intensity ($I_{UCL}$) versus the excitation power $P$ are shown for a Cs$_2$NaErF$_6$ crystal. For the up-conversion process, $I_{UCL}$ is proportional to the $n$th power of $P$, i.e. $I_{UCL} \sim P^n$ [30] where $n$ is the number of pump photons absorbed per up-converted photon emitted. A plot of log $I_{UCL}$ versus log $P$ yields a straight line with slope $n$. For green emissions that occur from the $^2H_{11/2}$ and $^4S_{3/2}$ states, for the slope of this dependence $n=2.1$ (524 nm) and 1.9 (557 nm), which means that two pump photons are required to populate the above mentioned states. There is the same situation for red emission from the $^4F_{9/2}$ state at 660 nm where $n=2.1$. Normally, excitation of Er$^{3+}$ ions to the higher lying excited states is achieved in two steps, for example ground-state absorption (GSA) $^4I_{15/2}$ followed by excited-state absorption (ESA) from the $^4I_{11/2}$ or the $^4I_{13/2}$ states. For Cs$_2$NaErF$_6$, cross-relaxation (CR) between the adjacent Er$^{3+}$ ions, which can participate as an additional mechanism for the population of the $^4F_{9/2}$ state, seems to be very weak. Indeed, the R/G ratio for UCL is not enhanced when the Er$^{3+}$ concentration in Cs$_2$NaYF$_6$ increases from 10 to 100 at%, Fig. 7(a). This well correlates with the large distance between the isolated Y$^{3+}$ sites in the Er$^{3+}$-Cs$_2$NaYF$_6$ crystal, so the probability of CR is not varied with the increase of the Er$^{3+}$ concentration in the elpasolite hosts. No significant dependence of R/G ratio on the excitation power was detected.

Similar slopes ($n=2$) for the log–log plots of the UCL intensity vs. the excitation power are observed also for a 1 at% Er$^{3+}$, 10 at% Yb$^{3+}$: Cs$_2$NaYF$_6$ crystal, Fig. 8(b). In this case, the first step of the UCL mechanism is the excitation of Er$^{3+}$ ions through the GSA $^2F_{7/2}$ followed by excited-state absorption (ESA) from the $^4I_{11/2}$ or the $^4I_{13/2}$ states. For Cs$_2$NaErF$_6$, cross-relaxation (CR) between the adjacent Er$^{3+}$ ions, which can participate as an additional mechanism for the population of the $^4F_{9/2}$ state, seems to be very weak. Indeed, the R/G ratio for UCL is not enhanced when the Er$^{3+}$ concentration in Cs$_2$NaYF$_6$ increases from 10 to 100 at%, Fig. 7(a). This well correlates with the large distance between the isolated Y$^{3+}$ sites in the Er$^{3+}$-Cs$_2$NaYF$_6$ crystal, so the probability of CR is not varied with the increase of the Er$^{3+}$ concentration in the elpasolite hosts. No significant dependence of R/G ratio on the excitation power was detected.

Under excitation into the $^2G_{9/2}$ or the $^2H_{11/2}$ states of Er$^{3+}$ in Cs$_2$NaYF$_6$ at 355 nm or 520 nm, respectively, all the crystals singly doped with Er$^{3+}$ ions demonstrate emission spectra similar to those obtained under near-IR excitation. Figs. 9(a), 3(a) and 7(a). The corresponding color coordinates can be found in Table 4. However, for a 1 at% Er$^{3+}$, 10 at% Yb$^{3+}$: Cs$_2$NaYF$_6$ crystal the spectra are different from those of Er$^{3+}$ doped Cs$_2$NaYF$_6$ crystals. In particular, a broad emission band spanning from 940 to 1050 nm is detected. This band is clearly different from the luminescent band related to the $^4I_{15/2}$ to $^4I_{13/2}$ transition of Er$^{3+}$ ions and has the spectral features of emission on the Yb$^{3+}$ ions is due to the so-called down-conversion (‘‘quantum cutting’’) process for the Er$^{3+}$–Yb$^{3+}$ ion pairs [32,33].

It should be also noted that enhancement of the efficiency of the up- and down-conversion processes in cubic elpasolites is possible with the ytterbium compositions Cs$_2$NaEr$_{1-x}$Yb$_x$:Cs$_2$NaYF$_6$ containing relatively high Er$^{3+}$ concentrations.

4. Conclusions

To conclude, we have studied absorption and luminescence of Er$^{3+}$ and Yb$^{3+}$ ions in cubic elpasolite Cs$_2$NaYF$_6$ crystals as well as in crystals of Cs$_2$NaEr$_{1-x}$Yb$_x$:Cs$_2$NaYF$_6$ synthesized under hydrothermal conditions. Stimulated-emission and gain cross-sections have been determined for the Yb$^{3+}$-$^2F_{5/2}$, $^2F_{7/2}$ and the Er$^{3+}$-$^4I_{15/2}$ transitions in 10 at% Yb$^{3+}$:Cs$_2$NaYF$_6$ and 10 at% Er$^{3+}$:Cs$_2$NaYF$_6$ at room temperature. The maximum $\sigma_{SE}$ values are $1.8 \times 10^{-21}$ cm$^2$ at 993 nm (Yb$^{3+}$) and $3.8 \times 10^{-21}$ cm$^2$ at 1535 nm (Er$^{3+}$). The possibility of dual-wavelength laser operation and wide tuning range exceeding 100 nm for laser emission are...
expected for Yb$^{3+}$:Cs$_2$NaYF$_6$ crystals. Due to their structure peculiarities, elpasolite crystals provide exceptionally long radiative lifetimes of the excited-states for both Yb$^{3+}$ and Er$^{3+}$ ions, \(\tau_{(2F_{5/2})} = 6.3\) ms and \(\tau_{(4I_{13/2})} \sim 32\) ms, respectively, together with relatively weak UCL, which makes them attractive for high pulse energy Q-switched lasers. Under excitation at 960 nm, Cs$_2$NaErF$_6$ crystals provide yellowish–green UCL with CIE coordinates \(x = 0.353, y = 0.656\). Down-conversion is detected for Er$^{3+}$:Yb$^{3+}$:Cs$_2$NaYF$_6$ crystals.

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References