Experimental report

31/05/2017

Proposal:	**5-11-417**	**Council:**	4/2016

Title: Determination of lithium positionsin the crystal structure of lithium-modified $Ca_3Nb_2Ga_3O_{12}$ laser garnet

Research area: Materials

This proposal is a new proposal

Main proposer: **Concepcion CASCALES**

Experimental team: Concepcion CASCALES

Local contacts: Maria Teresa FERNANDEZ DIAZ

Samples: $Ca_3Li_{0.275}Nb_{1.775}Ga_{2.95}O_{12}$

Instrument	Requested days	Allocated days	From	To
D9	5	5	20/06/2016	25/06/2016

Abstract:

Disordered Yb:$Ca_3Nb_{1.5}Ga_{3.5}O_{12}$ (CNGG) garnets are ultrashort pulse lasers due to the relatively broad Yb emission bandwith. In the Ia-3d garnet structure Ca occupies 24c sites, and Nb and Ga are mainly in 16c and 24d, furthermore, to maintain charge neutrality, vacancies in the three positions as well as antisited Nb and Ga are present. Yb replaces Ca, and the diverse site substitutions with cations of different size and charge around YbO_8 offers the possibility of a record broadening of Yb optical bands. However, the Yb incorporation into CNGG is limited by the electric charge mismatch with Ca. This incorporation is favored by doping with monovalent alkalis, i.e., 2 Ca substituted by a pair A-Yb. Notwithstanding the relevance of Li-modified Yb:CNGG (CLNGG) crystals, which support laser pulses as short as 55 fs, there is not a experimentally confident structural model for cations and vacancies distributions in CLNGG. Thus, precise D9 neutron diffraction data are expected to clarify questions concerning the nature of Li sites and the relative cationic contents over crystal sites. This model will guide future modifications to enhance the Yb optical bandwidth beyond the present limits

Today there is a large scientific and industrial effort to produce compact and energetic solid state lasers in the sub 100 fs pulse duration domain (often named as "ultrashort" pulsed laser) at affordable prices, which would allow their widespread use in industrial (cutting and welding), medical (diagnosis and surgical knife) and environmental (LIDAR and heritage restoration) fields. Such systems are most commonly envisaged as Yb^{3+}-doped crystals directly pumped by a diode laser. Since light pulse duration and pulse bandwidth are related by the quantum uncertainty principle, the main requirement of the Yb^{3+}-doped media is to have the broadest possible emission bandwidth along with favorable thermophysical properties. Yb^{3+} partially fulfilled this condition because its $4f^{13}$ electronic configuration is only weakly shielded from the interaction with the neighboring crystal lattice (at difference with other laser lanthanides). To extend the Yb^{3+} emission bandwidth beyond this the *disordered* crystal concept was developed.

Such disordered crystals are those having a large number of neighbor cationic distributions around Yb^{3+}, inducing a multiplicity of crystal field potentials, thus a near to continuous shift of the electronic levels of Yb^{3+} (even though Yb^{3+} may sit in a unique crystallographic site). Such distributions may be based on the change of the ionic radius of the cationic neighbors or in the change of their ionization state.

Different disordered crystals have been tested as Yb^{3+} hosts for ultrashort lasers. Our group has a extended experience on disordered double tungstate and double molybdate crystals and we have demonstrated pulses of 53 fs by modelocking of Yb^{3+}-doped $NaY(WO_4)_2$ crystals.[1] However, these crystals are tetragonal and have relatively poor thermal conductivity what limits the energy scalability. Many others of the disordered crystals developed are either optically uniaxial or biaxial, but for laser simplicity isotropic crystals are desirable. Our recent interest was focused in garnets with cubic crystal structure (space group $Ia\overline{3}d$) and large thermal conductivity, κ. The well known YAG ($Y_3Al_5O_{12}$) laser crystals is an example of this structure (κ= 10 W/mK, for undoped YAG).

In garnets with the general formula $\{M\}_3[N]_2(R)_3O_{12}$, $\{M\}$, $[N]$ and (R) being cations at dodecahedral (24*c*), octahedral (16*c*) and tetrahedral (24*d*) sites, respectively, Yb^{3+} enters exclusively in the dodecahedral position. Each YbO_8 dodecahedron shares edges with four other dodecahedra at ≈3.82 Å of distance, see their dense packing in Figure 1a, and it is also surrounded by four corner-sharing octahedra (16*a* site) at ≈3.49 Å, Figure 1b, and by six tetrahedra (24*d* site), two of them at ≈ 3.12 Å sharing edges and the four remaining linked by shared corners at ≈ 3.82 Å, see Figure 1c. This close packing offers the possibility of modifying the Yb^{3+} electronic levels, thus engineering the Yb^{3+} optical bandwidth, through different substitutions over the three crystallographic positions.

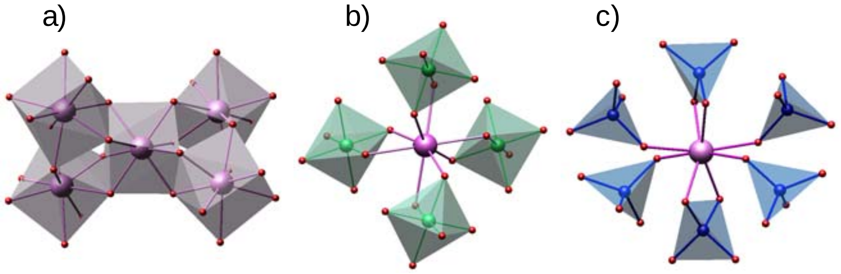

Figure 1. Cationic distributions around dodecahedral 24*c* sites occupied by Yb^{3+} in cubic garnets. (a) Nearest cations at dodecahedral 24*c* sites. (b) Nearest cations at octahedral 16*a* sites. (c) Nearest cations at tetrahedral 24*d* sites.

A drastic change over Yb^{3+} electronic levels is found with heterovalent substitutions. A remarkable example of this is the $Ca_3Nb_{1.5}Ga_{3.5}O_{12}$ (CNGG) crystal family, which hosts Ca^{2+} and Nb^{5+} on dodecahedral and octahedral sites, respectively. In order to maintain charge neutrality, the crystal also contains cationic vacancies in the three positions as well as antisited Nb^{5+} and Ga^{3+}, i.e. Nb^{5+} in 24*d* and Ga^{3+} 16*c* sites. The large number of site substitutions with cations of different ionic radii and charges give rise to a record broadening of the Yb^{3+} optical bands, however Yb^{3+} incorporation to the host is limited by electric charge mismatch induced by the substitution of Ca^{2+} by Yb^{3+}.

Yb^{3+} incorporation into the CNGG garnet lattice is favored by further doping with monovalent alkali cations, i.e. two Ca^{2+} substituted by one monovalent alkali cation plus one Yb^{3+}. In fact, Li^+-modified CNGG (CLNGG) crystals are known for some time, and very recently we have demonstrated for the first time the growth and optical properties of Na^+-modified CNGG (CNNGG) crystals.[2] Despite Na^+ and Li^+ are close alkali ions, their role in the CNGG structure and derived properties seems to be rather different. In the literature it is commonly assumed that Li^+ fills cationic vacancies at the octahedral and tetrahedral sites (although there is not direct experimental evidence of such assumption), while Na^+ occupies dodecahedral sites (as documented by us in Ref. 2 based on single crystal X-ray diffraction technique).

The relevance of Yb^{3+}-doped CLNGG crystals is demonstrated by the fact that laser pulses as short as 55 fs with 60 mW of average power were obtained directly from a SESAM drove oscillator cavity. Furthermore the direct comparison of the cw laser properties of Yb^{3+}-doped CNGG and Yb^{3+}-doped CLNGG crystals shows smaller pump laser threshold and larger output powers and slope efficiencies in the latter crystals.[3]

As a first effort to understand the effect of the different crystal environments on the Yb^{3+} electronic levels, some preliminary spectroscopic experiments have been already conducted by us. The electronic configuration of Yb^{3+} is simply constituted by two multiplets, ground $^2F_{7/2}$ and excited $^2F_{5/2}$, split by the crystal field into 4 and 3 Stark energy levels, respectively. At room temperature electronic transitions from several Stark levels of the ground multiplet to the excited multiplet, $^2F_{7/2}(0, 1, 2, 3) \rightarrow {}^2F_{5/2}(0', 1', 2')$, can be observed, moreover most of these transitions are phonon assisted, giving rise to a spectrum rich in bands, so room temperature spectroscopy is of little utility for investigation of the Yb sites. However, at low temperatures (< 10 K) only the ground $^2F_{7/2}(0)$ level is populated and the optical absorption spectrum shows a well resolved $^2F_{7/2}(0) \rightarrow {}^2F_{5/2}(0)$ band for each Yb^{3+} center present in the crystal. Figure 2 shows the comparison of such optical absorption of low (0.3at%) Yb^{3+}-doped CNGG, 8at% Yb^{3+}-doped CNGG and 8at% Yb^{3+}-doped CLNGG crystals. The coexistence of several Yb^{3+} main centers is observed in all cases.

To discern the origin of the spectral contributions to the Yb^{3+} bandwidth we envisaged a procedure that combines the analysis of the above Yb^{3+} $^2F_{7/2}(0) \rightarrow {}^2F_{5/2}(0')$ transition of CNGG and CLNGG garnets (including low temperature optical absorption and selectively excited photoluminescence spectra as well as Yb^{3+} lifetime measurements) with a structure-based modeling of Yb^{3+} crystal field interactions in these disordered hosts. Although some attempts were made in the past for such Yb^{3+} CLNGG optical bandwidth modeling, they lacked an accurate crystallographic basis to establish the distribution of cations and their occupancies over available crystal sites.[4,5]

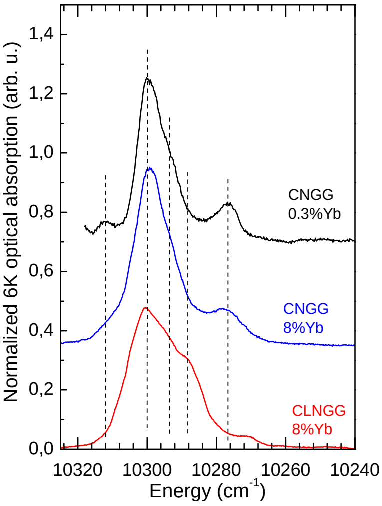

Figure 2. 6 K optical absorption of the $^2F_{7/2}(0) \rightarrow {}^2F_{5/2}(0')$ transition of Yb^{3+} in several Ca-Nb-Ga garnets: 0.3at% Yb:CNGG (black line); 8at% Yb:CNGG (blue line); 8at% Yb:CLNGG (red line).

A previous structure refinement using single crystal X-ray diffraction (scXRD) data of CLNGG was performed in the cubic space group $Ia\bar{3}d$, and the final refinement cycle leading to the lowest discrepancy factor R_1 $[I>2\sigma(I)] = 0.0116$ included along with the unit cell parameter and oxygen positional coordinates the occupancy factors of Ca^{2+}, Nb^{5+} and Ga^{3+} over available 24*c*, 16*a*, and 24*d* garnet crystal sites. However, from these scXRD data the determination of a reliable location of Li^+ ions in the garnet structure is not possible. Fitting attempts considering 16*a* sites, in fact almost fully occupied by Nb^{5+} and Ga^{3+} cations, do not provide conclusive results. Moreover, taking into account the previously observed non negligible concentration of vacancies over 24*d* sites in the CNGG crystal structure,[2] any attempt of structure refinement introducing a Li^+ population in this site is uncertain using scXRD data.

The purpose of the experiment using the D9 diffractometer was to solve the above structure uncertainty by determining the site(s) and occupancy factor(s) of Li^+ in the garnet lattice. For this experiment single crystal samples with two sizes (~3x3x3 mm^3 and ~3x1.7x1.6 mm^3), from a large Czochralski grown crystal with nominal composition $Ca_3Li_{0.275}Nb_{1.775}Ga_{2.95}O_{12}$, were provided. The first crystal was discarded after an initial test. With the smallest CLNGG crystal complete sets of reflections at room temperature (1396 integrated reflections, $-10 \leq h \leq 22$, $-10 \leq k \leq 22$, $-2 \leq l \leq 22$, from which 334 unique reflections) and at 20 K to minimize de Li^+ delocalization (1651 integrated reflections, $-19 \leq h \leq 22$, $-19 \leq k \leq 22$, $-3 \leq l \leq 22$, from which 401 unique reflections) were collected (λ=0.84090 Å). After the integration of reflections, a serious problem of extinction was detected in the crystal, even for 20 K data. Thus neither Fourier analysis nor tentative Rietveld profile refinements by using previous scXRD data were able to yield reliable structure data. It is expected that the crystal structure of CLNGG will be solved by applying extinction corrections and by using power neutron diffraction data.

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