Journal of Luminescence 144 (2013) 217–222

Contents lists available at SciVerse ScienceDirect

Journal of Luminescence

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

Investigation of visible emission induced by infrared femtosecond pulses in erbium-doped YVO_4 and $LuVO_4$ single crystals

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ARTICLE INFO

Article history:
Received 20 February 2013
Received in revised form
9 May 2013
Accepted 9 July 2013
Available online 16 July 2013

Keywords:
Vanadate crystals
Up-conversion phenomena
Femtosecond pulses excitation

ABSTRACT

Illumination of single crystal samples of erbium-doped YVO_4 and $LuVO_4$ by infrared femtosecond pulses brings about an intense green luminescence assigned to the $^4S_{3/2}$ - $^4I_{15/2}$ transition of Er^{3+} ions. When lowering the sample temperature an additional broad band in the blue related to the VO_4^{3-} emission appears and next grows steadily. It has been observed that the variation of wavelength of incident infrared femtosecond pulses in the region 800 nm–1600 nm affects weakly the intensity of both the blue and green luminescence bands. Analysis of luminescence dynamics made it possible to reveal that upon infrared excitation the rise time of the $^4S_{3/2}$ luminescence is longer by a factor of four, roughly as compared to that recorded upon direct excitation into high energy levels of Er^{3+}. Observed temperature dependence of up-converted blue and green luminescence implies that the energy transfer from vanadate groups cannot be considered as a main mechanism involved in the excitation erbium ions. It has been supposed that erbium ions are likely to be excited by energy transfer from free electrons created in the conduction band of the host by multiphoton excitation and /or by non-resonant multi-step ETU process involving absorption of infrared light in multiphonon side bands of electronic transitions. Creation of free electrons has been corroborated by changes of electrical conductivity of crystals induced by an illumination with infrared femtosecond pulses.

1. Introduction

Knowledge on phenomena related to propagation of powerful ultrashort light pulses in transparent media has increased markedly during last two decades as a consequence of accumulation of experimental data. Among early works devoted to this topic a significant comprehensive investigation reported by Brodeur and Chin [1] has provided a comparison of experimental data acquired for various liquid and solid state media and an assessment of importance of particular mechanisms involved. To account for observed phenomena, in particular for a transformation of incident light pulses into a “white light continuum” or “supercontinuum” a number of mechanisms, in particular self-phase modulation (SPM), group-velocity dispersion (GVD) and self-focusing have been considered. Relevance of creation of free electrons by multiphoton excitation (MPE) to the limitation of self focusing has been revealed. With this contribution the interplay between various mechanisms involved in the supercontinuum generation is generally understood. Subsequent investigation have shown that phenomenological laws established based on several model materials, especially the effect of bandgap of a medium on the spectral broadening, are not generally valid [2]. The fascinating phenomenon of spectral and energetical transformation of ultrashort light pulses in dielectric media is not precisely a topic of the present work. The information summarized above is relevant to understanding of the excitation mechanisms of localized levels of rare earth in crystals, however.

Knowledge on phenomena and mechanisms of excitation of up-converted visible luminescence from rare earth impurities in transparent media by infrared femtosecond pulses is poor. Up-converted visible emission in praseodymium-doped Y_2SiO_5 crystal has been observed upon femtosecond pulse excitation in infrared at 800 nm and attributed to three-photon absorption [3]. Up-converted visible emission in samarium-doped $ZnO–B_2O_3–SiO_2$ glass has been observed upon femtosecond pulse excitation in infrared at 800 nm and attributed to two-photon absorption process [4]. Up-converted luminescence of a pure YVO_4 single crystal has been excited by femtosecond pulses at 800 nm and attributed to simultaneous absorption of three photons [5]. In virtually all investigations reported thus far the phenomena of up-conversion were observed upon excitation at a wavelength of incident pulses fixed to 800 nm as provided by a titanium–sapphire laser and attributed to a resonant process consisting of simultaneous absorption of several photons.

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0022-2313/$ - see front matter © 2013 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.jlumin.2013.07.004

In the present work the up-conversion phenomena in erbium-doped YVO_4 and $LuVO_4$ single crystals are investigated as a function of wavelength of incident femtosecond pulses varied in the 800–1600 nm region. The choice of materials for the study follows from well documented knowledge on their structural features and fundamental optical properties. In fact, extensive spectroscopic study of undoped YVO_4 and YVO_4:Eu^{3+} systems performed in the past by Hsu and Powell [6] has revealed the nature of the host luminescence and peculiarities of the host-activator energy transfer. Capobianco et al. [7] reported the basic spectroscopic properties of Er^{3+} in YVO_4 crystals, such as transition intensities, radiative transition rates and energy level structure. Relaxation of excited states of rare earth ions including Er^{3+} has been studied by Gołąb et al. [8]. Spectroscopic features of a $LuVO_4$:Er^{3+} system have been reported recently by Lisiecki et al. [9]. The choice was affected also by an excellent structural and optical quality of vanadate crystals fabricated during our previous investigation devoted to laser performance of YVO_4:Er^{3+} system [10].

The intention of the study is to get a more close insight into processes and mechanisms of interaction of ultrashort light pulses with rare earth-doped inorganic crystals. It will be shown in the following that phenomena induced by an ultrashort excitation differ markedly from those observed when exciting with nanosecond or longer lasting light pulses.

2. Experimental

Single crystals of undoped YVO_4 and $LuVO_4$ as well as YVO_4: 0.5at% Er^{3+} and $LuVO_4$:1at% Er^{3+} were grown by the Czochralski technique. From as-grown crystal boules samples in the form of polished parallelepipeds with dimensions $5\times6\times8\ mm^3$ were fabricated.

Experiments were accomplished using an excitation source consisting of a femtosecond laser (Coherent Model "Libra") coupled to optical parametric amplifier (Light Conversion Model "OPerA"). The system delivers 100 fs pulses at repetition rate regulated up to 1 kHz at wavelength tuned between 230–2800 nm. The pulse energy is comprised between 6 and 150 μJ, depending on the spectral region. Excitation light was focused on single crystal samples using a lens having a focal length of 30 cm.

Location of the focus with respect to the sample surface was changed by moving the lens farther or closer to the sample. Luminescence emerging from the sample was observed in the direction perpendicular to the excitation beam. Appropriate long- and short-pass filters have been used to eliminate unwanted radiation. To record preliminary survey luminescence spectra a micro spectrometer (Hamamatsu Multichannel Analyzer PMA–12) was employed. High resolution luminescence spectra and luminescence decay curves were recorded with a grating spectrograph (Princeton Instr. Model Acton 2500i) coupled to a streak camera (Hamamatsu Model C5680) operating in the 200–1100 nm spectral region with a temporal resolution of 20 ps. To perform measurements at low temperature, the samples were installed in a continuous flow liquid helium cryostat equipped with a temperature controller.

3. Results and discussion

It was observed that incident femtosecond pulses at any wavelength in the infrared region between 800 nm and 1600 nm bring about an intense green luminescence in YVO_4:Er and $LuVO_4$: Er samples and considerably weaker blue luminescence in undoped YVO_4 and $LuVO_4$ samples. It has been ascertained also that spectral features of luminescence in both Er-doped and undoped samples are not influenced by a photon energy of exciting infrared femtosecond pulses. As an example, Fig. 1 compares survey luminescence spectra recorded at room temperature for YVO_4:Er sample upon excitation at 1200 nm, 1320 nm and 1520 nm. Essentially the same spectra were acquired for a $LuVO_4$: Er sample. The spectra consist of a green band in the vicinity of 550 nm, related to transitions from the $^2H_{11/2}$, $^4S_{3/2}$ group of levels to the ground $^4I_{15/2}$ state and a band in near infrared around 850 nm related to the $^4S_{3/2}\rightarrow{}^4I_{13/2}$ transition of Er^{3+}. It should be noticed here that solely the excitation at 1520 nm matches the absorption transition of Er^{3+} ions, in this particular case the $^4I_{15/2}\rightarrow{}^4I_{13/2}$ transition. In principle, several different mechanisms may be involved in the process of conversion of incident infrared radiation to visible emission (up-conversion) of rare earth ions in crystals. Stepwise mechanism consisting of sequential excitation of intermediate states by excited state absorption (ESA) and/or by nonradiative energy transfer up-conversion (ETU) is the most commonly known and well documented in numerous reports because it occurs at relatively low excitation powers, e.g. [11,12]. The stepwise mechanism and its implications to experimentally observed phenomena have been considered thoroughly in the paper by Pollnau and Gudel [13]. When the power of incident radiation becomes high enough a multiphoton excitation mechanism (MPE) consisting of simultaneous absorption of several photons that are needed to raise electrons from the ground state to a given excited state of a rare earth ion may happen [14]. To be effective the mechanisms mentioned above must fulfill condition of resonance in that the energy of incident photons (or of their sum for the MPE mechanism) should match energy difference between states involved. Two additional mechanisms should be considered when extremely powerful femtosecond light pulses propagate in rare earth-doped crystals, namely excitation by photons from generated broad-band supercontinuum (if present) and/or indirect process consisting of transition of electrons from the valence band to the conduction band of the host crystal induced by multiphoton excitation followed by an energy transfer from the host to rare earth impurities. To determine the pertinence of the former mechanism the energy density of femtosecond pulses in samples was varied by changing the position of the sample with respect to the focus point of incident excitation light in order to achieve a stable supercontinuum generation. It was found that well above the threshold the spectrum of the supercontinuum did not depend of the pump wavelength in the 800–1600 nm region. Its anti-Stokes parts recorded for YVO_4 and $LuVO_4$ crystals pumped at 1300 nm and 1500 nm are compared in Fig. 2.

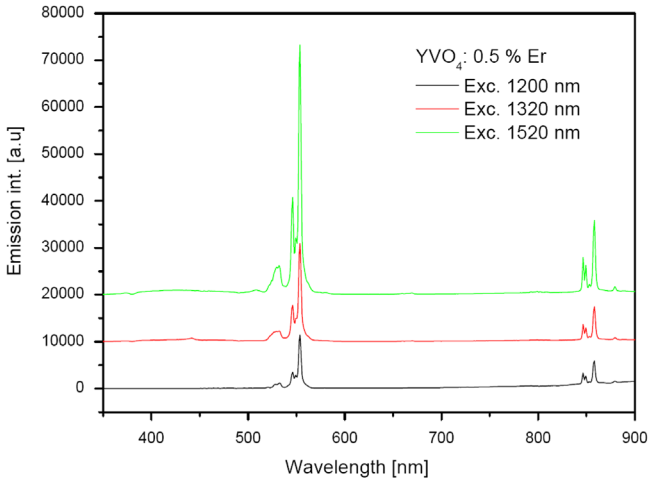

Fig. 1. Survey room temperature emission spectra of YVO_4:0.5%Er^{3+} single crystal recorded upon infrared femtosecond pulse excitation. Excitation wavelengths are indicated in the figure.