Electronic Supplementary Information

A probe of radiation field magnetic component based on octahedral Yb³⁺ in the CaNbGa garnet -CNGG- single crystal

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(i) Yb³⁺ Spectroscopy in Garnets

The Yb³⁺ spectroscopy in dodecahedral sites of garnets is quite well documented both in ordered crystals, such as Y₃Al₅O₁₂ -YAG-, and in other single crystal garnets with some degree of disorder. The optical absorption exhibits a well resolved 0-0' transition near 970 nm (969 nm for YAG and 972 nm for CNGG = $\{Ca \square_D\}_3[Nb_{1-x}Ga_x \square_O]_2(Ga_1)$ $_{\rm v}Nb_{\rm v}\square_{\rm T}$)₃O₁₂), but the resolution of 0-1' and 0-2' ones is compromised by phonon coupling and inhomogeneous broadening associated to static random environments. Among the disordered garnets, CNGG has been particularly studied for its application as a mode-locked laser systems for ultrashort (fs) laser pulse production. The lanthanide absorption and emission bands are spectrally broadened, see Fig. ESI.1 for Yb doped crystals, due to the presence of vacancies (\Box) in the three crystallographic sites of the garnet structure as well as to the Nb⁵⁺ and Ga³⁺ simultaneous occupation of the octahedral and tetrahedral garnet sites, even though with specific occupancy factors. [Kaminskii et al., Inorg. Mat. 22, 927, 1986] Further, the crystal can be modified by the incorporation of Li⁺ and Na⁺, although each one plays a quite different role: Li exclusively incorporates in tetrahedral sites, while Na⁺ is found exclusively in the dodecahedral site. Nevertheless, the similarity of the Yb³⁺ spectra in YAG and CNGG garnets shows that in both cases the common center is dodecahedral Yb³⁺.



Fig. ESI.1 Comparison of the room temperature optical spectroscopy of Yb^{3+} in 5at%Yb:YAG (black lines) and in 8at%Yb:CNNG (red lines) single crystal garnets. All spectra are normalized to their total area equal to unity. (a) Optical absorption. (b) Photoluminescence excited in the 920-940 nm region.

Recently, a site selective excitation study resolved different dodecahedral Yb³⁺ sites in CNGG associated to the electric charge in the two edge-sharing nearby tetrahedra, i.e. either vacant or Li⁺, Mg²⁺, Ga³⁺ or Nb⁵⁺ occupancy, shifting the 0 \rightarrow 0' band to larger energy as the charge increases [*M. D. Serrano et al, J. Mat. Chem. C 5, 11481, 2017*]. Fig. ESI.2 shows evidence of these dodecahedral centers excited inside the 0-0' Yb³⁺ linewidth (λ = 970-972 nm). The spectral distribution of the emission bands depends on the excitation wavelength. The excitation spectra of these emissions recorded in the 0.3at%Yb:CNGG crystal of interest in this work show bands at 960.3 nm and 968.7 nm in addition to the bands expected for the dodecahedral Yb, see Fig. ESI.2a, but interestingly the relative intensities of these two bands remain similar independently of the used λ_{EMI} , and they vary differently with regards to the intensity of the main peak at λ = 970.8 nm. These results from 6 K PL spectra indicate a same origin for OA bands at 960.3 nm and 968.7 nm, that is, they should correspond to ²F_{7/2}(0) \rightarrow ²F_{5/2}(0', 1') electronic transitions associated to 16*a* Yb³⁺, and furthermore the above four PL emission bands observed in Fig. 2 of the main text after excitation in any of these two bands should arise from 16*a* Yb³⁺ 2F_{5/2}(0') \rightarrow ²F_{7/2}(n=0, 1, 2, 3) transitions.



Fig. ESI.2 6 K photoluminescence spectra of 0.3at%Yb:CNGG crystal. (a) Comparison of the excitation spectra at several emission wavelengths λ_{EMI} with the 6 K optical absorption (AO) spectrum. (b) Photoluminescence emission for different excitation wavelengths inside the 0 \rightarrow 0' transition of dodecahedral Yb³⁺ centers.



Fig. ESI.3 Room temperature photoluminescence of 0.3at%Yb:CNGG single crystal excited at different wavelengths. (a) PL excited at the inhomogeneously broadened $0\rightarrow 0'$ dodecahedral Yb³⁺. (b) Comparison of the PL corresponding to the octahedral Yb³⁺ center (excited at λ_{EXC} = 960.3 nm) with that corresponding to dodecahedral Yb³⁺ (excited at λ_{EXC} = 920, 933, 944 and 982 nm).



Fig. ESI.4 6 K photoluminescence intensity decay of the 16*a* Yb^{3+ 2}F_{5/2} multiplet of 0.3at%Yb:CNGG crystal, λ_{EXC} = 960.3 nm, and λ_{EMI} corresponding to transitions to different ${}^{2}F_{7/2}$ mJ energy levels. The circles are the experimental results and the lines are the exponential fits of the long component of the corresponding decay. (a) λ_{EMI} = 967.6 nm. (b) λ_{EMI} = 997 nm. (c) λ_{EMI} = 1008 nm. (d) λ_{EMI} = 1080 nm.

The room temperature time-integrated PL emission of dodecahedral Yb³⁺ in CNGG is little sensitive to the excitation wavelength. In addition to the 0' \rightarrow 0 emission at 972 nm two broad bands at about 1000 and 1025 nm are observed, see Fig. ESI.3. Further, the corresponding RT PL emission of the 16*a* octahedral Yb³⁺ is basically undistinguishable from that observed for the dodecahedral one. Apart from PL reabsorption, fast excitation diffusion between both center types may be responsible of this fact.

As explained in the main text, the PL of the octahedral $16a \text{ Yb}^{3+}$ is characterized by a long time constant in the order of some ms. Fig. ESI.4 shows the $16a \text{ Yb}^{3+}$ PL intensity decay kinetics (excited at $\lambda = 960.3 \text{ nm}$) for several temperatures and emissions wavelengths associated to the emissions of the octahedral Yb^{3+} center. Results are quite independent of the monitored emission wavelength while the time constant decreases with increasing temperature.

Figs. ESI.5 and ESI.6 show some further information of the time-resolved PL results of 0.3at%Yb:CNGG crystal. Fig. 5a of the main text showed that optical absorptions of the dodecahedral and octahedral Yb centers in CNGG overlap at 960.3 nm. Fig. ESI.5 shows the low temperature (6 K) time-resolved PL excited at this wavelength after normalization to the most intense emission peak (λ = 1025 nm). The selection of long times for the analysis promotes the strength of the emissions assigned to the octahedral 16*a* Yb³⁺ center, λ = 968.7, 996.7, 1008.7 and 1080.6 nm. On the other hand, Fig. ESI.6 shows the comparison of the time-resolved PL of the octahedral center for low (6 K) and room temperatures. Although worse resolved at 300 K, the same bands are observed at both temperatures. The only noticeable change is the presence of a 1080 nm satellite band at 1068 nm, its origin was explained in the main text.



Fig. ESI.5 Comparison of the 6 K time-resolved PL contributions of dodecahedral (black line, delay 5 μ s and gate width 250 μ s) and octahedral (red line, delay 2.5 ms and gate width 8 ms) centers in 0.3at%Yb:CNGG. λ_{EXC} = 960.3 nm.



Fig. ESI.6 Comparison of the 6 K (black line) and 300 K (red line) time-resolved PL contributions of the octahedral center in 0.3at%Yb:CNGG. λ_{EXC} = 960.3 nm. Delay 2.5 ms and gate width 8 ms.

(ii) Crystal Field Analysis

The CF potential of the $C_{3i} (\equiv S_6)$ symmetry of the 16*a* site is described by nine nonzero CF parameters, B_0^2 , B_0^4 , B_3^4 , iB_3^4 , B_0^6 , B_3^6 , iB_3^6 , B_6^6 and iB_6^6 , which can be reduced to eight by a proper choice of the reference axis system, which cancels iB_3^4 . The use of some calculation model for CF interactions to derive an initial set of C_{3i} CF parameters should be the usual first approach, however given the reduced number of energy levels of the Yb³⁺ configuration the modeling with such a large number of parameters is unrealistic. Instead, we start considering the undistorted octahedral (O_h) symmetry, and then the introduction of additional CF parameters will allow accounting for the distorted real symmetry ("descent of symmetry" method). To obtain an initial set of O_h CF parameters we applied the semi-empirical Simple Overlap Model (SOM), which estimates them from crystallographic positions and distances of oxygen ligands around $16a \text{ Yb}^{3+}$. After that, the calculation of the sequence of energy levels requires only two free-ion parameters, E^0 , and the spin-orbit coupling constant, ζ , whose variation with the crystal host is theoretically predicted to be weak for a given Ln³⁺ ion, and consequently can be reasonably taken from the literature. These calculations were performed by using the program REEL [P. Porcher, Fortran routines REEL and IMAGE for simulation of d^N and f^N configurations involving real and complex crystalfield parameters, unpublished].

By choosing the threefold rotation axis as the *z*-axis, the O_h CF potential is described by the parameters B_0^4 , B_3^4 , B_0^6 , B_3^6 and B_6^6 , among which only B_0^4 and B_0^6 are independent parameters, since the B_3^4/B_0^4 , B_3^6/B_0^6 , and B_6^6/B_0^6 ratios are symmetry restricted. [*C. Görller-Walrand and K. Binnemans, Rationalization of crystal-field parametrization, Handbook on the Physics and Chemistry of Rare Earths vol 23, eds. K. A. Gschneidner Jr. and L. Eyring (Amsterdam: North-Holland), 1996.*] Obtained SOM values for B_0^4 and B_0^6 were 1603.14 cm⁻¹ and 75.58 cm⁻¹, respectively. Attempts of least square minimization fits of the experimental 16*a* Yb³⁺ energy levels (0 cm⁻¹, 290 cm⁻¹, 410 cm⁻¹ and 1069 cm⁻¹, of the ²F_{7/2} multiplet, and 10323 cm⁻¹, 10413 cm⁻¹ and 11161 cm⁻¹ of the excited ${}^{2}F_{5/2}$) to the calculated ones by using as starting CFPs the above trigonal set with SOM derived values were unsuccessful. Furthermore, the fit was also attempted by using as starting CF parameters the trigonal B_{0}^{2} , B_{0}^{4} , B_{3}^{4} , B_{0}^{6} , B_{3}^{6} and B_{6}^{6} set indicated for 16*a* Yb³⁺ in the Na₃Sc₂V₃O₁₂ garnet, [*Liu et al, Phyl. Magazine 88, 3075, 2008*] also with unsuccessful result.

Alternatively, if the fourfold rotation axis is chosen as the *z*-axis, the octahedral CF potential is described by the parameters B_0^4 , B_4^4 , B_0^6 and B_4^6 , with B_0^4 and B_0^6 being the independent parameters, and the relationships $B_4^4/B_0^6 = \sqrt{5/14}$ and $B_4^6/B_0^6 = -\sqrt{7/2}$. By using the SOM values of this set of CF parameters the least squares minimization fit seemed to be much better than previously with the threefold axis as *z*-axis. Taking into account that the tetragonal bipyramid, with symmetry D_{4h} , is the higher symmetry polyhedron with coordination number CN=6 which can be considered as a distortion of the octahedron, and whose CF potential is described by tetragonal CF parameters, the following step was to include in the fitting process the effect of the additional B_0^2 to the earlier set of O_h CF parameters, to describe the D_{4h} CF potential, now with all CF parameters freely varying. All the 6 K experimentally determined 16a Yb³⁺ energy levels of CNGG were perfectly reproduced by using the set of D_{4h} CF parameters included in the Table 1 of the main text.

This centrosymmetric D_{4h} potential can be understood as the actual distortion of an "ideal" O_h octahedral symmetry around Yb³⁺, by the removal of the C₃ symmetry axis, an effect that could be associated with some local modification, due to the structural disorder, in the neighborhood of the 16*a* Yb³⁺ site in this host.

(iii) $^2\!F_J$ crystal field splitting and the barycenter law

The ${}^{2S+1}L_J$ CF energy splitting, ΔE_J , was been shown to be linearly proportional to the scalar CF strength parameter N_J defined as [F. Auzel et al, *J. Physique*, 44, 201, 1983]

$$N_{j} = \left[\sum_{k} \sum_{q} \left(B_{q}^{k}\right)^{2} \frac{4\pi}{2k+1}\right]^{1/2}.$$
[1]

For the particular case of Yb³⁺, $\Delta E({}^{2}F_{7/2})= 0.261 \times N_{7/2}$ holds. [P. Haumesser et al., J. Phys.: Condens. Matter 13, 5427 2001]

Using the CF parameters determined in Table 1, $N_{7/2}$ = 3569 cm⁻¹ is obtained for the CF strength of the 16*a* octahedral Yb³⁺ center in the 0.3at%Yb:CNGG crystal. This corresponds to a theoretical $\Delta E(^{2}F_{7/2})$ = 931 cm⁻¹ which, taken into account that the constant relating ΔE_{J} and N_{J} is sensitive to the equidistance of the mJ sublevels,[*P*. *Haumesser et al., J. Phys.: Condens. Matter 13, 5427 2001*] supposes a good approximation of the 1069 cm⁻¹ experimental value determined, and in any case it confirms the high CF strength on Yb³⁺ in the octahedral CNGG center.

Another test of confidence on the determined mJ levels is provided by the "barycenter law". [*P. Haumesser et al, J. Phys.: Condens. Matter 13, 5427, 2001*] It establishes a linear relationship between the barycenters (\bar{E}) of the energy positions of

mJ levels of different ^{2S+1}L_J multiplets. For the Yb³⁺ case it reads as \bar{E} (²F_{5/2})= 10080 + 0.95 \bar{E} (²F_{7/2}). This law is represented in Fig. ESI.7 along with the position of a large number of ionic compounds, including the position corresponding for the octahedral 16*a* Yb³⁺ center in CNGG which mJ energy levels were given in Table 1 of the main text.



Fig. ESI.7 Plot of the barycenter energies of ${}^{2}F_{5/2}$ versus ${}^{2}F_{7/2}$ multiplets for several Ybdoped crystals (black diamonds). The line is a visual help. The red circle corresponds to the octahedral 16*a* Yb³⁺ center of the CNGG crystal.

For reference, Tables ESI.1 and ESI.2 provide values of ${}^{2}F_{J}$ splittings and barycenters for sexquioxides (Lu₂O₃) and garnets, respectively. In the first case including the comparison between centers with (C_{3i}) and without (C_{2}) center of symmetry.

Table ESI.1 Values of splittings and barycenters (in cm⁻¹) of six-fold oxygen coordinated Yb³⁺ for ${}^{2}F_{7/2}$ (0, 1, 2, 3) and ${}^{2}F_{5/2}$ (0', 1', 2') levels in C_{2} and centrosymmetric C_{3i} centers of Lu₂O₃ [*Y. Guyot et al J. Lumin. 170, 513, 2016*]

| Site symmetry | ² F _{7/2} | | ${}^{2}F_{5/2}$ | |
|-------------------|-------------------------------|------------|-----------------|------------|
| | Splitting | Barycenter | Splitting | Barycenter |
| C_2 | 988 | 463 | 820 | 10620 |
| $C_{3\mathrm{i}}$ | 1193 | 588 | 1073 | 10738 |

Table ESI.2 Comparison of splitting and barycenter values (in cm⁻¹) of ${}^{2}F_{7/2}$ (0, 1, 2, 3) and ${}^{2}F_{5/2}$ (0', 1', 2') Yb³⁺ levels in octahedral CNGG site and in the usually determined dodecahedral garnet site for YAG= Y₃Al₅O₁₂, YbAG= Yb₃Al₅O₁₂, LuAG= Lu₃Al₅O₁₂, GGG= Gd₃Ga₅O₁₂, YGG= Y₃Ga₅O₁₂ and YbGG= Yb₃Ga₅O₁₂. Ref 1 : [*G. A. Bogomolova et al, Sov. Phys. JETP 42, 440, 1976*]. Ref 2: [*R. A. Buchanan et al, Phys. Rev. 159, 245, 1967*]. Ref. 3: [*A. Brenier et al, J. Opt. Soc. Am. B 23, 676, 2006*]. Ref. 4: [*Liu Hong-Gang et al, J. Lum. 131, 2690, 2011*]. Ref 5: [*Y. Guyot et al, Opt. Mater. 27, 1658, 2005*].

| Garnet host | ² F _{7/2} | | ² F _{5/2} | | Reference |
|----------------|-------------------------------|------------|-------------------------------|------------|-----------|
| | Splitting | Barycenter | Splitting | Barycenter | |
| YAG | 785 | 490.5 | 352 | 10543.3 | 1 |
| YAG | 782 | 500.8 | 353 | 10538.3 | 2 |
| YAG | 786 | 496.5 | 600 | 10629.3 | 3 |
| YbAG | 766 | 521.3 | 352 | 10549.3 | 4 |
| LuAG | 762 | 499.3 | 570 | 10625.0 | 3 |
| GGG | 657 | 414.8 | 502 | 10567.3 | 5 |
| YGG | 642 | 446 | 428 | 10546.0 | 1 |
| YbGG | 624 | - | 434 | 10559.7 | 2 |
| CNGG | 1069 | 442 | 838 | 10632 | This work |