Optical Materials 78 (2018) 495–501

Contents lists available at ScienceDirect

Optical Materials

journal homepage: www.elsevier.com/locate/optmat

Spectroscopy of Tb^{3+} ions in monoclinic $KLu(WO_4)_2$ crystal application of an intermediate configuration interaction theory

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ARTICLE INFO

Article history:
Received 5 February 2018
Received in revised form
27 February 2018
Accepted 7 March 2018

Keywords:
Double tungstates
Terbium ions
Absorption
Luminescence
Judd-Ofelt theory
Stimulated emission

ABSTRACT

The spectroscopic properties of Tb^{3+} ions in monoclinic $KLu(WO_4)_2$ double tungstate crystal are studied with polarized light. The absorption spectra in the visible, near- and mid-IR including the transitions to all lower-lying ^7F_J ($J = 0 \ldots 5$) excited states are measured. The maximum absorption cross-section for the $^7F_6 \rightarrow {}^5D_4$ transition is 3.42×10^{-21} cm^2 at 486.7 nm for light polarization $\boldsymbol{E} \parallel N_m$. The transition probabilities for Tb^{3+} ions are calculated within the Judd-Ofelt theory modified for the case of an intermediate configuration interaction (ICI). The radiative lifetime of the $^5D_4$ state is 450 μs and the luminescence quantum yield is >90%. The polarized stimulated-emission cross-section spectra for all $^5D_4 \rightarrow {}^7F_J$ ($J = 0 \ldots 6$) emission channels are evaluated. The maximum σ_{SE} is 11.4×10^{-21} cm^2 at 549.4 nm (for $\boldsymbol{E} \parallel N_m$). Tb^{3+}:$KLu(WO_4)_2$ features high transition cross-sections for polarized light being promising for color-tunable visible lasers and imaging.

1. Introduction

Among the trivalent rare-earth ions (RE^{3+}), Sm^{3+}, Eu^{3+}, Tb^{3+} and Dy^{3+} are rather attractive for obtaining multi-color laser emission in the visible [1]. In particular, the Tb^{3+} ions (electronic configuration: [Xe]$4f^8$) are featuring a higher-lying (energy: ~20500 cm^{-1}) metastable excited state ($^5D_4$) and a set of lower-lying ^7F_J states ($J = 6 \ldots 0$ in order of increasing energy) [2]. This leads to multiple visible emissions due to the $^5D_4 \rightarrow {}^7F_J$ transitions that fall into the blue, green, yellow and red spectral ranges [3]. The $^5D_4$ state is long-living (from hundreds of μs to few ms) [3] and the corresponding luminescence quantum yield can be high due to the weak non-radiative (NR) processes even in oxide matrices with high phonon energies. The $^5D_4 \rightarrow {}^7F_5$ transition at ~545 nm is the most probable one and a purely green emission from Tb^{3+} has been observed [4]. The rich structure of higher-lying excited-states of Tb^{3+} allows for efficient UV excitation of these ions.

Aside from the interest to Tb lasers, there are multiple studies of Tb^{3+}-based green phosphors based on various matrices, i.e., glasses, glass-ceramics and nanoparticles [5–10]. This extended the understanding of Tb^{3+} spectroscopy. In recent years, the main interest shifted towards (Eu^{3+}, Tb^{3+}) and (Yb^{3+}, Tb^{3+}) codoped materials. The former codoping scheme brings the advantage of continuous color tuning (from red for singly Eu^{3+} doping to green for the Tb^{3+} one) [11,12]. The second codoped system is promising for down-conversion (DC) suitable to enhance the efficiency of silicon solar cells [13,14]. Such DC materials provide emission of up to 2 near-IR (~1 μm) photons from Yb^{3+} ions after the absorption of a single UV photon by a Tb^{3+} ion [13].

There are several early reports about the stimulated-emission from a Tb^{3+}-doped glass [15], an organic solution [16] and a Tb:$LiYF_4$ crystal [17] under broadband flashlamp-pumping, and from a Tb^{3+}-doped fiber laser [18]. Recently, efficient room-temperature (RT) Tb lasers were demonstrated using various fluoride crystals, namely $LiYF_4$, $LiLuF_4$, KY_3F_{10}, BaY_2F_8, CaF_2, LaF_3 and TbF_3 [3,19]. Lasing at ~545 nm (in the green, $^5D_4 \rightarrow {}^7F_5$ transition) and at ~585 nm (in the yellow, $^5D_4 \rightarrow {}^7F_4$ transition) were achieved. In the study of Metz et al., a highly-doped (28 at.%)

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https://doi.org/10.1016/j.optmat.2018.03.014
0925-3467/

Tb:LiLuF$_4$ laser pumped by a frequency-doubled optically pumped semiconductor laser (2ω-OPSL) at 486 nm (to the $^5D_4$ state) generated a maximum green output power of 1.13 W with a slope efficiency of 52% with respect to the absorbed pump power. In Ref. [19], wavelength tuning of Tb:CaF$_2$ and Tb:LiLuF$_4$ lasers between ~540 and 550 nm was also demonstrated.

The physical reason for application of fluoride crystals in Tb lasers is the following. Among the RE^{3+} ions, Tb^{3+} has one of the lowest energy separations between the multiplets of the 4f^8 configuration and the 4f^{8}5 d^1 excited one [20]. The 4f^8 → 4f^{8}5 d^1 transitions (e.g., the excited-state absorption (ESA)) are parity-allowed and thus more intense than the 4f^8 → 4f^8 transitions. Such interconfigurational ESA can strongly affect the laser performance [1,3]. For fluoride crystals, the so-called crystal field depression (CFD, which determines the splitting of the 4f^{8}5 d^1 levels and depends strongly on the host material) is small [20]. Thus, the unwanted interactions with the excited configuration are diminished. However, as it was shown by Metz et al., different host materials even with high CFD (e.g., oxide crystals) can be potentially suitable for Tb lasers.

Among the oxide crystals, the monoclinic double tungstates (MDTs) having a chemical formula of KRE(WO$_4$)$_2$ (shortly KREW) where RE stands for Y, Gd, Lu or Yb, are very attractive for RE^{3+} doping [21]. The two main features of MDTs are the high transition cross-sections for polarized light and high available RE^{3+} doping levels accompanied by weak luminescence quenching. Besides the ions suitable for near-IR lasers (at ~1 μm and at ~2 μm) [21], MDTs are recognized to be promising for visible lasers [22,23]. Dashkevich et al. presented a RT Eu:KGdW laser operating at 702 nm [23]. Stimulated-emission of Dy^{3+} ions in KYW (at 574 nm and 664 nm) was observed by Kaminskii et al. [24] at low temperature. Concerning Tb^{3+}-doped MDTs, very scarce data can be found in the literature. The previous work on Tb:KLuW focused only on the crystal growth and thermal properties [25]. In Refs. [26–28], the luminescence of Tb^{3+} ions in isostructural KYW and KYbW crystals was studied. In particular, Loiko et al. reported on the polarized spectroscopy of Tb^{3+} ions in KYbW [28]. However, this is a stoichiometric crystal and it is less attractive for laser applications due to the possible Yb^{3+} ↔ Tb^{3+} energy-transfer processes.

The aim of the present work is to study the optical absorption and emission of Tb^{3+} ions in the monoclinic KLuW crystal with polarized light and to calculate the Tb^{3+} transition probabilities using the modified Judd-Ofelt theory.

2. Crystal growth

The KLuW crystal doped with 3 at.% Tb^{3+} ($N_{Tb} = 1.93 \times 10^{-20}$ cm^{-3}, crystal density, $\rho = 7.613$ g/cm^3) was grown by the Top Seeded Solution Growth (TSSG) Slow-Cooling method using potassium ditungstate, $K_2W_2O_7$, as a solvent, see more details in Ref. [21]. The starting materials, K_2CO_3, Lu_2O_3, Tb_2O_3 and WO_3, were from Aldrich and Fluka (>99.9% purity). A seed from an undoped KYW crystal was used for starting the nucleation and was oriented along the [010] crystallographic axis. The structure of the grown crystal was confirmed with X-ray powder diffraction. Tb:KLuW is monoclinic (space group C^6_{2h} – $C2/c$, No. 15, point group: 2/m). The as-grown crystal was transparent, it was free of cracks and inclusions. The crystal had a slight yellow-brown coloration due to the Tb^{3+} ions.

3. Experimental

The MDT crystals, including Tb:KLuW, are optically biaxial and have three principal refractive indices, $n_p < n_m < n_g$ [21]. The spectroscopic properties are then characterized in the frame of the optical indicatrix, with the three orthogonal axes, denoted as N_p, N_m and N_g, respectively. For all monoclinic crystals, one of the optical indicatrix axes (it is N_p for MDTs) is parallel to the C_2 symmetry axis (or ***b*** crystallographic one). The two remaining optical indicatrix axes are located in the orthogonal mirror plane (the ***a*-*c*** plane). For KLuW, the angles $N_m \hat{} a = 59.3°$ and $N_g \hat{} c = 18.5°$ [21].

For the spectroscopic studies, we cut and polished a parallelepiped sample from the 3 at.% Tb:KLuW crystal with thicknesses t of 4.25 mm and 5.00 mm along the N_g- and N_p-axes, respectively, and thus giving access to all three principal polarizations.

The RT (293 K) absorption spectrum in the visible (0.36–0.51 μm) was measured with a Varian CARY-5000 spectrophotometer (Agilent). The spectral bandwidth (SBW) was 0.01 nm. The absorption cross-section was calculated from the absorption coefficient, $\sigma_{abs} = \alpha/N_{Tb}$. The RT absorption spectrum in the near-IR (1800-6200 cm^{-1}) was measured using a FTIR spectrometer Bruker Tensor 27 with a spectral resolution of 1 cm^{-1}. The spectra were measured for polarized light using a Glan-Taylor polarizer.

The polarized RT emission spectra of Tb:KLuW were measured with a Renishaw inVia confocal micro-Raman microscope with a ×50 objective and an 1800 l/mm grating. The excitation wavelength λ_{exc} was 458 nm or 488 nm. The spectra were combined to cover the 0.48–0.7 μm spectral range. The spectral resolution was ~1 cm^{-1}.

For the RT luminescence decay studies, a Cary Eclipse fluorescence spectrometer (Agilent) was used. The excitation wavelength λ_{exc} was 365, 380 or 475 nm. The decay from the $^5D_4$ state was monitored at 545 nm. The decay time τ_{lum} was determined according to a single-exponential law, $I_{lum}(t) = I_0 \exp(-t/\tau_{lum})$.

4. Results and discussion

4.1. Absorption

The absorption spectra of Tb^{3+} ions in KLuW are shown in Fig. 1

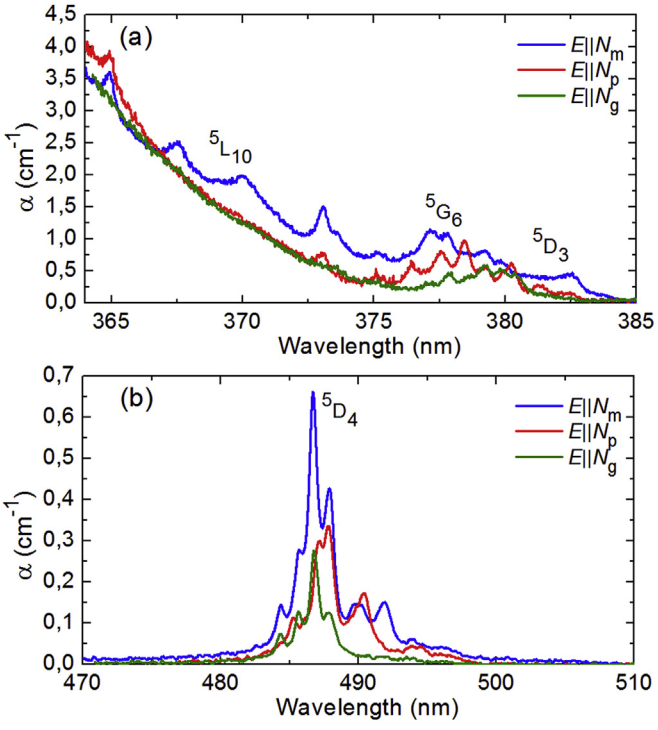

Fig. 1. Visible absorption spectra of a 3 at.% Tb:KLuW crystal with polarized light at RT: Transitions $^7F_6 \rightarrow {}^5D_3$, $^5G_6$, $^5L_{10}$ (a) and $^7F_6 \rightarrow {}^5D_4$ (b).