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Photoluminescence and up-conversion of Er^{3+} in tetragonal $NaBi(XO_4)_2$, X=Mo or W, scheelites

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Abstract

Er doped $NaBi(XO_4)_2$, X=Mo or W, single crystals with tetragonal structure have been grown with optical quality by the Czochralski method. Er concentrations up to 1.4×10^{20} cm^{-3} and 1.3×10^{20} cm^{-3} have been attained in Mo and W compounds respectively. $^4S_{3/2}\rightarrow{}^4I_{15/2}$ emission of Er^{3+} has been achieved at room temperature by up-conversion exciting the $^4I_{11/2}$ or $^4I_{9/2}$ multiplets. This green emission is strongly polarised parallel to the crystallographic **c**-axis. The efficiency of the up-conversion process in tetragonal $NaBi(MoO_4)_2$ and $NaBi(WO_4)_2$ crystals are similar and also similar to that found in monoclinic $KGd(WO_4)_2$ crystal. The slope of the logarithmic dependence between up-converted and pump intensities suggests a two-photon excitation process. A schematic model of the up-conversion process is outlined.

Keywords: Luminescence; Optical properties; Disordered systems

1. Introduction

Double tungstate and molybdate single crystals are attractive materials as laser hosts because of their large rare-earth ion admittance. The crystallographic structure of these compounds is related to the scheelite structure of $CaWO_4$. The divalent Ca cation can be substituted by a combination of a monovalent alkaline metal and trivalent transition metal or rare-earth cations. The most popular double tungstate laser hosts, i.e. $KX'(WO_4)_2$, X′=Y, La or Gd, after solidification in a high temperature β-phase, undergo upon cooling a transition to a low temperature α-phase [1], which deteriorates the crystal quality. Therefore, these crystals must be grown using high temperature solvents which leads to low growth rates. Other scheelite-related materials do not undergo this polymorphism. In particular, $NaBi(MoO_4)_2$ (hereafter NBMo) and $NaBi(WO_4)_2$ (hereafter NBW) solidify congruently into a tetragonal phase with the $I\bar{4}$ (N°82) space group [2,3]. This allows the use of the Czochralski method for crystallisation achieving larger growth rates. Single crystals of the NaBi double tungstates have been already used as efficient solid state Raman shifters [4], however, most of the optical properties of these matrices are not well known. Particularly, up-conversion in Er doped materials provides an efficient conversion of infrared diode laser emissions into green laser light [5], but it has not been demonstrated in these lattices. In this work, we show that green up-conversion fluorescence is produced in Er doped $NaBi(XO_4)_2$, X=Mo and W, with an efficiency which compares well with that found in monoclinic $KGd(WO_4)_2$ [6].

2. Experimental techniques

Erbium doped NBMo and NBW single crystals have been grown by the Czochralski technique. Er^{3+} was incorporated into the melt as Er_2O_3. Details of the crystal growth of the matrix have been given previously [7]. Single crystals about 20 mm of diameter and 50 mm long were obtained at a typical growth rate of 2.5 mm/h. The concentration in the crystal was determined by ionic coupled plasma (ICP) spectrometry with an uncertainty of ±15%. The maximum Er concentration achieved with good optical quality was $[Er]=1.4\times10^{20}$ cm^{-3} and $[Er]=1.3\times10^{20}$ cm^{-3} for Mo and W compounds, respectively.

Up-conversion has been excited at room temperature using a cw Ti-sapphire laser. The emission wavelength of this laser was calibrated with a Burleigh wavemeter, model WA-2500, with an accuracy of ±0.1 nm. The up-conversion emission was dispersed by a Spex 340-E spectrometer ($f=34$ cm) and detected using a cooled Hamamatsu R928

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photomultiplier and a lock-in. Polarised optical absorption spectra were recorded with a Varian 5E spectrophotometer and Glan-Taylor polariser.

3. Experimental results

In a separate work we have studied the Er^{3+} energy level positions in NBW and NBMo crystals at the liquid–He temperature range [8]. From these measurements the relative energy of the levels with regards to the first Stark level of the ground $^4I_{15/2}$ multiplet have been established. Only minor differences between NBW and NBMo were observed, hereafter the optical absorption properties of the two crystals will be treated in a unified mode. Fig. 1 shows a schematic diagram showing the energy positions and widths of the Er^{3+} multiplets in NBMo and NBW.

Fig. 2a shows the room temperature ground state optical absorption (GSA) coefficient, α_{GSA}, of the $^4S_{3/2}$, $^4I_{9/2}$ and $^4I_{11/2}$ multiplets of Er^{3+} in NBW recorded with light polarised parallel to the crystallographic **c**-axis (π polarisation) and to the **a**-axis (σ polarisation). The intensity of the GSA at $\lambda = 552$ nm, a relevant emission wavelength for the purposes of this work, is somehow sensitive to the polarisation of the light. It is worth noting that the peak intensities of the GSA corresponding to $^4I_{9/2}$ and $^4I_{11/2}$ multiplet are similar. These two multiplets are used for excitation of the up conversion, therefore, a priory an efficient excitation may be expected either at $\approx$980 nm ($^4I_{11/2}$) or $\approx$800 nm ($^4I_{9/2}$). Table 1 gives the room temperature ground state absorption cross sections, $\sigma_{GSA} = \alpha_{GSA}/[Er]$, for some relevant wavelengths.

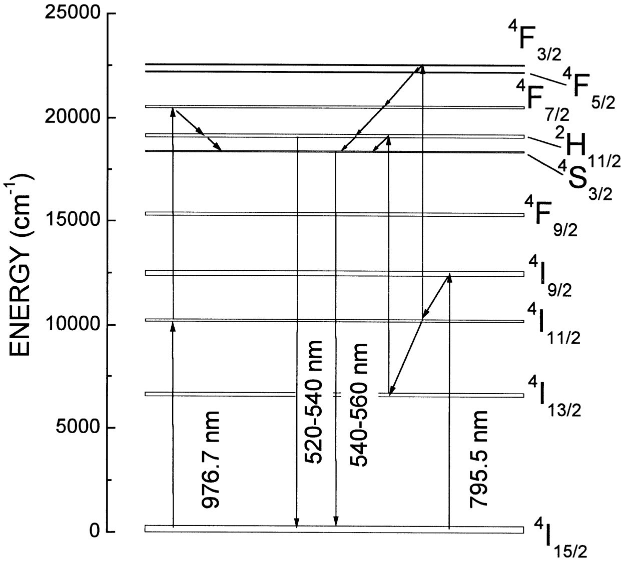

Fig. 1. Energy level diagram of the Er^{3+} multiplets involved in up-conversion processes in $NaBi(MoO_4)_2$ and $NaBi(WO_4)_2$ single crystals. Continuous arrows indicate pumping and radiative emission channels for up-conversion. Dashed arrows indicate non-radiative relaxation transitions.

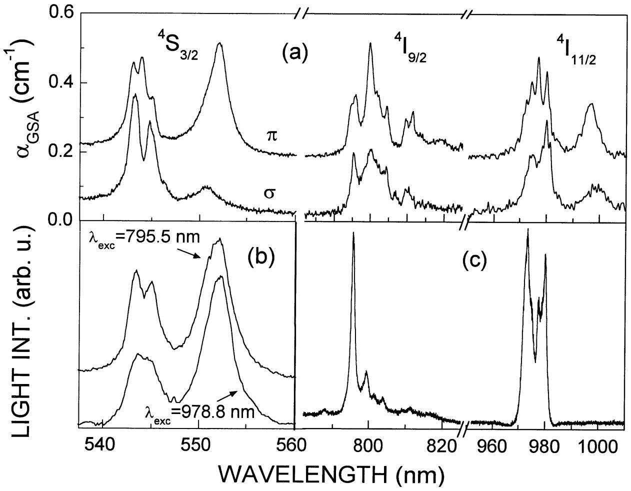

Fig. 2. 300 K optical measurements in $NaBi(WO_4)_2$:Er, $[Er] = 0.94 \times 10^{20}$ cm^{-3}. (a) Polarised ground state optical absorption corresponding to $^4I_{15/2} \rightarrow {}^4S_{3/2}$, $^4I_{9/2}$ and $^4I_{11/2}$ transitions. (b) π-polarised (parallel to the **c**-axis) up-conversion emission spectra. The spectra are excited parallel to the **c**-axis either at $^4I_{9/2}$ ($\lambda_{EXC} = 795.5$ nm) or $^4I_{11/2}$ ($\lambda_{EXC} = 978.8$ nm) multiplets of Er^{3+}. (c) π-polarised excitation spectra of the green up-conversion emission, $\lambda_{EMI} = 552$ nm. The emission is recorded non-polarised.

Fig. 2b and c show the up-conversion emission and its excitation spectrum respectively. The excitation is achieved either pumping into the $^4I_{11/2}$ ($\approx$970–980 nm) multiplet or in the $^4I_{9/2}$ ($\approx$795–805 nm) one. In both cases, the same complex emission is observed: two well separated emission bands in the 540–560 nm region corresponding to the $^4S_{3/2} \rightarrow {}^4I_{15/2}$ decay. These emissions are strongly π-polarised ($I_\pi / I_\sigma = 5$–6). In addition, others bands not shown were observed in the 520–540 nm region, which corresponds to the $^2H_{11/2} \rightarrow {}^4I_{15/2}$ Er^{3+} decay. For NBMo similar GSA, up-conversion emission and excitation spectra are observed, with the unique difference of a slight wavelength shift (see Table 1).

In order to enhance the fluorescence yield, we have increased the Er concentration. Our attempts to grow NBMo and NBW crystals with Er concentrations higher than 1.4×10^{20} cm^{-3} leaded to the appearance of crystal cracks. Fig. 3 shows a comparison of the $^4S_{3/2} \rightarrow {}^4I_{15/2}$ integrated emission intensity for both crystals as a function of the Er concentration, moreover the evolution of the up-conversion of Er^{3+} in $KGd(WO_4)_2$ is included for comparison. Up to the erbium incorporation limit only little differences between the efficiency of the three hosts considered may be observed.

Fig. 4 shows a log–log plot of the up-conversion intensity (I_{up}) as a function of the pumping light intensity (I_p). A linear regime is found according to the law, $I_{up} \propto I_p^s$. The slope found in Fig. 4 for the Er^{3+} emission in NBMo is $s = 2.0 \pm 0.07$.

Table 1
300 K ground state absorption, σ_{GSA}, and emission, σ_{EMI}, cross sections for relevant wavelengths of several Er^{3+} multiplets in NBW, NBMo, $KGd(WO_4)_2$ and $YLiF_4$ hosts[a]

	$NaBi(WO_4)_2$			$NaBi(MoO_4)_2$			$KGd(WO_4)_2$			$YLiF_4$		
	λ (nm)	π–σ_{GSA} (10^{-21} cm^2)	π–σ_{EMI} (10^{-20} cm^2)	λ (nm)	π–σ_{GSA} (10^{-21} cm^2)	π–σ_{EMI} (10^{-20} cm^2)	λ (nm)	σ_{GSA} (10^{-21} cm^2)	σ_{EMI} (10^{-20} cm^2)	λ (nm)	π–σ_{GSA} (10^{-21} cm^2)	π–σ_{EMI} (10^{-20} cm^2)
$^4S_{3/2}$	543.2	2.8	0.89	543.4	2.1	0.68	543.9	π–, 4.3	π–, 1.1			
	545.0	1.8	0.63	545.5	1.6	0.65						
	552.0	3.5	4.90	552.2	2.9	4.60	552.4	σ–, 2.7	σ–, 2.6	551	1.5	2.0
β			0.68–0.69					0.68			0.67	
$^4I_{9/2}$	795.5	1.9		796.0	1.4					792	1.0	
	800.0	3.4		801.0	2.6		801.5	π–, 3.3		810	0.5	
$^4I_{11/2}$	974.4	2.3		975.5	1.6					966	0.7	
	976.7	3.1		977.6	3.3					970	2.5	
	979.8	2.6		980.8	2.5		981.0	π–, 5.1				

[a] β is the branching ratio of the $^4S_{3/2}\rightarrow{}^4I_{15/2}$ transition.

4. Discussion

The maximum up-conversion efficiency in NBW (or NBMo) is found exciting at 795.5 nm (796 nm) for the $^4I_{9/2}$ multiplet and at 974.4 (975.5) or 979.8 (980.8) nm for the $^4I_{11/2}$ multiplet. Some intensity differences with light polarisation have been observed in the $^4I_{15/2}\leftrightarrow{}^4S_{3/2}$ GSA and emission. Fig. 2a shows that at $\lambda = 552$ nm, π-GSA is stronger than σ-GSA, the corresponding emission is also π-polarised. Rare earth impurities in NBMo and NBW substitute Bi^{3+}, therefore, a local symmetry S_4 is expected [2,3]. Er^{3+} has half-integer angular momentum J and for this symmetry point group the energy levels can be labelled with two non-equivalent irreducible representations, IR. All transitions are observed in σ configuration, while transitions from one IR to the other are additionally observed in π configuration. This is likely the reason of the higher GSA and emission cross sections in π spectra at $\lambda = 552$ nm. This conclusion stands either for NBMo or NBW crystals.

Fig. 2a and c provide a comparison between the GSA and up-conversion excitation spectra. It can be observed that although the excitation takes place inside the GSA band, the relative intensity of the peaks change from absorption to excitation. This is particularly clear for the $^4I_{9/2}$ multiplet. The two most common mechanisms giving rise to up-conversion are the excited state absorption (ESA) and the energy migration from excited ions. The comparison between GSA and up-conversion excitation suggests that for the used Er concentrations the dominant pumping mechanism is ESA, since minor differences between GSA and up-conversion excitation are expected when energy migration dominates. Moreover, for the upper limit erbium concentration, $[Er] \approx 1.4 \times 10^{20}$ cm^{-3}, the

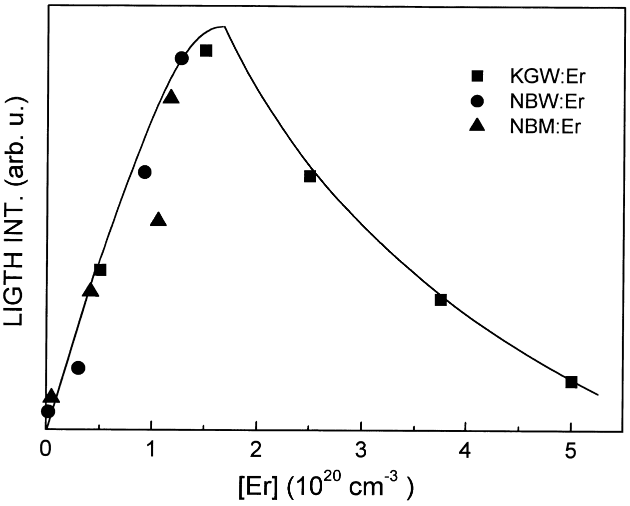

Fig. 3. Evolution of the integrated intensity of the up-conversion emission in $NaBi(WO_4)_2$ (●), $NaBi(MoO_4)_2$ (▲) and $KGd(WO_4)_2$ (■) vs. erbium concentration, [Er]. The continuous line is only a help to the eye. [Er] has been determined from ICP measurements in NBW and NBMo and from electron probe microanalysis measurements in $KGd(WO_4)_2$.

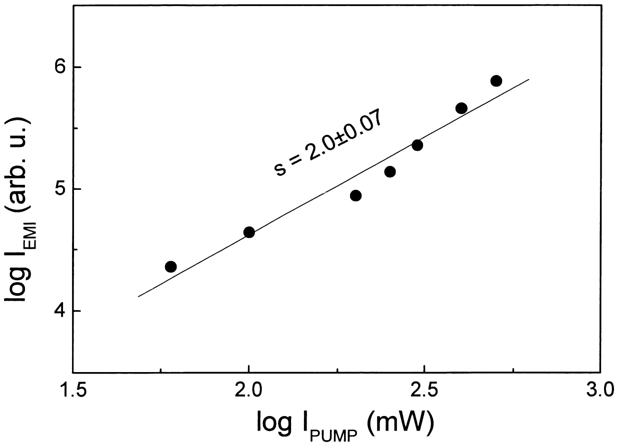

Fig. 4. Logarithmic plot of the 300 K integrated up-conversion emission intensity (I_{up}) versus the pumping intensity (I_p) exciting the $^4I_{9/2}$ multiplet of Er^{3+} in $NaBi(MoO_4)_2$. s is the slope of the fit.

average Er–Er distance, $r=(4\pi[\mathrm{Er}]/3)^{-1/3}\approx 1.2$ nm, is only at the distance onset for efficient energy migration.

Under these pumping conditions, the whole efficiency of up-conversion depends on the absorption of the ground and excited states as well as on the emission efficiency of the $^4S_{3/2}$ level. From the Judd–Ofelt theory the branching ratio for the $^4S_{3/2}\rightarrow{}^4I_{15/2}$ Er^{3+} transition in NBW and NBMo are obtained as $\beta=68$–69% [8]. Moreover, the emission cross section of this transition for a selected wavelength ($\lambda=c/\nu$), σ_{EMI}, can be obtained according to the reciprocity principle [9] as

$$\sigma_{\mathrm{EMI}}=\sigma_{\mathrm{GSA}}\frac{Z_l}{Z_u}\exp\left(\frac{E_{zl}-h\nu}{k_\beta T}\right),$$

where Z_l and Z_u are the partition functions of the lower and upper multiplets, respectively; and E_{zl} is the energy difference between the lowest Stark levels of the two multiplets considered. Using the energy level positions determined previously at 7 K [8] and the π-σ_{GSA} of the $^4S_{3/2}$ level given in Table 1, we have calculated the π emission cross sections, π-σ_{EMI}, of Er^{3+} for some relevant wavelengths. The obtained values are similar or even higher that those found in Er-doped $\mathrm{KGd(WO_4)_2}$ or $\mathrm{YLiF_4}$ laser hosts. The latter being considered a reference material for Er^{3+} up-conversion. Unfortunately, at present ESA of the $^4I_{9/2}$ and $^4I_{11/2}$ multiplets in $\mathrm{NaBi(XO_4)_2}$ crystals are not available for a more thorough comparison.

Another important difference of the present materials with other Er laser hosts is the relative GSA of the $^4I_{9/2}$ and $^4I_{11/2}$ multiplets. Usually the GSA of $^4I_{9/2}$ is less than a half of that observed for the $^4I_{11/2}$ multiplet. In our case, this ratio is about 1, therefore a very efficient up-conversion pumping at the $^4I_{9/2}$ multiplet could be expected.

The enhancement of the Er concentration is expected to improve the up-conversion efficiency due to the increase of the GSA and ESA, however, at some Er concentration energy migration from the radiative level imposes an upper limit to the expected improvement. Fig. 3 shows the expected up-conversion efficiency improvement with Er concentration for the NBW, NBMo and $\mathrm{KGd(WO_4)_2}$ hosts, up to reaching $[\mathrm{Er}]\approx 1.5\times 10^{20}$ cm^{-3}. Within the experimental uncertainty in the actual Er concentration in the samples used, the three crystal hosts considered behave in the same manner. In $\mathrm{KGd(WO_4)_2}$, the intensity of the up-conversion is limited at $[\mathrm{Er}]\approx 1.5$–2×10^{20} cm^{-3} by non-radiative energy transfer between Er ions, which produces a non-exponential behaviour of the radiative lifetime of the $^4S_{3/2}$ multiplet [6]. Erbium concentrations above this limit have not been achieved in NBW and NBMo. Slightly higher Er incorporations could be achieved in a future improving the growing conditions, however, in view of the comparison with $\mathrm{KGd(WO_4)_2}$ properties, likely this will not improve the up-conversion yield.

Due to the relatively large cut-off phonon frequency of double tungstate crystals (900–1000 cm^{-1}) in comparison to the reference $\mathrm{YLiF_4}$ host (440–460 cm^{-1}), we expect higher non-radiative losses in tungstates due to de-excitation from a given level to the low lying multiplets. Fig. 1 shows a schematic diagram of the expected excitation paths for double tungstate hosts. Most of the excitation to the $^4I_{9/2}$ multiplet is expected to be relaxed to the $^4I_{13/2}$ one, from which the $^2H_{11/2}$ multiplet is resonant to the pumping photon energy. A similar resonance from the $^4I_{13/2}$ multiplet can not be achieved exciting at 978.8 nm ($^4I_{11/2}$), therefore, a second photon absorption should promote electrons directly from the $^4I_{11/2}$ multiplet to the $^4F_{7/2}$ one. In both cases two photon processes should occur. For low depletion of the population of metastable multiplets, the s exponent of the $I_{\mathrm{up}}\propto I_{\mathrm{p}}^{s}$ law is expected to be equal to the number of photons involved in the excitation [10]. Fig. 4 shows that this condition is fulfilled for the NBMo sample analysed.

5. Conclusions

Er doped $\mathrm{NaBi(WO_4)_2}$ and $\mathrm{NaBi(MoO_4)_2}$ single crystals can be grown with optical quality by the Czochralski method. The maximum efficiency of green ($\lambda\approx 552$ nm) up-conversion has been achieved at 300 K using Er^{3+} concentrations $\approx 1.4\times 10^{20}$ cm^{-3}. At this wavelength, the emission is strongly polarised parallel to the **c**-axis (π-polarisation).

Only small differences are found between the NBMo and NBW hosts. Moreover, the $^4S_{3/2}\rightarrow{}^4I_{15/2}$ Er^{3+} emission cross sections and branching ratios in these double tungstates are similar or higher than those found in the reference $\mathrm{YLiF_4}$ host, however, larger thermal non-radiative losses are expected in tungstates.

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