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Cooperative emission study in ytterbium doped $NdVO_4$

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ABSTRACT

The infrared and visible cooperative emissions of ytterbium ions are studied in Yb-doped $NdVO_4$ single crystals. The absorption of optical phonons allows the emissions at room temperature when a Nd:YAG laser is used. Low temperature emissions are observed due to the $Nd^{3+} \rightarrow Yb^{3+}$ energy transfer following an argon ion laser excitation of the Nd^{3+} ions. Analysis of the cooperative emission at low doping concentration (1%) indicates that it is generated by distant pair forming Yb^{3+} ions while at high doping concentration ($\geq$ 5%) close ions magnetically coupled and superexchange mechanisms prevail in the emitting process.

1. Introduction

Interest in Yb^{3+} ($4f^{13}$) ion based solid state lasers has been growing due to the simple Yb^{3+} two manifold crystal-field (CF) levels $^2F_{7/2}$ ground state and $^2F_{5/2}$ excited state, which prevents cross-relaxation quenching and up-conversion effects [1,2]. For Yb^{3+} the radiative lifetime is longer as compared to Nd^{3+} activated solids, and highly doped miniaturized devices in low thermal loading materials could thus be envisaged for various applications [3]. In addition, enhanced cooperative emission, in which two infrared excited Yb^{3+} ions undergo a simultaneous de-excitation process emitting one photon in the visible, could be realized [4]. Cooperative emission has been proposed for applications in three-dimensional solid state fluorescence display [5] and optical bistability effects that are important in optical communication and optical computing. Such effects have been observed in Yb-doped materials [6,7]. Interest in crystalline hosts with high optical conversion efficiency, high birefringence and good thermal conductivity such as the vanadates is becoming important [3]. In particular, the high solubility of Yb in $LuVO_4$ and $NdVO_4$ non-hygroscopic and thermally stable crystals is noteworthy.

In the host lattice, the Yb^{3+} CF levels are doubly degenerate (Kramers doublets). However for close enough ions, Yb^{3+}–Yb^{3+} pair CF degeneracies are lifted under magnetic interactions, and additional CF excitations are observed [8]. Such interacting pairs play a major role in energy transfer and cooperative emission [9]. Strongly dependent on pair distances and bondings, either forced dipole–dipole and dipole–quadrupole [10,11] or super exchange mechanisms are expected to prevail [12].

Recently, Yb^{3+} ion $^2F_{7/2}$ ground states and $^2F_{5/2}$ excited states in Yb-doped $LuVO_4$ (Yb:LVO) and $NdVO_4$ (Yb:NVO) have been measured, as a function of doping concentration, by infrared absorption and luminescence [13,14]. Also, the Raman active phonons were detected and analyzed in order to determine the doping effects on the crystalline quality and the phonon contributions to the crystal-field vibronics. Neither defects nor local modes were detected and the phonon frequencies were linear between the end members $YbVO_4$ and $LuVO_4$, $NdVO_4$. In the case of Yb:NVO, the observed Yb^{3+} CF infrared active bands corresponded to two site occupations, namely Nd substitutional site and interstitial octahedral site [14].

In both Yb:LVO and Yb:NVO satellites to CF excitations, associated with Yb^{3+}–Yb^{3+} pairs of ions coupled by superexchange interactions, have been observed. The pair interactions were described using an effective spin-Hamiltonian $H = -2J\boldsymbol{S_A}\boldsymbol{S_B}$ that acts as a perturbation on the pair lifting for each ion its lowest ground state level $^2F_{7/2}(0)$ Kramers doublet degeneracy while its $^2F_{7/2}(1, 2, 3)$ and $^2F_{5/2}(0, 1, 2)$ levels remain degenerate [15]. Satellites are predicted at $\Delta + J/2$ and $\Delta - 3J/2$ energies where Δ corresponds to the rare earth isolated ion CF transition energy and J to the pair exchange coupling constant (>0 for ferromagnetically coupled pairs and <0 for antiferromagnetically coupled pairs). Three different exchange Yb^{3+}–Yb^{3+} coupled pairs have been observed in Yb-doped Y_2SiO_5 with $J = 6.5$, 7.9 and $-4.5\ cm^{-1}$, indicating possible ferromagnetic and antiferromagnetic pair interactions [8]. The J values are comparable with those reported for Yb^{3+}–Yb^{3+} in (Yb:LVO) [13] and for Nd^{3+}–Nd^{3+} pairs in YVO_4 and $YLiF_4$ [15].

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In the case of Yb:NVO, the pair satellite absorption bands correspond to Δ (site I)$=10152\pm1$ cm^{-1} and Δ (site II)$=10170\pm1$ cm^{-1} for the isolated Yb^{3+} ions with their associated J constants -6.5, 7 and -11.5, 6.5 cm^{-1} (±1 cm^{-1}) for sites I and II, respectively [14].

A general theory of superexchange between neighboring lanthanide ions in dielectric crystals has been elaborated in the context of the development and the search of efficient up-conversion lasers [12,16]. It proposes a method for calculating an effective Hamiltonian of the generalized superexchange interaction without empirical parameters. Nevertheless, the difficulties of calculation originate from the great number of the excited charge-transfer states in real systems when the lanthanide ion 4f electrons exceed one. For the simplest f^1–f^1 pair, an order of magnitude of around 1 cm^{-1} of the exchange coupling constant is estimated and the energy transfer rate in the case of exchange interaction greatly exceeds the one of dipole–dipole interaction [12].

In this study taking advantage of Nd^{3+} sensitizer character and corresponding transfer energy between Nd^{3+} and Yb^{3+} [17], we focus on the Yb^{3+} cooperative emission in Yb:NVO as obtained by exciting Yb^{3+} in the infrared (9394 cm^{-1}) and by exciting the Nd^{3+} ions in resonance in the visible (19,436 cm^{-1}) region. The objectives are (i) to determine the adequate conditions for maximizing the cooperative emission depending on the exciting sources in the infrared and the visible and (ii) to identify the role played by the Yb^{3+}–Yb^{3+} pairs that are coupled by the exchange interaction as compared to the electric multipolar interacting pairs.

2. Experiments

NdVO$_4$ has a tetragonal crystal structure belonging to the D$^{19}_{4h}$ space group. The lattice parameters are $a=b=7.329$ and $c=6.496$ Å [18]. Nd^{3+}–Nd^{3+} pairs are characterized by first, second and third nearest neighbors of distances 4.003, 6.061 and 6.436 Å, respectively. The difference in ionic radii between the Yb^{3+} and Nd^{3+} ions in eight-fold coordination, 0.985 and 1.109 Å, respectively [19], favors in addition to the Nd^{3+} substitution the location of Yb^{3+} ions in interstitial octahedral sites in NdVO$_4$. Single crystals of NdVO$_4$ doped with Yb (Yb$_x$Nd$_{1-x}$VO$_4$ where $x=1\%$, 5%, 10% and 15%) were prepared by the flux growth method as described in Ref. [14,9] and transparent crystals with an average size of $3\times2\times1$ mm^3 elongated in the direction of the crystallographic c axis of the tetragonal structure were obtained.

A Raman Fourier spectrometer (Bruker 100), equipped with a Janis cryostat, a Ge detector and a continuous wave Nd:YAG laser (9394.6 cm^{-1}), was used for the observation of the infrared and cooperative emission as well as an argon ion laser (19,436 cm^{-1}), a Spex double monochromator and a nitrogen cooled CCD detector for the excitation in resonance of Nd^{3+}.

Infrared transmission measurements were obtained as a function of temperature and doping concentration in the 9000–15,000 cm^{-1} energy range using a Fourier transform interferometer (BOMEM DA3.002) equipped with a quartz–halogen source, a quartz beamsplitter and a Si detector.

3. Results and discussion

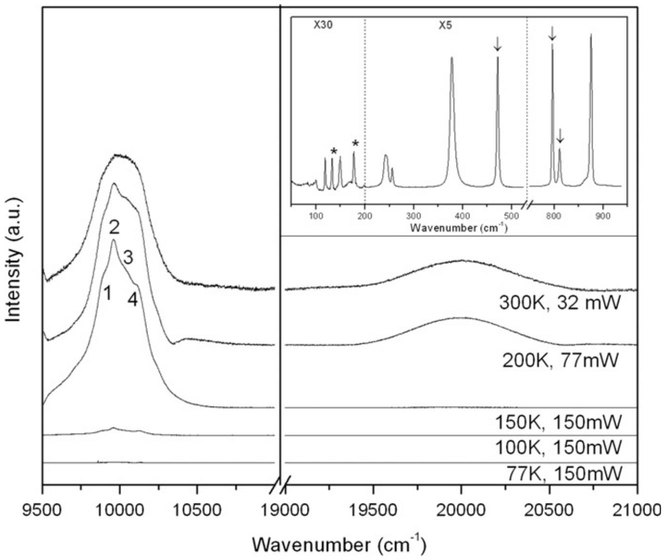

Fig. 1. Infrared and cooperative emission spectra in Yb$_{0.1}$Nd$_{0.9}$VO$_4$ as a function of temperature. Pump (9394 cm^{-1}) intensity is adjusted to maximize the cooperative emission when present (see text for description of peaks 1–4). Inset: Raman active phonons of Yb$_{0.1}$Nd$_{0.9}$VO$_4$ (↓) contributing to the Yb^{3+} excitation at 10 K. * indicates plasma lines.

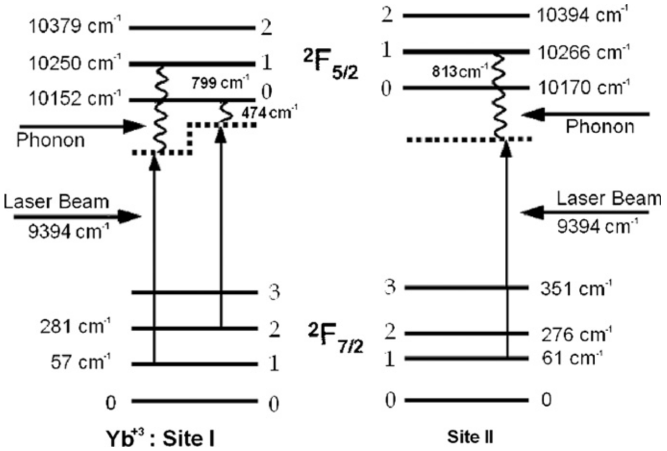

Fig. 2. Crystal-field energy diagram at 10 K for the two sites Yb^{3+} ions in NdVO$_4$.

In Fig. 1 infrared and visible luminescence bands of Yb$_{0.1}$Nd$_{0.9}$VO$_4$ are shown as a function of temperature under the 9394 cm^{-1} Nd:YAG laser excitation in the 9500–11,000 and 19,000–21,000 cm^{-1} energy ranges, respectively. At room temperature both luminescences are observed. For the same observation at 200 K, the excitation energy needs to be doubled. At 150 K, only the infrared emission band, which almost vanishes at 100 K, is observed after doubling again the excitation energy. As shown in Fig. 2, such behavior is consistent with the absorption of Raman active optical phonons (e.g. 474, 799, 813 ± 0.5 cm^{-1} inset of Fig. 1) that are less numerous at low temperatures. These phonons compensate for the mismatch between the excitation energy and the Yb^{3+} CF levels as detected for the two occupation sites (see Ref. [14]). Same excitation processes with the 9394 cm^{-1} Nd:YAG laser excitation implying optical phonons have been reported for Yb^{3+} doped tellurite glasses and their blue cooperative emission [20]. In NdVO$_4$, Yb^{3+} ion $^2F_{7/2}$ ground state and $^2F_{5/2}$ excited state split in four (0, 1, 2, 3) and three (0,1, 2) levels, respectively (Fig. 2). The strongest infrared emission bands, resolved (±5 cm^{-1}) at 150 K, correspond to site II transition (peak 1: $^2F_{5/2}(0)\rightarrow{}^2F_{7/2}(2)$: 9894 cm^{-1}), site I transition (peak 2: $^2F_{5/2}(1)\rightarrow{}^2F_{7/2}(2)$: 9969 cm^{-1}) and site II transitions (peak 3: $^2F_{5/2}(2)\rightarrow{}^2F_{7/2}(3)$: 10,043 cm^{-1}) (peak 4: $^2F_{5/2}(0)\rightarrow{}^2F_{7/2}(1)$: 10,109 cm^{-1}) while additional emissions due to the Yb^{3+}–Yb^{3+} pairs contribute to the total infrared band. Between 300 and 200 K, the infrared