Growth, Thermal and Spectral Properties of Er^{3+} -Doped and $\text{Er}^{3+}/\text{Yb}^{3+}$ -Codoped $\text{Li}_3\text{Ba}_2\text{La}_3(\text{WO}_4)_8$ Crystals

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Abstract

This paper reports the growth and spectral properties of Er^{3+} -doped and $\text{Er}^{3+}/\text{Yb}^{3+}$ -codoped $\text{Li}_3\text{Ba}_2\text{La}_3(\text{WO}_4)_8$ crystals. The Er^{3+} : $\text{Li}_3\text{Ba}_2\text{La}_3(\text{WO}_4)_8$ crystal with dimensions of 56 mm×28 mm×9 mm and $\text{Er}^{3+}/\text{Yb}^{3+}$: $\text{Li}_3\text{Ba}_2\text{La}_3(\text{WO}_4)_8$ crystal with dimensions of 52 mm×24 mm×8 mm were obtained by the top-seeded solution growth (TSSG) method. Thermal expansion coefficients and thermal conductivity of both crystals were measured. The spectroscopic characterizations of both crystals were investigated. The spectroscopic analysis reveals that the $\text{Er}^{3+}/\text{Yb}^{3+}$: $\text{Li}_3\text{Ba}_2\text{La}_3(\text{WO}_4)_8$ crystal has much better optical properties than the Er^{3+} : $\text{Li}_3\text{Ba}_2\text{La}_3(\text{WO}_4)_8$ crystal, thus it may become a potential candidate for solid-state laser gain medium material.

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Introduction

Er^{3+} is a well-known active ion for the solid-state laser in near infrared and up-conversion emission [1–3]. The $^4\text{I}_{13/2} \rightarrow ^4\text{I}_{15/2}$ transition has attracted much attention because its eye-safe emission around 1.55 μm has potential use in optical communication, range finding and medical treatment [4,5,6]. The green output emission of Er^{3+} ions has already been used in various fields, such as data storage and laser display [7,8]. Unfortunately, the optical absorption band of the excited energy level ($^4\text{I}_{11/2}$) is weak, which means Er^{3+} ions cannot be effectively pumped. This problem is normally solved by adding a certain amount of Yb^{3+} sensitizing ions, since Yb^{3+} ions have a broad and high absorption band around 980 nm and the energy transfer from Yb^{3+} to Er^{3+} ions is efficient [9,10,11,12]. Laser oscillation has been observed in several Er^{3+} and Yb^{3+} codoped laser hosts, such as YAG, Y_2SiO_5 [13], $\text{YCa}_4\text{O}(\text{BO}_3)_3$ [4], $\text{GdCa}_4\text{O}(\text{BO}_3)_3$ [5], YVO_4 [14], $\text{YAl}_3(\text{BO}_3)_4$ [15], and $\text{NaCe}(\text{WO}_4)_2$ [16]. Among them, the slope efficiencies of $\text{Er}^{3+}/\text{Yb}^{3+}$ codoped $\text{YCa}_4\text{O}(\text{BO}_3)_3$ and $\text{GdCa}_4\text{O}(\text{BO}_3)_3$ crystals are the highest, and exhibit a better thermal property than phosphate glass [4,5]. However, the full widths at half the maximum (FWHM) of absorption bands around 980 nm of the $\text{Er}^{3+}/\text{Yb}^{3+}$ codoped $\text{YCa}_4\text{O}(\text{BO}_3)_3$ (4 nm) and $\text{GdCa}_4\text{O}(\text{BO}_3)_3$ (3 nm) crystals are narrow [4,5,17,18]. The narrow absorption bands need crucially temperature controlling, because the emission wavelength of the pumping diode changes at 0.2–0.3 nm/°K with the operating temperature of the laser device [19,20]. As a consequence, it is necessary to explore novel materials with large absorption bandwidths for solid-state laser application.

$\text{Li}_3\text{Ba}_2\text{Ln}_3(\text{WO}_4)_8$ (Ln = La–Lu, Y) belongs to the monoclinic system with space group $\text{C}2/c$, which was firstly discovered by our

group [21]. Due to the existence of a statistical distribution of Ln and Li atoms, these crystals have a high structure disorder, which results in the absorption and emission lines broadening homogeneously when rare-earth ions are doped and occupy the positions of Ln^{3+} ions [22]. $\text{Li}_3\text{Ba}_2\text{La}_3(\text{WO}_4)_8$ (hereafter denoted as LBLW) is a member of this family. In this work, the thermal expansion coefficients and thermal conductivity of Er^{3+} : LBLW and $\text{Er}^{3+}/\text{Yb}^{3+}$: LBLW single crystals grown by TSSG method were measured. The room-temperature polarized absorption and fluorescence spectra as well as the up-conversion mechanism of both kinds of crystals were reported and analyzed.

Materials and Methods

1. Crystal Growth

The Er^{3+} : LBLW and $\text{Er}^{3+}/\text{Yb}^{3+}$: LBLW crystals were grown by the top-seeded solution growth (TSSG) method from a flux of Li_2WO_4 . The crystal growth was carried out in a vertical tubular furnace. The schematic diagram of crystal growth apparatuses is same as that in Ref. [23]. The furnace temperature was controlled by an AL-708 controller with controlling accuracy of ± 0.1 K. The raw materials of Er^{3+} : LBLW and $\text{Er}^{3+}/\text{Yb}^{3+}$: LBLW were synthesized by the solid-state reaction. The chemicals used were WO_3 , Li_2CO_3 , BaCO_3 , La_2O_3 , Er_2O_3 and Y_2O_3 with the purity of 99.99%. The solutions were composed of 25 mol% of solute (LBLW) and 75 mol% of solvent (Li_2WO_4). The crystal growth procedure is similar to that in Ref [23]. When the growth ended, the crystals were drawn out of the solution and cooled down to room temperature at a cooled rate of 15 K/h. Fig. 1 shows the grown Er^{3+} : LBLW and $\text{Er}^{3+}/\text{Yb}^{3+}$: LBLW crystals with dimensions of 56 mm×28 mm×9 mm and 52 mm×24 mm×8 mm, respectively.

Figure 1. LBLW crystals grown from TSSG method: (a) facets marked by Miller indices (hkl); (b) Er³⁺: LBLW crystal; (c) Er³⁺/Yb³⁺: LBLW crystal.

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The concentrations of rare earth ions were determined to be 0.41 at.% Er³⁺ in Er³⁺: LBLW crystal and 0.48 at.% Er³⁺ and 3.18 at.% Yb³⁺ in Er³⁺/Yb³⁺: LBLW crystal by the inductively coupled plasma atomic emission spectrometry (ICP-AES, Ultima2, Jobin-Yvon).

2. Thermal Properties

The thermal expansion of crystal is an important thermal factor for the crystal growth [24,25]. The thermal expansion coefficients were measured using a thermal expansion dilatometer (NETZSCH DIL 402 PC). The linear thermal expansion coefficient is defined as:

$$\alpha = \frac{1}{L_0} \frac{\Delta L}{\Delta T} \quad (1)$$

where L_0 is the initial length of the sample at room temperature, and ΔL is the change in length when the temperature changes ΔT .

Since the LBLW crystal with monoclinic is of anisotropy, the thermal expansion coefficient α_{ij} is a second rank tensor with four nonzero components in the orthogonal crystallo-physical axes (a , b , c^*) [26]. Thus, in order to obtain thermal expansion ellipsoid, the measurement should be carried out along at least four different directions. Therefore, four rectangular samples were cut from both the Er³⁺-doped and Er³⁺/Yb³⁺-codoped LBLW crystals, of which three were along the crystallographic a -, b - and c^* -axis and the fourth, namely c' , was cut with the anti-clockwise angle (ϕ) 45° with respect to the c -axis. During the measurement, the samples were heated at a heating rate of 5 K/min in the range of 300~1100 K in the air atmosphere.

The processes to determine the thermal expansion tensor in both crystals is similar, therefore here, for brevity, we mainly discuss the Er³⁺-doped one. The measured thermal expansion ratios $\Delta L/L_0$ versus T are shown in Fig. 2 (a). It can be found that when the temperature is below 450 K, the value of $\Delta L/L_0$ rise nonlinearly with the temperature. This may be due to the error caused by the thermal dilatometer at temperature below 450 K

Figure 2. Thermal expansion properties of Er³⁺: LBLW crystal: (a) thermal expansions measured along the crystallo-physical axes (a , b , c^*) and along the anti-clockwise 45° with respect to the c -axis (c'); (b) Orientation relationship among the crystallo-physical axes (a , b , c^*), principal axes (X_I , X_{II} , X_{III}) and optical indicatrix axes (X , Y , Z).
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[27,28]. By linear fitting of the curves above 450 K, the values of the thermal expansion coefficients along a , b , c^* and c' axes are derived as $\alpha_a = 11.3 \times 10^{-6} \text{ K}^{-1}$, $\alpha_b = 8.07 \times 10^{-6} \text{ K}^{-1}$, $\alpha_{c^*} = 8.82 \times 10^{-6} \text{ K}^{-1}$ and $\alpha_{c'} = 9.81 \times 10^{-6} \text{ K}^{-1}$, respectively. The values of the diagonal elements in the crystallo-physical axes are $\alpha_{11} = \alpha_a$, $\alpha_{22} = \alpha_b$ and $\alpha_{33} = \alpha_{c^*}$. $\alpha_{13} = \alpha_{31}$ can be deduced from the equation [26],

$$\alpha_{13} = \frac{\alpha_{c'} - (\alpha_{11} - \alpha_{33}) \times \sin 2\phi/2}{\cos 2\phi} = 0.25 \times 10^{-6} \text{ K}^{-1} \quad (2)$$

Thus, the thermal expansion tensor for the Er³⁺-doped LBLW crystal in the crystallo-physical axes can be written as

$$\alpha_{ij} = \begin{pmatrix} \alpha_{11} & 0 & \alpha_{13} \\ 0 & \alpha_{22} & 0 \\ \alpha_{31} & 0 & \alpha_{33} \end{pmatrix} = \begin{pmatrix} 11.30 & 0 & 0.25 \\ 0 & 8.07 & 0 \\ 0.25 & 0 & 8.82 \end{pmatrix} \times 10^{-6} \text{ K}^{-1} \quad (3)$$

The next step is to find the values of the principal thermal expansion. For a monoclinic crystal, one of the principal axes (X_{III})

of the thermal expansion ellipsoid coincides with the crystallographic b -axis. The other two principle axes (X_I , X_{III}) which can be calculated from the secular equation $\det(\alpha_{ij} - \lambda \delta_{ij}) = 0$ [29] are in the (010) plane. For Er³⁺-doped LBLW crystal, the eigenvalues are $\alpha'_{11} = 11.33 \text{ K}^{-1}$ and $\alpha'_{33} = 8.80 \text{ K}^{-1}$, and the linear thermal expansion tensor in the principal axes is

$$\begin{pmatrix} \alpha'_{11} & 0 & 0 \\ 0 & \alpha'_{22} & 0 \\ 0 & 0 & \alpha'_{33} \end{pmatrix} = \begin{pmatrix} 11.33 & 0 & 0 \\ 0 & 8.07 & 0 \\ 0 & 0 & 8.80 \end{pmatrix} \times 10^{-6} \text{ K}^{-1} \quad (4)$$

the angle ρ between the crystallo-physical c^* -axis and principal X_{III} axis can be evaluated by

$$\tan 2\rho = \frac{2\alpha_{13}}{\alpha_{33} - \alpha_{11}} = -5.70^\circ \quad (5)$$

the minus value of ρ denotes the clockwise angle from c^* -axis to the X_{III} axis (see Fig. 2 (b)).

The values of the linear thermal expansion coefficients along the optical indicatrix axes are more important in practice because the laser elements are normally cut along these axes. The orientation

Table 1. Comparison of linear thermal expansion values of Er³⁺: LBLW and Er³⁺/Yb³⁺: LBLW with other crystals (in units 10^{-6} K^{-1}).

	Crystallo-physical axes			Principal axes			Optical indicatrix axes			Ref
	α_a	α_b	α_{c^*}	X_I	X_{II}	X_{III}	α_X	α_Y	α_Z	
Er ³⁺ :LBLW	11.30	8.07	8.82	11.33	8.07	8.79	11.17	8.07	8.94	This work
Er ³⁺ /Yb ³⁺ :LBLW	10.25	8.01	9.15	11.32	8.01	9.08	11.18	8.01	9.22	This work
KGd(WO ₄) ₂	13.6	2.8	20.5	10.6	2.8	23.4	14.56	2.8	19.54	[31]
KLu(WO ₄) ₂	10.6	3.35	15.1	8.89	3.35	16.72	11.19	3.35	14.55	[32]
Er ³⁺ : Li ₃ Ba ₂ La ₃ (MoO ₄) ₈	16.9	18.5	≈19.6							[33]

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Figure 3. Thermal conductivity properties of Er³⁺: LBLW and Er³⁺/Yb³⁺: LBLW crystals with each crystal measured along the crystallographic directions directions *a*, *b*, *c* and *c*^{*}, respectively: (a) for Er³⁺: LBLW crystal; (b) for Er³⁺/Yb³⁺: LBLW crystal.
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of the optical indicatrix axes (*X*, *Y*, *Z*) with respect to the crystallographic axes (*a*, *b*, *c*) is from that of Ref [30]: (*a*, *X*) = 19° and (*c*, *Z*) = 20° (see Fig. 2 (b)). Using the detailed procedure described in Ref. [26], the ellipsoid in the optical indicatrix axis can be determined as

$$\begin{pmatrix} 11.17 & 0 & -0.61 \\ 0 & 8.07 & 0 \\ -0.61 & 0 & 8.95 \end{pmatrix} \times 10^{-6} \text{K}^{-1} \quad (6)$$

The linear thermal expansion coefficient for the both Er³⁺-doped and Er³⁺/Yb³⁺-doped crystals along the directions of crystallo-physical axes (*a*, *b*, *c*^{*}), principal axes (*X*_I, *X*_{II}, *X*_{III}) and optical indicatrix axes (*X*, *Y*, *Z*) are included in Table 1. The values of α_b/α_a and α_c/α_{c^*} are 0.71 and 0.78, respectively. The thermal expansion exhibits a larger anisotropy than Li₃Ba₂La₃(MoO₄)₈ crystal [33], which means the LBLW crystal is easier to crack during the cooling process. Therefore, a slow annealing rate should be applied in the crystal growth procedure.

The thermal conductivity coefficient (κ) of both Er³⁺-doped and Er³⁺/Yb³⁺-doped crystals were measured by the laser-flash method (Model NETZSCH LFA 457, Germany) in the temperature range 350–700 K. Four samples along *a*, *b*, *c* and *c*^{*} crystallographic directions for each crystal were prepared for thermal conductivity measurements. The dimension of the samples was about 6 mm × 6 mm × 2 mm. Fig. 3 shows the evolution of κ with temperature of both kinds of crystals. The average values of thermal conductivity at 400 K are 0.95 and 0.94 Wm⁻¹K⁻¹ for Er³⁺-doped and Er³⁺/Yb³⁺-codoped LBLW, respectively. Compared with other typical tungstate crystals, such as KGd(WO₄)₂ (≈3.3 Wm⁻¹K⁻¹) [29], KY(WO₄)₂ (≈2.7 Wm⁻¹K⁻¹) [34] and KLu(WO₄)₂ (≈3.3 Wm⁻¹K⁻¹) [35], the thermal conductivity of the LBLW crystal is very low. The low thermal conductivity may be related to the disordered structure of LBLW crystal which can increase the probability of phonon-phonon scattering. In fact, NdGd(WO₄)₂ with disordered structure also has very low thermal conductivity (≈1.2 Wm⁻¹K⁻¹) [29].

3. Spectral Properties

Two cubic samples with dimensions of 7.4 mm × 3.8 mm × 5.8 mm and 7.2 mm × 2.4 mm × 4.7 mm were cut from the Er³⁺: LBLW and Er³⁺/Yb³⁺: LBLW crystals, respectively. Each face of samples was perpendicular to one of the optical indicatrix axes. All the surfaces of these cuboids were polished for spectral experiments. The polarized absorption spectra from 300 nm to 1700 nm were measured using a Perkin-Elmer UV-VIS-NIR spectrometer (Lambda 900). The polarized fluorescence spectra were recorded by a spectrophotometer (FLS920, Edinburgh) equipped with a xenon lamp as the excitation source. Two photomultiplier tubes (PMT) (Hamamatsu R955 and R5509) were used as the detectors in the VIS and NIR regions, respectively. Furthermore, the up-conversion spectroscopic experiments were carried out by a monochromator (Triax550,

Figure 4. Polarized absorption spectra of Er³⁺: LBLW and Er³⁺/Yb³⁺: LBLW crystals at room temperature.
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Table 2. Polarized oscillator strength parameters Ω_t , measured and calculated line strengths for polarized spectra of Er³⁺: LBLW crystal at room temperature.

J' -Manifold	$E X$			$E Y$			$E Z$		
	$\bar{\lambda}^a$ (nm)	S^{mea}	S^{cal}	$\bar{\lambda}$	S^{mea}	S^{cal}	$\bar{\lambda}$	S^{mea}	S^{cal}
		(10 ⁻²⁰ cm ²)		(nm)	(10 ⁻²⁰ cm ²)		(nm)	(10 ⁻²⁰ cm ²)	
⁴ I _{13/2}	1525	1.172	1.21	1516	2.21	2.18	1520	1.25	1.26
⁴ I _{11/2}	984	6.32	6.07	983	7.64	7.82	981	5.74	5.66
⁴ I _{9/2}	801	2.817	2.98	804	4.53	3.42	803	2.11	2.25
⁴ F _{9/2}	656	1.147	1.14	658	1.54	1.59	655	9.73	9.63
⁴ S _{3/2}	545	1.481	1.13	547	1.75	2.70	545	1.68	1.37
⁴ F _{7/2}	489	5.864	5.68	490	1.06	1.05	489	5.58	5.74
⁴ F _{5/2} + ⁴ F _{3/2}	450	2.109	1.79	449	4.55	4.29	447	2.19	2.18
² H _{9/2}	407	1.873	1.47	407	2.76	3.12	407	2.17	1.64
RMSΔS(10 ⁻²¹ cm ²) ^b	0.36			0.72			0.30		
Ω ^{X,Y,Z} (10 ⁻²⁰ cm ²)	14.31, 1.72, 0.51			10.52, 1.85, 1.21			11.0, 1.23, 0.63		
Ω ^{eff} (10 ¹⁻²⁰ cm ²)	11.94, 1.60, 0.78								

^a $\bar{\lambda}$ is the mean wavelength.^bRMSΔS is the root mean square deviation.

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Jobin-Yvon) excited at 976 nm with a diode laser, and the power range of the diode emission was from 40 to 1400 mW. The signals were detected with a PMT (R943-02, Hamamatsu). All measurements were performed at room temperature.

The absorption spectra of the Er³⁺: LBLW and Er³⁺/Yb³⁺: LBLW crystals at room temperature are shown in Fig. 4. These sharp absorption lines are attributed to the Er³⁺ ions except the broad absorption band at 900–1050 nm, which is the overlap of the ⁴I_{15/2}→⁴I_{11/2} transition of Er³⁺ ions and the ²F_{7/2}→²F_{5/2} transition of Yb³⁺ ions. In comparison with Er³⁺: LBLW crystal, such broad and strong absorption band around 900–1050 nm was mainly attributed to the ²F_{7/2}→²F_{5/2} transition of Yb³⁺ ions. The absorption coefficients for Er³⁺/Yb³⁺: LBLW crystal are 1.76 cm⁻¹ at 980 nm, 2.54 cm⁻¹ at 974 nm and 1.80 cm⁻¹ at 978 nm for *E*||*X*, *E*||*Y* and *E*||*Z* respectively. They are roughly ten times as large as those of the Er³⁺: LBLW crystal (0.15 cm⁻¹, 0.14 cm⁻¹ and 0.22 cm⁻¹ for *E*||*X*, *E*||*Y* and *E*||*Z*, respectively). Therefore, the crystal co-doped with Yb³⁺ ions can significantly

increase the absorption of the pump energy if pumped at around 980 nm. It should be also noted that the FWHMs of Er³⁺/Yb³⁺: LBLW crystal around 980 nm are 35 nm, 38 nm and 34 nm for *E*||*X*, *E*||*Y* and *E*||*Z*, respectively, and these values are larger than those of Er³⁺/Yb³⁺: YCa₄O(BO₃)₃ and Er³⁺/Yb³⁺: GdCa₄O(BO₃)₃ crystals [4,5]. The broad absorption bands which can relax the requirement of accurate temperature control of diode laser make Er³⁺/Yb³⁺: LBLW crystal suitable for diode laser pumping.

The Judd-Ofelt theory [36,37] has been widely used to analyze the spectroscopic properties of the rare earth ions except Yb³⁺ ion in crystals. The oscillator strength parameters Ω_t (*t* = 2, 4, 6) can be fitted from the room-temperature absorption spectra, then the spontaneous emission probabilities, radiative lifetime and fluorescence branching ratios can be obtained. The detailed calculation procedure is similar to that reported in Ref [38]. The reduced matrix elements values of unit tensor operators used in the calculation could be found in Ref [39,40]. Except for the two high

Table 3. Spontaneous emission probabilities $A_{JJ'}^{ed}$, fluorescence branching ratios β and radiative lifetimes τ_r for Er³⁺: LBLW crystal.

<i>J</i> → <i>J'</i>	<i>E</i> <i>X</i>				<i>E</i> <i>Y</i>		<i>E</i> <i>Z</i>		
	$\bar{\lambda}$	$A_{JJ'}^{ed}$	$A_{JJ'}^{ed}$	β	$A_{JJ'}^{ed}$	β	$A_{JJ'}^{ed}$	β	τ_r
	(nm)	(S ⁻¹)	(S ⁻¹)	(%)	(S ⁻¹)	(%)	(S ⁻¹)	(%)	(ms)
⁴ I _{13/2} → ⁴ I _{15/2}	1543	77.53	136.04	100.00	245.41	100.00	141.58	100.00	3.44
⁴ I _{11/2} → ⁴ I _{13/2}	2746	17.31	30.70	13.66	46.70	14.06	29.49	14.19	1.80
	988		303.54	86.34	391.43	85.94	283.13	85.81	
⁴ S _{3/2} → ⁴ F _{9/2}	3125		0.66	0.04	1.56	0.04	0.79	0.04	0.39
	1666		82.29	5.28	144.34	3.93	80.54	4.31	
	1215		36.16	2.32	79.35	2.16	41.27	2.21	
	842		428.09	27.49	1024.96	27.94	520.20	27.82	
	545		1010.05	64.86	2418.35	65.92	1227.38	65.63	

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Figure 5. Polarized stimulated emission cross-section versus wavelength for $^4I_{13/2} \rightarrow ^4I_{15/2}$ transition of $\text{Er}^{3+}/\text{Yb}^{3+}$: LBLW crystal calculated by F-L formula.
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absorption bands which centered at 524 nm and 379 nm, namely $^4I_{15/2} \rightarrow ^2H_{11/2}$ and $^4I_{15/2} \rightarrow ^4G_{11/2}$, respectively (see Fig. 4), all the other ones were chose to fit the oscillator strength parameters for $E||X$, $E||Y$ and $E||Z$ polarizations. Because those two transitions belong to hypersensitive transition [41,42], they are sensitive to the variation of local structure around Er^{3+} ions. Here, only the spectrum of the Er^{3+} : LBLW crystal was calculated for brevity. Table 2 lists the values of the measured (S^{mea}) and calculated (S^{cal}) line strengths, the intensity parameters $\Omega^{X,Y,Z}$ for each polarization as well as the effective intensity parameters which are defined as $\Omega^{eff} = (\Omega^X + \Omega^Y + \Omega^Z)/3$. After obtaining the oscillator strength parameters $\Omega^{X,Y,Z}$ for each polarization, the spontaneous emission probabilities of the electric- and magnetic-dipole transitions (named $A_{JJ'}^{ed}$ and $A_{JJ'}^{md}$, respectively), fluorescence branching ratio

Figure 6. Polarized gain cross sections of $\text{Er}^{3+}/\text{Yb}^{3+}$: LBLW crystal versus wavelength.
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β and radiative lifetime τ_r of some typical transitions could be gained. The values of these spectroscopic parameters are all outlined in Table 3.

The Er^{3+} : LBLW crystal could not be efficiently excited by Xenon lamp because of the weak absorption at 976 nm. Moreover, considering the small phonon energy of the $(\text{WO}_4)^{2-}$ groups (roughly 900 cm^{-1}) [43], the multiphonon relaxation from the $^4I_{11/2}$ to $^4I_{13/2}$ multiplets of Er^{3+} ions was slow. Therefore, the emission band surrounding 1550 nm ($^4I_{13/2} \rightarrow ^4I_{15/2}$) for Er^{3+} : LBLW crystal is too weak to be distinguished. Thus, the fluorescence spectra of the $\text{Er}^{3+}/\text{Yb}^{3+}$: LBLW crystal were only recorded (see Fig. 5). The stimulated-emission cross-sections were calculated by the Fuchtbauer-Ladenburg (F-L) formula [44,45],

$$\sigma_{F-L}^q = \frac{A^q \lambda^5 I^q(\lambda)}{8\pi c n^2 \int \lambda I^q(\lambda) d\lambda} \quad (7)$$

where A^q is the spontaneous emission probability for q polarization, $I^q(\lambda)$ is the fluorescence intensity as a function of wavelength. The peak emission cross-sections are about 0.81×10^{-20} , 1.23×10^{-20} and $0.84 \times 10^{-20} \text{ cm}^2$ for $E||X$, $E||Y$ and $E||Z$ respectively, which are comparable to other co-doped crystals, such as $1.89 \times 10^{-20} \text{ cm}^2$ for $\text{Er}^{3+}/\text{Yb}^{3+}$: KY(WO₄)₂ [46], $0.71 \times 10^{-20} \text{ cm}^2$ for $\text{Er}^{3+}/\text{Yb}^{3+}$: LaPO₄ [47] and $0.95 \times 10^{-20} \text{ cm}^2$ for $\text{Ce}^{3+}/\text{Er}^{3+}$: NaLa(MoO₄)₂ [48].

The Er^{3+} laser via the $^4I_{13/2} \rightarrow ^4I_{15/2}$ transition operates in a quasi-three scheme, therefore the re-absorption losses should be considered. The useful laser wavelength could be evaluated by the so-called effective gain cross section [49].

$$\sigma_{gain}^q = \beta \sigma_{em}^q - (1 - \beta) \sigma_{abs}^q \quad (8)$$

here, σ_{em}^q is the emission cross-section, σ_{abs}^q is the absorption cross-section and β is the population inversion of Er^{3+} ions. Results of the wavelength dependences around 1550 nm for several β values ($\beta = 0.4, 0.5, 0.6, 0.7$) are shown in Fig. 6. It can be noted that the wavelengths under the low population inversion, for all polarizations, are all located approximately 1590 nm. Additionally, a laser oscillating at shorter wavelength can also be realized by increasing the values of β .

Figure 7. Up-conversion fluorescence spectrum of Er^{3+} : LBLW and $\text{Er}^{3+}/\text{Yb}^{3+}$: LBLW crystals excited 976 nm radiation at room temperature.
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Figure 8. Transition mechanisms and simplified energy levels of Er³⁺/Yb³⁺: LBLW crystal.
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Fig. 7 shows the up-conversion fluorescence spectra for Er³⁺: LBLW and Er³⁺/Yb³⁺: LBLW crystals in the range from 500 to 700 nm excited at 976 nm radiation of diode laser. Note that the fluorescence intensity of Er³⁺/Yb³⁺ co-doped LBLW crystal is much larger than that of Er³⁺-doped LBLW. This means there existed fast and efficient Yb³⁺→Er³⁺ energy transfer in Er³⁺/Yb³⁺: LBLW crystal. Fig. 8 displays the up-conversion mechanisms and simplified energy levels of Er³⁺ and Yb³⁺ ions in Er³⁺/Yb³⁺: LBLW crystal. Two different mechanisms, namely Er³⁺ excited state absorption (ESA) and a two-step Yb-Er energy transfer (ET), may exist in the up-conversion process [5,20,50].

For the Er³⁺/Yb³⁺ crystal, the green emissions of 530 and 553 nm (²H_{11/2}→⁴I_{15/2} and ⁴S_{3/2}→⁴I_{15/2}, respectively) can be explained by the following steps: Firstly, the Er³⁺ ions were excited from ground state to the excited state ⁴I_{11/2} by means of ground state absorption (GSA) and by ET process from ²F_{5/2} level of Yb³⁺ to Er³⁺. The ET process is dominant because of the large absorption cross-section around 980 nm of Yb³⁺ ions. Secondly, some Er³⁺ ions at the ⁴I_{11/2} level were promoted up to the higher ⁴F_{7/2} level by ET process from ²F_{5/2} level of Yb³⁺ or by ESA of Er³⁺ ions, then the ions at the ⁴F_{7/2} level relaxed non-radiatively to the lower levels ²H_{11/2} and ⁴S_{3/2} owing to the small energy gap between them. When the Er³⁺ ions at the ²H_{11/2} and ⁴S_{3/2} levels transitioned to the ground state, they produced 530 and 553 nm green emissions, respectively. The green emissions of the Er³⁺: LBLW crystal also experienced the above processes except the lack of ET process. Because the lifetime of the ⁴S_{3/2} level is much longer than that of the ²H_{11/2} level [51], more ions would non-radiatively decay to the ⁴S_{3/2} level. As a consequence, the intensity of 553 nm is stronger than 530 nm.

For the red emission of 661 nm (⁴F_{9/2}→⁴I_{15/2}), population on the ⁴F_{9/2} might be accumulated by two ways: ESA and ET process. Both ways excited Er³⁺ ions from ⁴I_{13/2} to ⁴F_{9/2}. Besides, the ions at the ⁴S_{3/2} level also relaxed rapidly to the ⁴F_{9/2} level. The red emission intensity is also significantly weaker than that of

Er³⁺/Yb³⁺ crystal because of lacking of ET process in the Er³⁺: LBLW crystal.

The dependence of integrated up-conversion fluorescence intensity on the excitation power at 976 nm for Er³⁺/Yb³⁺ crystal is shown in Fig. 9. According to the relation $I_{up} \propto I^n$ [52], where n is the number of photon involved in the up-conversion process and I is the excitation power. The slopes (for green and red light are all near 2) indicate that two photon processed populated the ²H_{11/2}, ⁴S_{3/2} and ⁴F_{9/2} levels. However, due to the competition between the linear decay and the depletion of the intermediate excited states, the values of n may be lower than 2 (see Fig. 9) [53].

Figure 9. The ln-ln plots of integrated emission intensities versus the excitation power for Er³⁺/Yb³⁺ crystal.
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Results and Discussion

The Er³⁺: LBLW and Er³⁺/Yb³⁺: LBLW have been successfully grown by the TSSG method from the flux of Li₂WO₄. The thermal expansion coefficients in the optical indicatrix axes were $\alpha_X = 11.17 \times 10^{-6} \text{ K}^{-1}$, $\alpha_Y = 8.07 \times 10^{-6} \text{ K}^{-1}$ and $\alpha_Z = 8.94 \times 10^{-6} \text{ K}^{-1}$ for the Er³⁺: LBLW crystal, and $\alpha_X = 11.18 \times 10^{-6} \text{ K}^{-1}$, $\alpha_Y = 8.01 \times 10^{-6} \text{ K}^{-1}$ and $\alpha_Z = 9.22 \times 10^{-6} \text{ K}^{-1}$ for the Er³⁺/Yb³⁺: LBLW crystal. The anisotropy of thermal expansion indicates that the LBLW crystals are easier to crack; thus, slow cooling rate should be adopted after the crystals were withdrawn from the melt. The Er³⁺/Yb³⁺: LBLW crystal has broad absorption bands near 980 nm (35 nm, 38 nm and 34 nm for $E||X$, $E||Y$ and $E||Z$, respectively), which make it very suitable for diode pumping. The effective J-O intensity parameters of the Er³⁺: LBLW were calculated to be $\Omega_2^{eff} = 11.94 \times 10^{-20} \text{ cm}^2$, $\Omega_4^{eff} = 1.60 \times 10^{-20} \text{ cm}^2$, $\Omega_6^{eff} = 0.78 \times 10^{-20} \text{ cm}^2$, respectively. Considering the re-absorp-

tion losses of the quasi-three scheme, the effective emission cross-section around 1550 nm was also calculated. Under the 976 nm excitation, the up-conversion emissions of three visible optical bands, corresponding to the $^2H_{11/2} \rightarrow ^4I_{15/2}$, $^4S_{3/2} \rightarrow ^4I_{15/2}$ and $^4F_{9/2} \rightarrow ^4I_{15/2}$, respectively, for Er³⁺/Yb³⁺: LBLW crystal were observed. The investigation of up-conversion spectra denotes that the energy transfer between Yb³⁺ and Er³⁺ is efficient. The spectroscopic analysis reveals that the Er³⁺/Yb³⁺: LBLW crystal has much better optical properties than the Er³⁺: LBLW crystal. Therefore, the Er³⁺/Yb³⁺: LBLW crystal may become a potential candidate for solid-state laser gain medium material.

Author Contributions

Conceived and designed the experiments: BX GW. Performed the experiments: BX ZL. Analyzed the data: BX GW. Contributed reagents/materials/analysis tools: YH LZ. Wrote the paper: BX GW.

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