Optical Materials 34 (2012) 579–590

Contents lists available at ScienceDirect

Optical Materials

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

Anti-Stokes laser-induced cooling in rare-earth doped low phonon materials

J. Fernández [a,b,*], A.J. García-Adeva [a], R. Balda [a,b]

[a] Departamento Física Aplicada I, Escuela Técnica Superior de Ingeniería, Alda. Urquijo s/n, 48013 Bilbao, Spain
[b] Centro de Física de Materiales CSIC-UPV/EHU and Donostia International Physics Center, Apartado 1072, 20080 San Sebastián, Spain

ARTICLE INFO

Article history:
Received 11 February 2011
Accepted 26 May 2011
Available online 2 July 2011

Keywords:
Laser cooling
Rare-earths
Optical properties
Ytterbium
Erbium

ABSTRACT

In this work we discuss the anti-Stokes laser-induced cooling of two matrices doped with Yb^{3+} and Er^{3+}: a low phonon KPb_2Cl_5 crystal and a fluorochloride glass. In order to assess the presence of internal cooling in these systems we used photothermal deflection and conventional excitation spectroscopic techniques, whereas the bulk cooling in the Er^{3+}-doped materials was detected by means of a calibrated thermal sensitive camera. Furthermore, we also consider some of our findings on cooling processes occurring in Yb^{3+}-doped low phonon materials from a theoretical perspective. The experimental results are in good agreement with the predictions of a model based on the presence of a second order process in the cooling mechanism. The fluorescence excess shown by the excitation spectra of Yb^{3+}-doped sample obtained at high fluences, by pumping at wavelengths in the cooling region, has been explained in the framework of the configurational coordinate model by considering that the frequencies of the vibrational modes in the ground and excited states change at high pumping intensities (quadratic coupling mode). In the case of Er^{3+} ion, it is worthwhile to mention that the cooling was observed in the spectral region where some upconversion processes that initiate at the pumped $^4I_{9/2}$ level occur. Together with the spectroscopic characterization, a short discussion on the experimental and theoretical background of the cooling process including the possible influence of upconversion processes is presented.

1. Introduction

In 1929 Pringsheim [1] proposed the possibility of cooling matter by anti-Stokes fluorescence. Twenty years later, Kastler [2] suggested that rare-earth-doped crystals may provide a way to obtain solid state cooling by anti-Stokes emission (CASE). The first experimental attempt to demonstrate radiation cooling was performed by Kushida and Geusic in a Nd:YAG crystal [3] but only reduced heating rates were achieved. However, it was not until 1995 that the first solid-state CASE was demonstrated in an Yb^{3+} doped fluorozirconate glass by Epstein et al. [4]. From then on, several works have been published regarding topics as the composition requirements of the matrices to achieve cooling [5–7] or the temperature drop attainable in fiber configuration [8–10]. Throughout the last years laser cooling has been observed in ytterbium-doped $KGd(WO_4)_4$ [11], YAG [12], KPb_2Cl_5 [13], BaY_2F_8 [14], and YLF [15] crystals. Moreover, cooling has also been reported in liquids [16] and semiconductors [17].

Among the potential applications of anti-Stokes laser cooling of solids, two main fields seem to attract the interest in this effect: cryocoolers for aerospatial applications and high power solid state lasers in which no excess heat is generated. Regarding the later, Bowman [18] proposed to use radiation cooling by anti-Stokes fluorescence within the laser medium to balance the heat generated by the Stokes shifted stimulated emission (radiation balanced lasers). This could arise in very high power lasers in which limitations in beam quality and average power could be overcome. The studies carried-out by Bowman and Mungan to evaluate ytterbium doped laser materials for their utility in radiation balanced laser systems [19,11] predict that Yb^{3+} doped $KY(WO_4)_2$ and $KGd(WO_4)_2$ crystals will show the highest performance for this kind of applications. In these studies, fluorescence optical cooling in $KGd(WO_4)_2$ crystal was reported for the first time, opening up a very encouraging outlook for radiation balanced lasers.

In spite of the efforts to improve this process and to develop novel materials doped with rare-earth ions amenable to cooling, only a reduced number of Yb^{3+}-doped glasses and crystal matrices were able to produce CASE and, among other rare-earth ions, only a Tm^{3+}-doped heavy-metal fluoride glass was reported to be an efficient cooler [20,21]. Two of the requirements of the host material to obtain solid state cooling by anti-Stokes emission are to possess negligible nonradiative processes and to have near unity quantum efficiency of the anti-Stokes emission from the RE levels involved in the cooling process. This explains why most efforts have focused on obtaining laser cooling in ytterbium doped solids. The presence of only two levels ($^2F_{7/2}$ and $^2F_{5/2}$) separated by about 10,000 cm^{-1}

* Corresponding author at: Departamento Física Aplicada I, Escuela Técnica Superior de Ingeniería, Alda. Urquijo s/n, 48013 Bilbao, Spain.

E-mail address: wupferoj@bi.ehu.es (J. Fernández).

0925-3467/$ - see front matter © 2011 Elsevier B.V. All rights reserved.
doi:10.1016/j.optmat.2011.05.037

avoids some problems, such as excited-state absorption and cross-relaxation that are detrimental to the cooling process.

The investigation of new hosts for rare earth ions with low phonon energies appears to be a promising way to find efficient cooling materials, especially for dopant ions with low-energy band-gaps between active levels. The advantage of sulfide- and chloride- based hosts over the most extensively studied fluoride compounds is their lower phonon energy that leads to a significant reduction of the multiphonon relaxation rates. This allows an increased lifetime of some excited levels that can relax radiatively. However, these materials usually present poor mechanical properties, moisture sensitivity, and are difficult to synthesize. Potassium lead chloride, KPb_2Cl_5, has been studied as a promising host for RE ions [22] because it is non-hygroscopic and readily incorporates rare-earth ions. According to Raman-scattering measurements [23] the maximum phonon energy of optical phonons for this crystal is 203 cm^{-1}. On the other hand, divalent fluorochloride glasses – resistant to moisture – with lower phonon energies (370 cm^{-1}) than fluoride glasses open new possibilities to develop materials capable of producing cooling by anti-Stokes emission. Indeed, laser-induced internal cooling has been demonstrated in the past in these matrices doped with Yb^{3+} ions by the present authors [13,24].

In the first part of this manuscript, we present a theoretical interpretation of some recent findings related to cooling processes in Yb^{3+}-doped low phonon materials. In the second part, we discuss the demonstration of anti-Stokes laser-induced cooling in two matrices doped with Er^{3+}: a low phonon KPb_2Cl_5 crystal and a fluorochloride glass recently achieved by our group [25]. The analysis of the results in the Er^{3+}-doped matrices shows that some contribution to the observed cooling could arise from upconversion processes. We present a preliminary theoretical approach that could explain the influence of the observed upconversion processes on the anti-Stokes cooling, a possibility scarcely pointed out in the literature [17,21].

2. Yb^{3+}-doped materials

2.1. Experimental

Single crystals of non-hygroscopic Yb^{3+} doped KPb_2Cl_5 crystal were grown in our laboratory by the Bridgman technique in a chloride atmosphere with a two-zone transparent furnace, a temperature gradient of 18 °C/cm and a 1 mm per hour growth rate. Quartz ampoules with a pointed end were used to serve as seed selectors and to promote single crystal growth. The Yb^{3+} content was about 5×10^{19} ions/cm^3. The sample of CNBZn fluorochloride glass (CdF_2–$CdCl_2$–NaF–BaF_2–$BaCl_2$–ZnF_2) doped with 1 mol% of YbF_3 was prepared at the Laboratoire de Verres et Ceramiques of the University of Rennes (France). Fig. 1 shows a block diagram of the experimental set-up used in the photothermal deflection, absorption, and excitation measurements. The beam of a tunable (λ = 905–1090 nm) cw titanium-sapphire ring laser (8 GHz bandwidth) was modulated at 1.24 Hz by means of a mechanical chopper. A fraction of the incident power was used for signal normalization. A copropagating helium–neon probe laser beam (λ = 632.8 nm) was co-aligned with the pump beam through a dichroic element. Both pump and probe copropagating beams were focused into the middle of the sample with diameters of ~100 μm and ~60 μm respectively. After leaving the sample, the beams passed through a second identical lens separated from the first one by a distance twice the focal length (5 cm) to avoid high divergence of the emerging beams. A second dichroic beam splitter deviated the pumping beam to a pyroelectric detector which measured the transmitted pumping power. Before reaching a quadrant

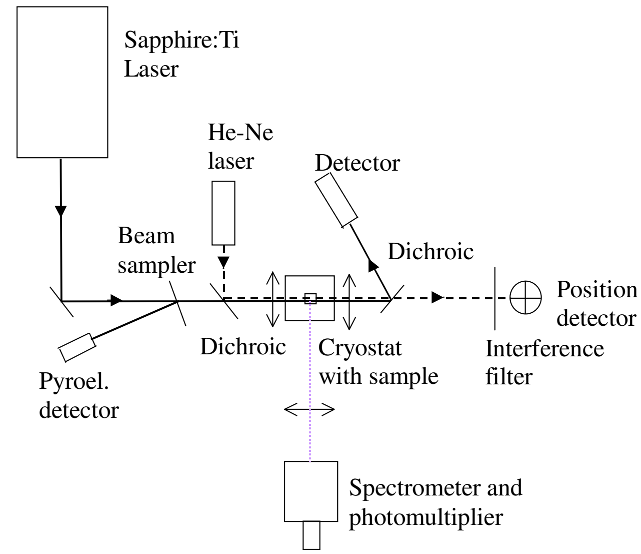

Fig. 1. Block diagram of the experimental set-up used in the photothermal deflection, absorption, and excitation measurements.

position detector the probe beam passed through an interference filter to eliminate residual pumping radiation. The excitation spectra were measured with the same configuration by collecting the fluorescence at a right-angle from the focused area of the pumping beam by means of a collimating lens, and focusing it with a second lens at the 100 μm entrance slit of a 0.22 m monochromator provided with an extended infrared photomultiplier. Lock-in detection was used in both experiments. Thermal deflection waveforms were detected by using a digital scope. The samples were placed on a Teflon holder inside a low vacuum (10^{-2} mbar) cryostat chamber.

2.2. Photothermal quantum efficiency measurements

The calculation of the quantum efficiency (QE), both in glass and crystal samples, was carried-out by considering a simplified model of the Yb^{3+} ions as a two level system (Fig. 2). We shall consider a typical process in which a photon with energy $\hbar\omega_L$ from the incident beam of intensity I_0, modulated at a frequency of ω_m, is absorbed by an electron that goes up to the excited state. The relaxation to the ground state can take place through radiative or non-radiative processes with probabilities W_R and W_{NR} respectively, at a mean energy of $\hbar\omega_0$. The energy difference between the incident and fluorescent photons is exchanged as heat with the host.

In this model, the heat the sample exchanges per unit time and unit volume in a typical heating process is

$$H = n_2[W_{NR}\hbar\omega_L + W_R\hbar(\omega_L - \omega_0)] \quad (1)$$

where n_2 is the population density of the excited state.

The excited state population is governed by the incident beam modulation frequency ω_m and the lifetime of the level, τ.

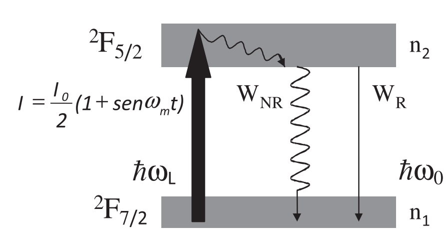

Fig. 2. Two level scheme of the Yb^{3+} ions in a typical heating process.