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Raman active phonon and crystal-field studies of Yb^{3+} doped $NdVO_4$

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ABSTRACT

The $^2F_{7/2}$ and $^2F_{5/2}$ crystal field energy levels of the Yb^{3+} ion are measured by infrared absorption in Yb doped $NdVO_4$, with concentrations ranging from 0.25% to 15%, as a function of doping, temperature and magnetic field. Two substitution sites are observed and the presence of Yb^{3+}–Yb^{3+} interacting pairs is confirmed. Also, the Raman active phonons are detected and analyzed in order to determine the doping effects on the crystalline quality and the phonon contributions to the crystal field vibronics.

1. Introduction

Interest in Yb^{3+} solid state lasers as possible substitutes for the Nd^{3+} lasers has been growing due to their small quantum defect and simple two-manifold crystal field (CF) levels ($^2F_{7/2}$ and $^2F_{5/2}$) that prevent self-quenching by cross-relaxation and up-conversion parasitic effects [1,2]. Thus the Yb^{3+} concentration can be made very high (tens of %), for miniaturized device applications, which can be pumped using commercially available InGaAs laser diodes. For instance, continuous wave laser operation of Yb^{3+} doped $LuVO_4$ (Yb:LVO) at 1.031 μm has been demonstrated with 43% optical conversion efficiency [3]. Also, in Yb^{3+} doped materials, emission bands are significantly broad allowing mode locked laser operation with short pulse durations.

The Yb^{3+} CF levels are doubly degenerate (Kramers doublets) in the case of isolated ions in the host lattice. However, for close enough ions, Yb^{3+}–Yb^{3+} pair CF degeneracies are lifted due to their magnetic interactions which depend on pair distances and bondings. Such interacting pairs give rise to additional CF excitations [4] and seem to play a major role in energy transfer and cooperative emissions with prevailing superexchange mechanisms [5].

To our knowledge, in spite of the growing interest in Yb doped rare earth vanadates as laser materials having remarkable spectroscopic performances [6,7], there has been no detailed experimental reports of their Yb^{3+} ion $^2F_{7/2}$ ground and $^2F_{5/2}$ excited states CF excitations except recently for Yb:LVO compounds [8].

In the parent compound, $YbVO_4$, the $^2F_{7/2}$ ground state multiplet CF excitations have been measured at 58, 281, 353 cm^{-1} by inelastic neutron scattering [9], and at 58, 277, 353 cm^{-1} by magnetic susceptibility [10] with two different sets of CF parameters calculated.

The Yb^{3+} isolated ion and Yb^{3+}–Yb^{3+} coupled ion pair CF excitations in Yb:LVO have been studied by infrared transmission and luminescence as a function of temperature allowing the determination of their corresponding set of CF Hamiltonian parameters [8].

Compared to Yb:LVO, the Yb^{3+} doped $NdVO_4$ (Yb:NVO) system presents additional possibilities for CF excitations with Nd^{3+} as sensitizer in the assisted cooperative emission. In such emission, Yb^{3+}–Yb^{3+} pairs (characterized by first, second and third nearest neighbors distances 4.003 Å, 6.061 Å, and 6.436 Å, respectively) play a major role. Also, the difference in ionic radii between the Yb^{3+} and Nd^{3+} ions in eightfold coordination (0.985 Å and 1.109 Å, respectively as compared to 0.977 Å for Lu^{3+} ion) may favor, in addition to the Nd^{3+} substitution, Yb^{3+} ions to enter interstitial octahedral sites in $NdVO_4$. Such site occupation has been observed in the case of Fe^{3+} in the zircon structure $ZrSiO_4$ [11] and should broaden further the various absorption and emission bands.

In this paper, we study the Yb^{3+} ion $^2F_{7/2}$ and $^2F_{5/2}$ CF excitations in Yb:NVO by infrared transmission and luminescence as a function of doping concentration (0.25–15%) and temperature (10–300 K) in the context where Yb^{3+} isolated ions and Yb^{3+}–Yb^{3+} interacting pairs are present. Also, in order to discriminate the vibronic sidebands associated with the CF absorption bands and determine if defects are generated by high doping concentrations, the Raman active phonon frequencies of the doped samples are

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measured and their linewidths are analyzed. Finally, if in addition to Yb^{3+} ions substituting for Nd^{3+} ions, Yb^{3+} ions locate also in octahedral sites, two sets of CF excitations should be observed.

2. Experiments

$NdVO_4$ has a tetragonal crystal structure belonging to the D_{4h}^{19} space group. The lattice parameters are: $a = b = 7.329$ and $c = 6.496$ Å [12]. Single crystals of $NdVO_4$ doped with Yb^{3+} were prepared by the flux growth method using $Pb_2V_2O_7$ as solvent [13]. Appropriate quantities of pure V_2O_5, PbO, $Na_2B_4O_7$, 99.99% Nd_2O_3 and Yb_2O_3, were used as starting materials; $Na_2B_4O_7$ was added as flux modifier to increase the size of the crystals [14]. The Yb^{3+} dopant was added with nominal concentrations in the 0.5–15 mol% range (substituting for Nd^{3+}). After careful mixing, the starting mixtures were put in Pt crucibles and heated up to 1270 °C in a horizontal programmable furnace. The melts were maintained at this temperature for 12 h (soaking time), then cooled to 800 °C at a rate of 1.8 °C h^{-1}; the crucibles were then drawn out from furnace and quickly inverted to separate the flux from the crystals grown at the crucible bottom. Transparent crystals having an average size $3 \times 2 \times 1$ mm^3 and elongated in the direction of the crystallographic c axis of the tetragonal structure were separated from the flux by dissolving it in hot diluted HNO_3.

Raman spectra with 0.5 cm^{-1} resolution were measured in the backscattering configuration using a He–Ne laser (632.8 nm) and a Labram-800 Raman microscope spectrometer equipped with ×50 objective, appropriate notch filter and nitrogen cooled CCD detector. The studied single crystals were mounted in a continuous flow temperature regulated liquid helium Janis cryostat and the laser power was kept at 0.8 mW to avoid local heating. With incident laser exciting light polarized either parallel to the c or a axes, A_{1g}, B_{1g}, B_{2g} and E_g Raman active phonons were detected for different doping concentrations using $YbVO_4$ and $NdVO_4$ phonons as templates.

Infrared transmission measurements were obtained as a function of temperature and magnetic field 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. For measurements under external magnetic field, the sample was placed in the bore of a superconducting magnet with the magnetic field parallel to the incident radiation. A Raman Fourier spectrometer (Bruker 100), equipped with a Janis cryostat, a Ge detector and a YAG laser (9394.6 cm^{-1}), was also used for the observation of the infrared luminescence.

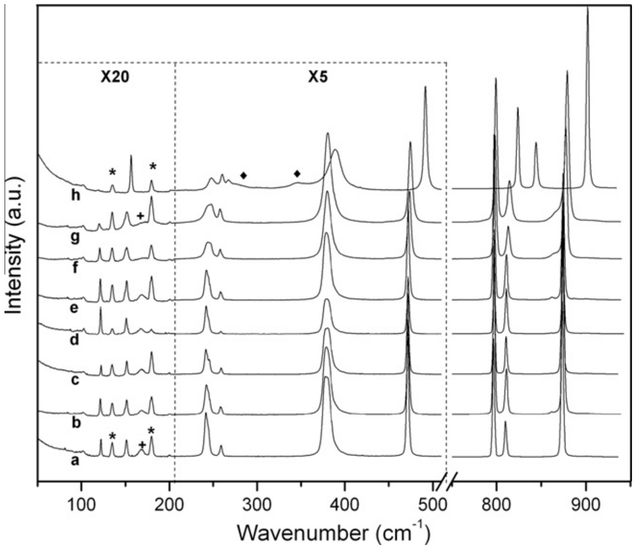

Fig. 1a. Raman active phonons of $NdVO_4$ (a), $YbVO_4$ (h), and Yb doped $NdVO_4$ at $T = 10$ K as a function of Yb concentration: (b) 0.25%, (c) 0.5%, (d) 1%, (e) 2.5%, (f) 10%, (g) 15%. * Indicates plasma lines, $+Nd^{3+}$ 168 cm^{-1} CF excitation and ♦ Yb^{3+} 279 and 351 cm^{-1} CF excitations.

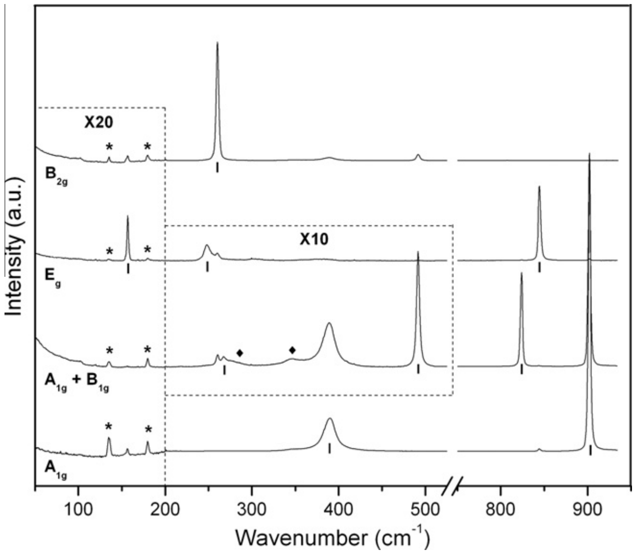

Fig. 1b. A_{1g}, B_{1g}, B_{2g} and E_g symmetry $YbVO_4$ Raman active phonons at $T = 10$ K.

3. Results and discussion

The Raman active phonons of $REVO_4$ (RE = rare earth) have been studied by Santos et al. [15]. Except the 375 cm^{-1} particular excitation reported in $NdVO_4$ by Nguyen et al. [16] and assigned to B_{2g} symmetry phonon, the observed phonon frequencies evolve systematically from $LaVO_4$ to $LuVO_4$. Typical low temperature Raman active phonons of Yb:NVO as a function of Yb concentration are shown in Fig. 1a and their symmetries are made explicit in the spectra of $YbVO_4$ (Fig. 1b). The detected $NdVO_4$ phonon frequencies at 10 K: A_{1g} (381, 873 cm^{-1} symmetric bending and stretching modes, respectively), B_{1g} (122, 245, 472, 797 cm^{-1}), B_{2g} (259 cm^{-1}) and E_g (151, 242, 810 cm^{-1} translational, rotational, and antisymmetric stretching modes, respectively) shift linearly with doping to the $YbVO_4$ corresponding at 10 K phonon frequencies: A_{1g} (389, 902 cm^{-1}), B_{1g} (267, 492, 824 cm^{-1}), B_{2g} (262 cm^{-1}) and E_g (157, 248, 844 cm^{-1}). Their bandwidths increase by approximately a factor of two when the Yb doping varies from 0.25% to 15%. Linear phonon frequency shifts as well as the absence of disorder induced local modes, attest of the Yb:NVO sample crystalline qualities even for high doping concentrations. It is worth noting that the additional excitation to the expected phonons observed at 375 cm^{-1}, in the case of $NdVO_4$ and Yb:NVO, could be associated with a Nd^{3+} ion CF excitation within the ground state multiplet as reported by Antic-Fidancev et al. [17].

CF vibronics that result from the coupling between odd parity infrared active CF excitations and even parity Raman active phonons, are often observed in Yb doped oxides and reflect strong e-phonon interactions [4]. They could complicate the analysis of the infrared transmission spectra and the identification of the Yb^{3+} ion CF levels.

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 in $NdVO_4$. In Fig. 2, Yb:NVO infrared CF absorption bands at 10 K are shown for various doping concentrations. Many satellite bands, in addition to the