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Crystal field study of ytterbium doped Lu_2SiO_5 and Y_2SiO_5 under a magnetic field

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Abstract

Yb^{3+} crystal field excitations in ytterbium doped Y_2SiO_5 and Lu_2SiO_5 single crystals and thin films are studied under an applied magnetic field. The ground and excited state g -factors that are needed for the calculation of reliable crystal field Hamiltonian parameters are determined. Some of the Yb^{3+} ions that substitute for the Y^{3+} or Lu^{3+} ions give rise to Yb^{3+} - Yb^{3+} magnetically interacting pairs as confirmed by their crystal field absorption bands under a magnetic field. The overall crystal field excitation characteristics confirm the strong similarities between the single crystals studied and thin films.

1. Introduction

Recently, interest in Yb^{3+} based laser materials as possible substitutes for the Nd^{3+} based solid state lasers has been growing. They present several advantages, such as a small quantum defect and a simple electronic structure, with two manifold crystal field (CF) levels ($^2\text{F}_{7/2}$ and $^2\text{F}_{5/2}$), that prevent self-quenching by cross-relaxation and up-conversion parasitic effects [1, 2]. Due to Yb^{3+} - Yb^{3+} pair interactions, their emission bands are broad, allowing mode locked laser operation with short pulse durations. For instance Yb doped Y_2SiO_5 (Yb:YSO) and Yb doped Lu_2SiO_5 (Yb:LSO) lasers, that combine high thermal conductivity with large tunability, emit pulses of ~ 200 fs around $1 \mu\text{m}$ and exhibit high optical conversion of more than 50% [3, 4]. Yb:YSO and Yb:LSO have been recently studied by means of Raman spectroscopy and infrared transmission [5–8]. Y_2SiO_5 crystallizes in the C_{2h}^6 monoclinic space group and Yb^{3+} ions enter two non-equivalent and equally populated Y_I and Y_{II} sites of C_1 symmetry [9]. In Yb:YSO and Yb:LSO, Yb_I and Yb_{II} isolated ion infrared absorption bands that correspond to $^2\text{F}_{7/2}$ (0, 1, 2, 3) \rightarrow $^2\text{F}_{5/2}$ (0, 1, 2) transitions have been observed in the 10 000–11 500 cm^{-1} range [5–8]. The Yb^{3+} CF interaction Hamiltonian can be written as [10] $H_{\text{CF}} = \sum_{k,q} B_{kq} [C_q^k + C_{-q}^k]$ where the functions C_q^k transform like

tensor operators under simultaneous rotation of the coordinates of all the f electrons, and the B_{kq} are the so-called CF parameters. Because of the Yb^{3+} ion low site symmetry group C_1 , 27 B_{kq} CF coefficients have to be calculated with relatively few detected levels (four $^2\text{F}_{7/2}$ and three $^2\text{F}_{5/2}$). Thus, the standard procedures that consider the CF parameters as adjustable variables are hopeless. In erbium doped Y_2SiO_5 [11], a very simple model in which ligand ions were considered as mere fixed point charges, in addition to various other approximations, was used with the objective of associating with each rare earth site its own crystal field levels. The B_{kq} parameters were calculated considering the average values $\langle r^2 \rangle$, $\langle r^4 \rangle$ and $\langle r^6 \rangle$ as adjustable parameters. In the case of Yb:YSO a point charge electrostatic model has been used to calculate Yb^{3+} energy levels by varying effective charges in a sphere of 130 Å radius in order to estimate the ytterbium manifold overall splitting [8]. Recently, Gaume *et al* [12] calculated semi-empirically Yb^{3+} energy levels in Yb: Sc_2SiO_5 with an overlap model in which the chemical bonding, restricted to the first coordination sphere of Yb^{3+} , was taken into account. In order for such methods to succeed in calculating reliably the CF parameters, additional experimental measurements such as g factor ones are needed.

In addition to the Yb^{3+} main infrared absorption bands in Yb:YSO and Yb:LSO, several weaker bands are observed

in the 10 000–11 500 cm^{-1} range. Campos *et al* [7] have conjectured either a crystal field perturbation at the main sites due to the presence of defects generated by Yb^{3+} ions at neighboring sites or a magnetic coupling between Yb^{3+} – Yb^{3+} pair ions [13]. As a continuation of previous investigations on the CF excitations of Yb:YSO we present in this paper infrared transmission measurements of Yb:YSO and Yb:LSO under a magnetic field. The objectives are on one hand to evaluate the g factors of the ${}^2F_{7/2}$ ground state and ${}^2F_{5/2}$ first excited state levels in order to provide more experimental grounds for the CF Hamiltonian modeling and, on the other hand, to allow determination of whether the observed satellites originate from Yb^{3+} – Yb^{3+} magnetic pair interactions that favor applications in cooperative emission [14] and possibly optical bistability [15].

2. Experiments

Y_2SiO_5 and Lu_2SiO_5 crystallize in the C_{2h}^6 monoclinic space group [9]. While the Y coordination octahedra share edges in the chains that are linked together by SiO_4 tetrahedra, the ions are arranged in compact chains running along the c -axis. Yb^{3+} ions substitute equally at the two non-equivalent C_1 symmetry (Y^{3+} or Lu^{3+}) sites of the host lattice, with coordination number (6 + 1) for Y_I , Lu_I (mean Y–O distance: 2.309 Å, Lu–O distance: 2.324 Å) and 6 for Y_{II} , Lu_{II} (mean Y–O distance: 2.269 Å, Lu–O distance: 2.226 Å) [16]. There are three mutually perpendicular optical extinction axes in $\text{Y}_2(\text{Lu})_2\text{SiO}_5$: the crystal's \mathbf{b} axis and the \mathbf{D}_1 and \mathbf{D}_2 axes that correspond to the optical extinction directions when the crystal is viewed along the \mathbf{b} axis between crossed polarizers [17]. Under an applied magnetic field each Y^{3+} or Lu^{3+} site gives rise to two non-equivalent sites unless the magnetic field is oriented parallel to \mathbf{b} or in the $\mathbf{D}_1\mathbf{D}_2$ plane. Y^{3+} , Yb^{3+} and Lu^{3+} have similar ionic radii, so no noticeable defects or strains are presumably introduced by substitution in Yb:YSO or Yb:LSO.

The samples studied were Yb 5%:YSO and Yb 8%:LSO single crystals grown by the Czochralski technique and [010] oriented Yb 2%:YSO, and Yb 10%:YSO thin films grown by liquid phase epitaxy [18]. For the infrared studies, the thin films were mounted perpendicular to the incident radiation and magnetic field. 0.5 cm^{-1} resolution transmission spectra at low temperature in a 1–7 T applied magnetic field were obtained in the 10 000–10 500 cm^{-1} range with a Fourier transform interferometer BOMEM DA3.002 equipped with a quartz–halogen source, a quartz beam splitter and a Si detector. Electron paramagnetic resonance EPR measurements were performed with a 9.5 GHz X-band Bruker ER 220 D spectrometer.

3. Results and discussion

In agreement with Campos *et al* [7], ${}^2F_{7/2}(0) \rightarrow {}^2F_{5/2}(0)$ absorption bands associated with Yb^{3+} isolated ions in sites I and II are observed at 10 189, 10 215 ($\pm 1 \text{ cm}^{-1}$) in Yb 5%:YSO and at 10 188, 10 216 cm^{-1} ($\pm 1 \text{ cm}^{-1}$) in Yb 8%:LSO respectively (figure 1). Several concentration

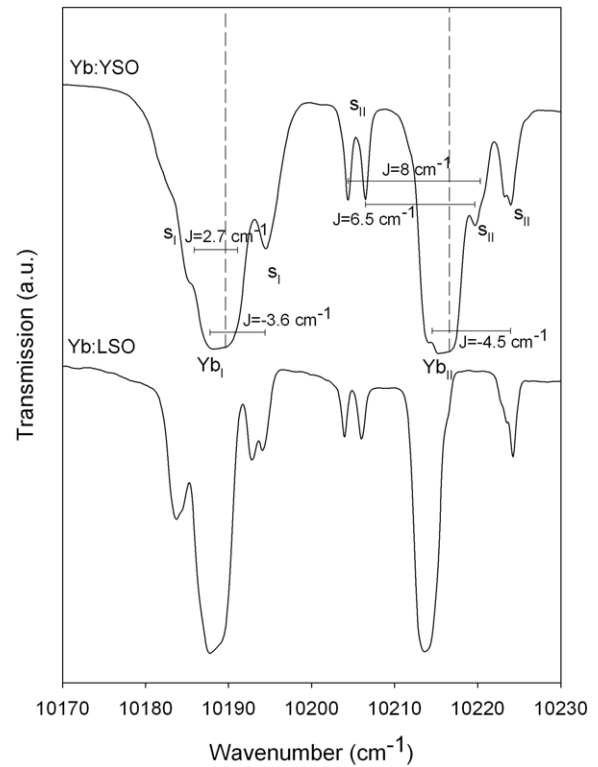


Figure 1. Infrared CF absorption bands at $T = 12$ K of Yb 5%:YSO and Yb 8%:LSO single crystals. Dashed lines indicate the isolated ion Yb_I and Yb_{II} absorption frequencies and S_I , S_{II} the pair satellites associated with sites I and II, respectively. J pair exchange constants are indicated.

dependent additional bands are also detected in both compounds around 10 185, 10 186, 10 190, 10 194, 10 205, 10 207, 10 214, 10 220, 10 221, 10 223 cm^{-1} ($\pm 1 \text{ cm}^{-1}$) (figure 1). We associate them with magnetically coupled Yb^{3+} – Yb^{3+} pairs. Since Y_I (Lu_I) and Y_{II} (Lu_{II}) ions in Y_2SiO_5 and Lu_2SiO_5 have seven neighbors at distances shorter than 4.695 Å with which they share one or two oxygens [9], many Yb^{3+} CF satellites for each site main line in Yb:YSO and Yb:LSO are expected, depending on pair distances and bondings. The CF Hamiltonian lifts the Yb^{3+} level 2F_j degeneracy into $2j + 1$ doubly degenerate states referred to as Kramers doublets. Guillot-Noël *et al* [13] have modeled the neighboring rare earth ion magnetic interactions, that lift the Kramers doublet degeneracy, with an effective spin Hamiltonian $H = -2 J \mathbf{S}_A \cdot \mathbf{S}_B$ acting as a perturbation. They have assumed that the pair ions A and B contribute mainly in their ground states to the interaction with their effective spins $S_A = S_B = 1/2$, and have predicted satellites at $\Delta + J/2$ and $\Delta - 3J/2$ energies. 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). In the case of Yb:YSO and Yb:LSO, and similarly to those for Nd:YLiF₄ and Nd:YVO₄ [19–21], the exchange coupling constants J as determined from the infrared absorption spectra are found between ~ -4.5 and 8 cm^{-1} (figure 1). Both positive and negative J values could be associated with the

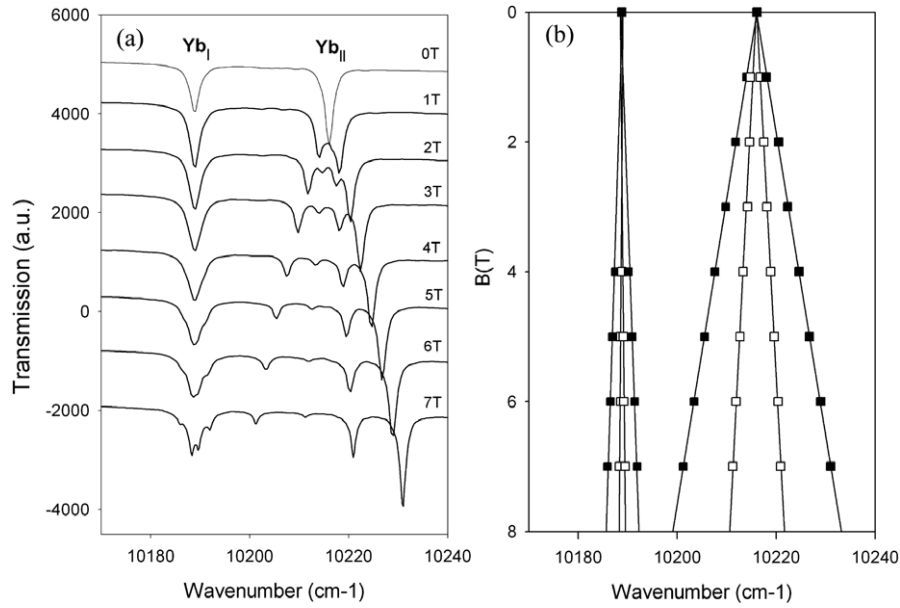


Figure 2. Infrared CF absorption bands, as a function of \mathbf{B} at $T = 12$ K, of Yb 2%:YSO thin film with $\mathbf{B} \parallel \mathbf{b}$. (a) Transmission, (b) frequencies. Squares indicate the measured frequencies.

satellites, namely $J = 2$, -3.6 cm^{-1} (site I), 6.5, 8 and -4.5 cm^{-1} (site II) (figure 1), indicating that direct exchange and superexchange processes involving the ligands contribute to pair interactions.

A generalization of the mechanism of superexchange between lanthanide ions bridged by ligands, designated as covalent coupling, has been proposed by Mironov and Kaminskii [22, 23]. They have particularly shown that calculations of strongly transfer integral dependent intensities are complex even for simple f^1-f^1 exchange coupled pairs. Such pair covalent coupling could be at the origin of the recently reported Yb:YSO cooperative emission that corresponds to a process in which two Yb^{3+} excited ions make downward transitions emitting one photon with the sum of the two transitions energies [14].

Under an applied magnetic field B parallel to the \mathbf{b} axis, non-equivalent magnetic sites remain unresolved. However, the twofold degeneracies of the isolated Yb^{3+} ion CF Kramers doublets in each site are lifted due to the first-order Zeeman splitting. A single optical transition at energy Δ' , between a ground state Kramers doublet and an excited state Kramers doublet with g -factors g_0 (ground state) and g_1 (excited state) respectively, splits into four transitions at energies $\Delta' \pm \mu_B B(g_0 \pm g_1)/2$. Infrared absorptions of [010] oriented Yb 2%:YSO thin film, as a function of applied magnetic field between 0 and 7 T (e.g. 10 189, $10\,216 \pm 1 \text{ cm}^{-1}$ at 0 T; and 10 186; 10 188; 10 189.5; 10 192; 10 201; 10 211; 10 221; $10\,231 \pm 1 \text{ cm}^{-1}$ at 7 T) allow the detection of four absorption bands associated with each Yb^{3+} site CF level (figure 2(a)). The low Yb concentration hinders pair formations and observation of their corresponding satellites. Slopes of the various lines joining the absorption band frequencies as a function of the applied magnetic field (0.43 ± 0.01 , 0.12 ± 0.04 , -0.09 ± 0.01 , $-0.38 \pm 0.04 \text{ cm}^{-1} \text{ T}^{-1}$) for Yb^{3+} site I and (2.13 ± 0.01 , 0.70 ± 0.01 ,

-0.68 ± 0.01 , $-2.12 \pm 0.1 \text{ cm}^{-1} \text{ T}^{-1}$) for Yb^{3+} site II (figure 2(b)), allow the g factor determinations. Hence for the isolated Yb^{3+} ions in sites I and II, $g_0 = 0.6 \pm 0.1$; $g_1 = 1.1 \pm 0.1$ and $g_0 = 5.64 \pm 0.03$; $g_1 = 2.86 \pm 0.03$ respectively. In order to observe the Zeeman splitting of the satellites and their corresponding g factors a higher Yb concentration sample, Yb 10%:YSO thin film, was used in the infrared transmission (figures 3(a) and (b)). The observed additional absorption band frequencies as a function of the magnetic field (e.g. 10 204, 10 206, $10\,223.5 \pm 1 \text{ cm}^{-1}$ at 0 T; and 10 188, 10 191, 10 209, 10 219, $10\,221$, $10\,237 \pm 1 \text{ cm}^{-1}$ at 7 T) show the same slopes for the frequency joining lines as for the isolated Yb^{3+} ions in site II. It can thus be concluded that they are characterized by the same g factors and that the Yb^{3+} ions involved in pair interactions are located at regular sites. Similarly in Yb 8%:LSO single crystal with $\mathbf{B} \parallel \mathbf{b}$, while the absorption bands for site I could not be unambiguously resolved (figure 4(a)), almost the same line slopes and g factors, $g_0 = 6.2 \pm 0.2$ and $g_1 = 3.1 \pm 0.15$ (figure 4(b)), are obtained for the isolated Yb^{3+} ions at sites II as well as for their satellites except for one possible irregular site (+ in figure 4(b)).

In order to confirm the isolated Yb^{3+} ion ground state g -factors, EPR measurements at 12 K for Yb 2%:YSO thin film were undertaken with $\mathbf{B} \parallel \mathbf{b}$. The splitting of the $S = 1/2$ ground state energy, $g\mu_B B$, under an applied magnetic field ($B < 1$ T), is of the order of GHz. For 9.5 GHz two absorption bands around $B = 1160$ and 8510 G are observed (figure 5). They correspond to Yb^{3+} ions in isolated site I and II absorptions with $g_0 = 0.8 \pm 0.2$ and 5.8 ± 0.2 respectively confirming the infrared absorption measurements.

4. Conclusion

Infrared CF absorptions of Yb^{3+} , in Yb:LSO and Yb:YSO single crystals and thin films, were studied at $T = 12$ K

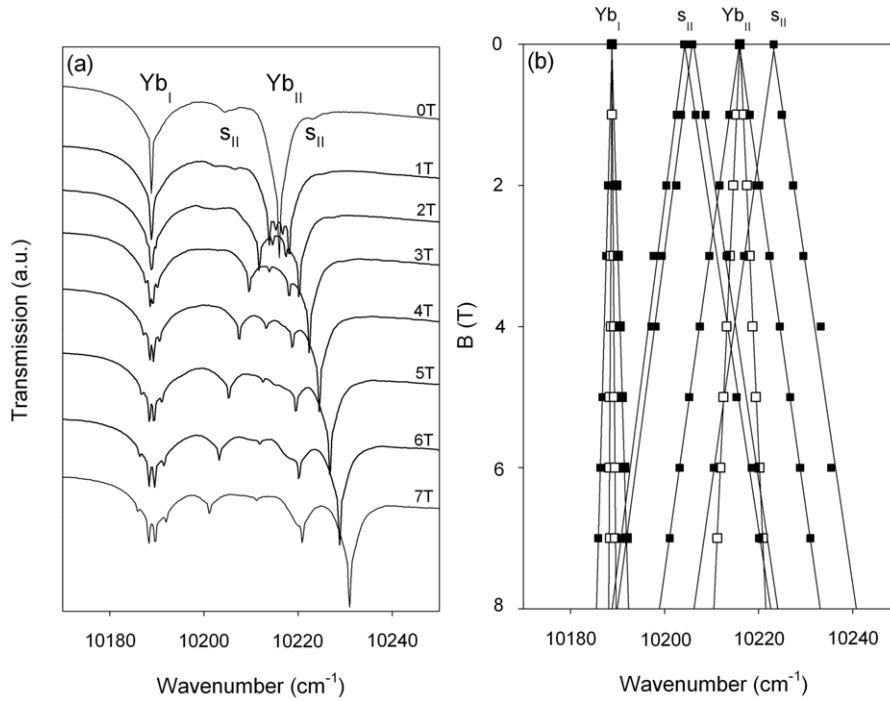


Figure 3. Infrared CF absorption bands, as a function of \mathbf{B} at $T = 12$ K, of Yb 10%:YSO thin film with $\mathbf{B} \parallel \mathbf{b}$. (a) Transmission (S_{II} : site II pair satellites), (b) frequencies. Squares indicate the measured frequencies.

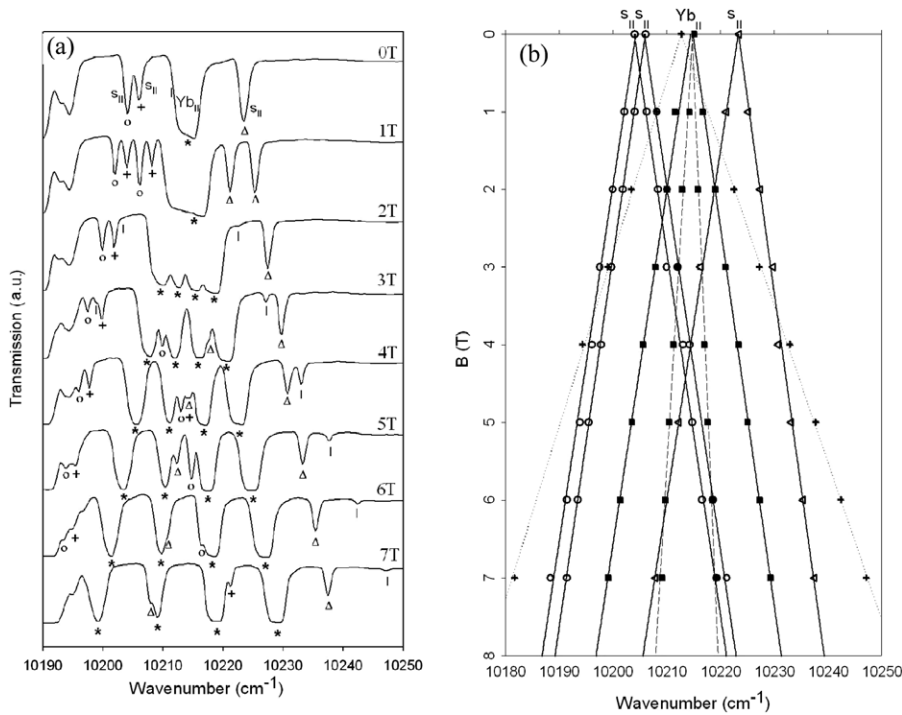


Figure 4. Site II infrared CF absorption bands, as a function of \mathbf{B} at $T = 12$ K, of Yb 8%:LSO single crystal with $\mathbf{B} \parallel \mathbf{b}$. (a) Transmission (*: isolated site; o, +, Δ : S_{II} pair satellites), (b) frequencies (square: isolated site; o, Δ : S_{II} pair satellites; +: defect).

under a magnetic field. In addition to the two Yb^{3+} site CF excitations, satellites that correspond to $\text{Yb}^{3+}\text{-Yb}^{3+}$ interacting pairs are observed. Such pairs are described using an effective spin Hamiltonian with positive and negative exchange constants that reflect a covalent coupling effective

in pair cooperative emission. For Yb:LSO and Yb:YSO single crystals and thin films, CF absorption frequencies and corresponding ground state and excited state g factors are almost identical. Such similarities indicate the absence of strains in the thin films and imply the same crystal field

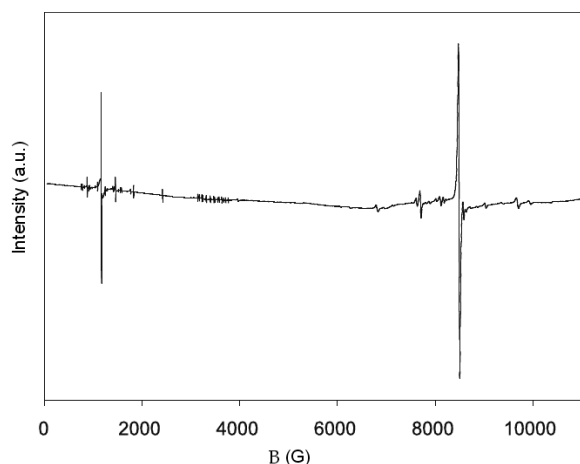


Figure 5. EPR measurements at $T = 13$ K for Yb 2%:YSO thin film with $\mathbf{B} \parallel \mathbf{b}$.

parameters as well as identical pair interactions for the two compounds.

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