Nd³⁺-doped Ca₃Ga₂Ge₃O₁₂ garnet: A new optical pressure sensor

U. R. Rodríguez-Mendoza,¹,a S. F. León-Luis,¹ J. E. Muñoz-Santiuste,² D. Jaque,³ and V. Lavin¹

¹Dpto. de Física Fundamental y Experimental, Electrónica y Sistemas, and MALTA Consolider Team, Universidad de La Laguna, 38200 San Cristóbal de La Laguna, Santa Cruz de Tenerife, Spain
²Dpto. de Física Aplicada, and MALTA Consolider Team, Escuela Politécnica Superior, Universidad Carlos III de Madrid, Avda. del Mediterráneo, 28913 Leganés, Madrid, Spain
³CGIEL, and Departamento de Física de Materiales, Facultad de Ciencias, Universidad Autónoma de Madrid, 28049 Cantoblanco, Madrid, Spain

(Received 23 January 2013; accepted 20 May 2013; published online 7 June 2013)

A pressure-induced shift of the emission spectrum corresponding to the near infrared $^{4}F_{3/2} \rightarrow ^{4}I_{9/2}$ transition of Nd³⁺ ions in a calcium gadolinium germanium garnet was obtained in the interval from ambient conditions up to 23 GPa in order to test its suitability as an optical pressure sensor. Although several Nd³⁺ non-equivalent centers are present in this garnet, which complicates the assignation of the optical transitions, the $R_1, R_2 \rightarrow Z_5$ transitions are unequivocally characterised and fit the requirements of an ideal optical pressure sensor. Results obtained for these emission peaks indicate large pressure coefficients of $-8.8$ and $-10.8$ cm⁻¹ GPa⁻¹; meanwhile, the rest of the $R_1, R_2 \rightarrow Z_1$ emissions remain almost unchanged under pressure. This behaviour is ascribed to the influence of the crystal-field at high pressure on the $Z_5$ Stark level of the ground state and can be easily reproduced exclusively by varying the cubic term of fourth rank of the crystal-field Hamiltonian, which accounts for the Nd³⁺ ions and is related to medium Nd³⁺-oxygen distances. These coefficients are larger than those found for the R-lines of Cr³⁺ in ruby, $-7.56$ cm⁻¹ GPa⁻¹, suggesting that this system may be a good candidate for a luminescence pressure sensor.

© 2013 AIP Publishing LLC. [http://dx.doi.org/10.1063/1.4809217]

I. INTRODUCTION

Matter under extreme pressure and/or temperature conditions is the subject of multidisciplinary studies that join diverse fields as physics, chemistry, geology, material science, microbiology, or food technology.¹⁻⁴ One of the fundamental goals of the high pressure technique is to mimic processes and phenomena that occur in the interior of the Earth and other planetary objects, such as phase transitions, chemical reactions, or microbiological activity, and to understand their physical, chemical, geological, and biological foundations and implications. In particular, the high pressure technique applied to optical spectroscopy provides a number of advantages over other techniques at ambient pressure conditions.³,⁴ On one hand, it provides a unique insight into the electronic structure and optical properties of materials doped with transition metals or rare earth ions, since it can vary the structure, the coordination environment and, consequently, the electric, magnetic, vibrational, and optical properties. On the other hand, by reducing the volume of the sample, it allows a wide range of structures and bindings of a particular chemical composition to be studied.³,⁴

Solid material can be compressed at high pressure with the help of an anvil cell.¹,² Choosing the type of anvil cell depends on the pressure range required. The most commonly used are sapphire, moissanite, and, especially, diamond. These devices allow a variety of optical, electrical, X-ray, and other studies over a wide range of the electromagnetic spectrum to be carried out at low and high temperature and high magnetic fields. A pre-indent metal gasket with a centred hole, together with both anvils, constitutes the hydrostatic chamber in which the sample, the hydrostatic medium, and the pressure sensor should be inserted. In order to achieve very high pressures, this chamber should be very small, typically 100 μm in diameter and 50 μm in height. The choice of the hydrostatic medium depends both on its chemical reactivity with the sample and on its hydrostaticity range. The determination of the pressure inside the hydrostatic sample chamber of the cell requires a calibrated standard. It is quite common to determine the working pressure through an in situ, indirect measurement of the calibrated pressure-sensitive luminescence of an optically active ion, i.e., transition metal or rare earth, in a micro-sized crystalline host located in the sample chamber.

The ideal optical pressure sensor for high pressure techniques needs to meet some general requirements, described by Barnett et al.⁵ as: (i) a single emitting line; (ii) with no significant broadening or weakening and little or no surrounding background; (iii) with a large shift with pressure $\Delta l/dP$; (iv) a small temperature dependent line shift $\Delta l/dT$; (v) for high sensitivity and precision, its linewidth $\Gamma$ should be small compared to the line shift, i.e., low $\Gamma^{-1}d\Delta l/dP$ factor; and, finally, (vi) the host lattice should be highly stable at high pressures and temperatures.

The most commonly used luminescence pressure sensor is the Cr³⁺:Al₂O₃ crystal (ruby),³,⁴,⁶ monitoring the wavelength red-shift of the lower energy $R_1$ emission line ($^{4}E \rightarrow ^{4}A_2$) with pressure. Its strong luminescence efficiency at around 700 nm
and the strong line shift relative to its linewidth that occurs when pressure is increased are its most important features. Moreover, it can be easily measured by exciting with commercial lasers (Ar⁺, violet and blue laser diode, or green diode-pumped solid state laser) and recorded with a conventional highly efficient photomultiplier tube. However, it has several drawbacks: temperature-induced broadening, which produces a strong overlap with the emission from the R2 line; luminescence quenching, which limits its application to below 500 °C; low pressure sensitivity below 1 GPa, a range especially important for life-related high pressure research; the signal overlap of the sample’s luminescence with the strong luminescence of ruby; and finally, the need to change the detector if the emission of the sample lies in other spectral range than the sensor. Thus, new sensors should resolve these problems, while preserving the advantages of ruby.

Due to all these requirements, special attention has been paid to rare-earth based sensors because the shielding of the 4f-electrons produces very sharp absorption and emission lines in the UV-VIS-near-infrared (NIR) optical range that are less sensitive to the environment compared to those of the 3d electrons of Cr³⁺. In this sense, the luminescence in systems such as Nd³⁺:doped YAlO₃ have been tested in the NIR range, studying the pressure shifts of the R₂ → Z₂ line of the ⁴F₉/₂ → ⁴I₀/₂ transition. Particularly interesting are the high pressure studies carried out in 1990s by Hua et al. in Nd³⁺:doped yttrium gadolinium (YAG), gadolinium gallium garnet (GGG), and gadolinium scandium gallium (GSGG) garnets, the latter co-doped with Cr³⁺, in which special attention was paid to the R₁,R₂ → Z₁ lines of the ⁴F₉/₂ → ⁴I₀/₂ transition. More complete high pressure studies were later carried out on similar garnets doped with Nd³⁺, in particular lanthanum lutetium gallium garnets (LLGO), gadolinium GSGG co-doped with Cr³⁺, yttrium aluminium garnets (YAG), and gadolinium gallium garnet (GGG), focusing on the R₁,R₂ → Z₁ lines of the ⁴F₉/₂ → ⁴I₀/₂ transition, where sensor applications have been found. Moreover, in the latter study, an extensive analysis of the crystal-field interaction in the environment of the rare earth ion was carried out.

In this paper, we study the high pressure luminescence properties of Nd³⁺ in a calcium gallium germanium garnet crystal (Nd³⁺:CGGG), analysing in detail the ⁴F₉/₂ → ⁴I₀/₂ emission. The advantage of this crystal over other garnets is that it possesses a lower melting point and is therefore less expensive to manufacture. The study of the evolution of its NIR emission spectrum when pressure increases, particularly the R₁,R₂ → Z₁ lines of the ⁴F₉/₂ → ⁴I₀/₂ transition, indicates that this crystal can be used as a pressure sensor in the NIR.

II. EXPERIMENTAL

The Nd³⁺:doped Ca₃Ga₂Ge₃O₁₂ (Nd³⁺:CGGG) crystal was grown by the Czochralski technique. The luminescence of the Nd³⁺ ions was excited either by the 488 nm line of an Ar⁺ laser (Spectra Physics 2065A-66 Beamlok) or the radiation of a 532 nm diode-pumped solid state laser and recorded using a 0.75 m single grating monochromator (Spex 750M) equipped with a cooled NIR extended photomultiplier (Hamamatsu R-5102), and using the lock-in technique (EG&G Princeton Applied Research model 5210). High pressure was generated with a miniature diamond anvil cell (mini-DAC) designed at The University of Paderborn (Germany). Four different high pressure experiments were performed in sample chambers of typical dimensions of Ø = 150 μm and h = 70 μm using ~10 μm ruby chips as pressure calibrant. A 16:4:1 methanol-ethanol-water mixture served as pressure medium, providing hydrostatic pressures of up to ~15 GPa. Low temperature experiments between 77 K and room temperature were achieved by mounting the mini-DAC in a continuous closed He cycle cryostat (PC202 AF Advanced Research System ARS).

III. RESULTS AND DISCUSSIONS

A. Ambient- and high-pressure luminescence

For optical applications, it is of particular interest to analyse the local structure around the rare earth ions in the matrix, since it rules the fine structure splitting of the free-ion multiplets and the forced intra-configurational 4f-4f electric-dipole transition probabilities. Garnet crystals belong to the 1a-3d cubic space group and have the general chemical formula A₃B₂C₃O₁₂, where A denotes the dodecahedral, B the octahedral, and C the tetrahedral sites in the lattice. For the Nd³⁺:Ca₃Ga₂Ge₃O₁₂ (CGGG) crystal, the Ca³⁺ ions are located in dodecahedral sites, and the Ga³⁺ and Ge³⁺ ions occupy octahedral and tetrahedral sites, respectively. The Nd³⁺ ion substitutes the Ca²⁺ ion in the dodecahedral site, and is surrounded by 8 oxygen ligands with a distorted cubic symmetry that will rise to a real D₂ orthorhombic local site symmetry. Moreover, the excess charge of the Nd³⁺ ions can be compensated by substituting Ge⁴⁺ ions with Ga³⁺ ions, as suggested by Eskov et al. Up to six different non-equivalent sites for the Nd³⁺ ions will be generated. Therefore, the crystal-field interaction acting on the Nd³⁺ ions has such a low symmetry that it will completely lift the degeneracy of the 2S+1L₁ multiplets of the free-Nd³⁺ ion energy level diagram and split them into J+1/2 crystal-field, or Stark, levels according to the double Kramer degeneracy. The energy level scheme of the Nd³⁺ ion is very similar for the family of garnet crystals (see Fig. 1), and no large changes in energy are expected for the Stark levels involving the ⁴F₉/₂ → ⁴I₀/₂ transition of interest for a pressure sensor.

The starting point is the double cubic group, which splits the ground ⁴I₀/₂ term in three levels, whose irreducible representations are denoted by Γ₆+2Γ₈, while keeping the lowest emitting ⁴F₉/₂ level as a singlet, denoted by Γ₈ (see Fig. 1). The orthorhombic distortion, superimposed on the main cubic field, lifts the remaining degeneracy and each Γ₈ level splits into two Stark doublets. As a result, the Γ₈(⁴F₉/₂) singlet splits into the R₁ and R₂ Stark levels, and the ⁴I₀/₂ state appears structured as four levels (Z₁ to Z₄), paired two on two (coming from 2Γ₆), with the last Z₂ Stark level (coming from Γ₈) slightly further away. The energy level scheme is depicted in Fig. 1, taking the Z₁ as the zero energy reference Stark level.

In this context, up to ten peaks may appear for each non-equivalent site, corresponding to transitions from the two Rₙ Starks of the ⁴F₉/₂ state to the five Zₗ Stark levels of...
the $^4I_{9/2}$ ground state, which may complicate the resolution of the peaks and the identification of the transitions. At ambient conditions, two main parts of the luminescence spectrum can be distinguished (see Fig. 2): the first, ranging from 11 000 cm$^{-1}$ to 11 600 cm$^{-1}$ has a complex structure of peaks; and the second, composed of two high intensity peaks red-shifted from the rest around 300 cm$^{-1}$ and easily identified as the $R_1, R_2 \rightarrow Z_j$ transitions.

Due to the fact that the $R_1$ and $R_2$ Stark levels are as close in energy as 100 cm$^{-1}$ at ambient pressure, they can be treated as thermalized levels. Thus their relative populations follow a Maxwell-Boltzmann distribution, which predicts that the population of the $R_2$ upper level will decrease when the temperature decreases, and consequently a quenching of the intensity of the $R_2$ emissions is expected respect to that of the $R_1$ emissions. Taking advantage of this feature, low temperature spectra were measured in order to identify those transitions associated to the $R_1$ and $R_2$ emissions by simply comparing the emission spectra of the $^4F_{3/2} \rightarrow ^4I_{9/2}$ band at RT and at 77 K, both at ambient pressure (see Fig. 2). The quenching of the intensity of the bands corresponding to the $R_2 \rightarrow Z_j$ emissions is clearly observed for the low temperature spectrum, which allows us to identify all the $R_i \rightarrow Z_j$ transitions.

Moreover, slight differences can also be observed in the position and linewidths of these bands as a function of temperature. It is worth noting that despite the six non-equivalent sites found for the Nd$^{3+}$ ions in the CGGG garnet structure, the emission spectra of these transitions do not change significantly with the excitation pumping wavelength, after testing with four different lines of the Ar$^+$ laser and a 532 nm laser diode radiation. Thus the average positions at ambient conditions have been selected in order to elaborate a partial energy diagram (see Fig. 1).

The room temperature emission spectra of the Nd$^{3+}$ ions in the CGGG garnet crystal associated with the $^4F_{3/2} \rightarrow ^4I_{9/2}$ transition are presented in Fig. 3 as a function of pressure from ambient conditions up to 23 GPa. It is worth noting that inhomogeneous broadening increases for all the emission peaks above 15 GPa, which can be associated with the initial stages of loss of the hydrostatic condition of the transmitting medium in the pressure chamber, checked by analysing the broadening of the ruby lines. This fact, along with the overlapping of the $R_{1,2} \rightarrow Z_j$ ($j = 1-4$) transitions, makes the identification of the emission peaks at high pressure a difficult task. However, the main feature is that the most sensitive transitions to pressure are those between the $R_1$, $R_2$, and the
Z₅ Stark levels, which show significant red-shifts, meanwhile the rest of the transitions do not change significantly, except the R₂→Z₁ which has a slight red-shift. The Stark energy levels of the ⁴I₉/₂ ground state obtained from the emission spectra under pressure. Solid lines are obtained by superimposing a constant orthorhombic splitting (~100 cm⁻¹) to the Γ₉ cubic energy levels (see text for details).

B. Crystal-field analysis

The shifts of the emission peaks of the Nd³⁺ ion can be correlated to variations in the energies of the ⁴S⁺¹L₉ states and their hyperfine structure with pressure. Microscopically, these pressure-induced changes are related to variations of three major interactions, i.e., the Coulomb repulsion and the spin-orbit coupling, mainly responsible for the shift of the barycenters of the ⁴S⁺¹L₉ multiplets, and the crystal-field (CF) interaction, which accounts for the breakdown of the degeneracy of the multiplets into the Stark levels and the optical properties of the rare earth ion in the solid.¹⁹

The CF theory describes the inter-electronic interaction between the electrons of the inner 4f shell of the rare earth ion and the charge of its host ligands, all distributed in a particular local point symmetry. Rare earth ions are properly described in the weak-field limit by using a one-electron CF Hamiltonian, in which a small group of phenomenological parameters allow to reproduce the rare earth energy level diagram. In the framework of the Racah algebra, these phenomenological parameters are numeric coefficients that multiply the tensor operators. This interaction can be described as follows:²⁰

\[
H^{(\text{Even})}_{\text{CF}} = \sum_{k} B^{k}_q (C^{(k)}_q) = \sum_{k} \sum_{q=2}^{q=6} B^{k}_q (C^{(k)}_q) + (-1)^q C^{(k)}_q

+ iB^{k}_q \left[ C^{(k)}_q - (-1)^q C^{(k)}_q \right],
\]

where real \(B^{k}_q\) and imaginary \(B^{k}_q\) CF parameters are radial integrals, while the angular components of the renormalized spherical tensor operators \(C^{(k)}_q\) can be precisely calculated with the help of the Racah algebra and the group theory.²⁰

When increasing pressure an enhancement of the CF interaction is expected and, in general, increased splitting of the multiplets is observed. In the description of the CF theory, it is useful to define a scalar, rotationally invariant parameter known as the overall CF strength parameter. According to Auzel et al.²¹,²² and Chang et al.,²³ it can be written as

\[
S = \left[ \frac{1}{3} \sum_{k} \frac{1}{2k+1} \left( |B^{k}_q|^2 + 2 \sum_{q=3/2}^{|q|} \left( |B^{k}_q|^2 + |B^{k}_q|^2 \right) \right) \right]^{1/2}.
\]

Roughly speaking, the maximum splitting of each ⁴S⁺¹L₉ multiplet depends linearly on the overall CF strength. For the D₂ symmetry at the Nd³⁺ sites in garnets, the CF Hamiltonian is

\[
H_{\text{CF}} = B^{0}_0 C^{0}_0 + B^{2}_2 (C^{2}_2 + C^{2}_2) + B^{4}_4 C^{4}_4 + B^{6}_6 (C^{6}_6 + C^{6}_6) + B^{8}_8 (C^{8}_8 + C^{8}_8) + B^{10}_10 (C^{10}_{10} + C^{10}_{10})
\]

with 9 real, non-vanishing CF parameters. However, adequate reproduction of the variation of the energy level positions under pressure is not possible due to the scarcity of available levels in the luminescence spectra measured. Thus, in order to describe the interaction between the rare earth ion and its oxygen ligands in garnets, it is often convenient to assume that the local environment of the rare earth ions is characterized by an orthorhombic distortion of a main cubic symmetry. Thus the complete (free ion + CF) Hamiltonian can be written as

\[
H = H_{\text{FREE-Nd}^{3+}} + \{ B^{k}_0 (C^{k}_0 ± \sqrt{5}/14 (C^{k}_{-4} + C^{k}_{4}))

+ B^{k}_0 (C^{k}_0 ± \sqrt{13}/2 (C^{k}_{-4} + C^{k}_{4})) \}_{\text{cubic}}

+ \{ B^{k}_2 (C^{k}_2 + C^{k}_2) + B^{k}_4 (C^{k}_{-2} + C^{k}_{2}) + B^{k}_6 (C^{k}_6 + C^{k}_6) + B^{k}_8 (C^{k}_{-6} + C^{k}_{6}) \}_{\text{non-cubic}}.
\]

where two contributions must be taken into account: the cubic symmetry component that can be represented by only the \(B^{0}_0\) and \(B^{10}_0\) CF parameters, since the \(B^{k}_0\) and \(B^{k}_0\) are then obtained by specific ratios,²⁰ and the non-cubic symmetry component that accounts for the real D₂ symmetry at the

FIG. 4. (Left) The dependence of the ⁴I₉/₂ cubic splitting on the cubic \(B^{4}_4\) and \(B^{6}_6\) CF parameters (solid lines) in the range of values of the overall CF strength for the CCGG garnet under study from ambient pressure up to 25 GPa. The dependence only on the \(B^{4}_4\) CF parameter (dotted lines) is also given. (Right) Stark energy levels (■) of the ⁴I₉/₂ ground state obtained from the emission spectra as a function of pressure are given in Fig. 4(right). In the framework of the Racah algebra, these

\[ \text{Pressure (GPa)} \]
\[ 0 \quad 5 \quad 10 \quad 15 \quad 20 \quad 25 \]
\[ \text{Energy (cm}^{-1}) \]
\[ 1000 \quad 600 \quad 400 \quad 200 \quad 0 \]
\[ 700 \quad 800 \quad 900 \quad 1000 \]
\[ \Gamma_6 \quad \Gamma_8 \quad \Gamma_8 \]
\[ \text{Cubic} \]
\[ Z_5 \quad Z_7 \quad Z_9 \]
Nd$^{3+}$ sites, and is governed by the appearance of other $B^k_0$ ($k = 2, 4, 6; -k \leq |q| \leq k; q$ even) CF parameters and the deviation from the cubic ratios of the resulting fourth and sixth rank CF parameters.

Although 11 real CF parameters appear in this Hamiltonian, seeming to be a more complicated point of view, this description has some evident advantages. As already mentioned, the cubic group splits the $^4I_{9/2}$ ground term into three levels, $\Gamma_6, 2\Gamma_8$, while keeping the lowest emitting $^4F_{3/2}$ level as a $\Gamma_8$ singlet (see Fig. 1). The superimposed non-cubic distortion removes the remaining degeneracy and each $\Gamma_8$ cubic-level splits into two Stark doublets to finally give five $^4I_{9/2}$ Stark $Z_j$ levels and two $^4F_{3/2}$ Stark $R_j$ levels (see Fig. 1). The main fact is that, since in a cubic symmetry the $^4F_{3/2}$ emitting multiplet of the Nd$^{3+}$ ion is still a singlet, the non-cubic part of the CF Hamiltonian must be directly responsible for the observed splitting of the $^4F_{3/2}$ state into the $R_j$ and $R_j$ Stark emitting levels (ruled by the second rank $B^2_0$ CF parameters). Thus, this splitting may be used as a rough measurement of the magnitude of the non-cubic distortion from the main cubic crystal-field.

Comparing the $R_1-R_2$ splitting at ambient conditions ($\sim 100 \text{ cm}^{-1}$) to the $^4I_{9/2}$ splitting ($\sim 800 \text{ cm}^{-1}$), we can estimate that the contribution to the overall CF strength of the non-cubic distortion is lower than 15% of the overall splitting and, therefore, the main contribution of the overall CF strength ($\sim 85\%$) comes from the cubic part of the CF Hamiltonian. Moreover, it can be observed that increasing pressure induces different rates of red-shifts of the $R_1, R_2 \rightarrow Z_3$ transitions (see Fig. 3), closing the energy gap between them from around $100 \text{ cm}^{-1}$ at ambient pressure to $50 \text{ cm}^{-1}$ at 23 GPa. This reduction of the Stark splitting of the $^4F_{3/2}$ multiplet can only be associated with the decrease of the orthorhombic distortion or, in other words, the CF symmetry over the Nd$^{3+}$ site in the garnet lattice becomes more cubic when pressure is increased. Similar results have been found by Hua et al. in various garnets. Thus, these facts allow us to make a simplified analysis of the pressure effect on the $^4I_{9/2}$ energy level position using only the cubic part of the CF Hamiltonian and disregarding the effect of the orthorhombic distortion.

In the garnet under study, the $Z_{1,4}$ Stark levels of the $^4I_{9/2}$ ground state show a very low sensitivity to pressure variations (see Figs. 3 and 4(right)), and their energy separations remain mainly constant, whereas there is a strong variation of the energy position of the $Z_3$ Stark level that points out larger splittings of the $^4I_{9/2}$ ground multiplet and stronger CF strengths felt by the Nd$^{3+}$ ions as the pressure increases. Although the energy positions of $R_j \rightarrow Z_j$ lines are related to all the CF parameters, due to the Nd$^{3+}$ environment’s abovementioned tendency toward cubic symmetry under pressure, an early analysis might be that the increase in overall CF strength at the Nd$^{3+}$ site must be associated primarily with variations in the cubic part of the CF Hamiltonian. In this framework, a small variation of the cubic $B^6_0$ CF parameter strongly changes the energy position of all $Z_j$ Stark levels, whereas only the energy position of the $Z_3$ Stark level appears to be particularly dependent on the fourth rank cubic part of the CF Hamiltonian. In fact, increasing the $B^6_0$ by around 50% over its ambient pressure value allows the observed behaviour under pressure of all the $R_j \rightarrow Z_j$ transitions, and hence of all the energy dependence of the $Z_j$ Stark levels, to be reasonably reproduced (see dotted lines in Fig. 4(left)).

In order to delve into this dependency, a brief look must be taken at the theoretical models describing the CF interaction. The simplest, and therefore rather unrealistic, description of the solid and its effect on the RE$^{3+}$ ion is the point charge electrostatic model (PCEM). The fundamental idea is that, associated with each ligand ion, there is a charge concentrated at the atomic position of the ligand, and the electrostatic field acting on every 4f electron of the rare earth ion is generated by this set of point charges. Therefore, the site symmetry of the local environment of the rare earth ion is taken into account through the lattice sum, and the resulting CF parameters are given by

$$
B^k_q = \sum_{L=1}^{N} (Ze)^2 \frac{(l^k)}{R^k_L} \sqrt{\frac{4\pi}{2k+1}} Y^*_{kq}(\theta_L, \varphi_L),
$$

where $(l^k)$ are the radial integrals of the rare earth ion wavefunction; $(Ze)_L$ represents the charge of ligands; $R_L$ their distance from the central rare earth ion; and the spherical harmonics $Y^*_{kq}(\theta_L, \varphi_L)$ describe the angular dependence.

According to Eq. (5), radial dependences in the form $1/R^{k+1}$ are expected for the $k$th rank CF parameters in the PCEM. Thus an increase of 50% in the cubic fourth rank CF parameter, which means a coupled increase of 76% in the cubic sixth rank CF parameter, translates to a disproportionate decrease of around 22% in the local volume of the RE$^{3+}$ ion, which is absurd for one of the hardest materials, the garnets, in the pressure range under study. This result has to be understood as a failure of the PCEM, which has many approaches, such as neglecting the finite extension of the charge densities of the ligands or the overlap of the wave functions of electrons 4f ions with those of the ligands. That is why the PCEM is taken only as a very rough approximation to the problem, especially for less ionic systems.

Much more realistic results in the simulation of the $^4I_{9/2}$ Stark level fine structure are obtained by using the Superposition Model. This model was developed to separate the geometrical and physical information contained in the CF parameters, which are expressed as a sum of individual contributions from the nearest ions in the host crystal lattice, each one being the product of a purely angular part and a radial part that depends on the rare earth-ligand (RE$^{3+}$-L) distance,

$$
B^k_q = \sum_{L} g_{k,q} g_{\mathbf{R}_L}(\theta_L, \varphi_L),
$$

where $g_{k,q}$ are normalized spherical harmonic functions, and $R_L, \theta_L, \varphi_L$ locate the position of ligand L in the lattice coordination environment. The so-called intrinsic CF parameter $B^k_q(R_L)$ is characteristic for a specific ligand type, and depends only on the distance between the RE$^{3+}$ ion and the ligand L. A power law dependence is usually assumed in the form.
\[ B_k(R_L) = B_k(R_0)(R_0/R_L)^t_k, \]

where \( R_0 \) is a specific or reference distance, and \( t_k \) are power law exponents that reflect the distance dependence of the RE\(^{3+}\)-L interaction.

For our simulation, we took a characteristic distance of \( R_0 = 2.3 \text{ Å} \) and intrinsic parameters \( B_k(R_0) = 980 \text{ cm}^{-1} \) and \( B_0^c = 575 \text{ cm}^{-1} \), since these values are quite similar to others reported for the Nd\(^{3+}\) ion with oxygen ligands.\(^{28}\) With these values and a cubic, eight-fold coordinated oxygen structure, it is easy to simulate the effect of pressure forcing a reduction of the RE\(^{3+}\)-L distances, while keeping the cubic angular positions fixed. Power law values of \( t_4 = 12 \) and \( t_6 = 6 \), previously reported for the Nd\(^{3+}\):YAG system,\(^{27}\) were used.

At ambient conditions, an Nd\(^{3+}\)-O\(^2-\) distance of 2.363 Å was used and \( B_0^c = -2200 \text{ cm}^{-1} \) and \( B_0^e = 870 \text{ cm}^{-1} \) were obtained, giving rise to an overall CF strength \( S = 682 \text{ cm}^{-1} \). Thus the ambient pressure \( t_4 \) in Pt cubic Stark levels are at 0 (\( \Gamma_8 \)), 240 (\( \Gamma_8 \)), and 770 (\( \Gamma_6 \)) cm\(^{-1}\), respectively (see Fig. 4(left)). On the other hand, the highest pressure conditions at 23 GPa were reached with a Nd\(^{3+}\)-O\(^2-\) distance of 2.278 Å, for which \( B_0^c = -3152 \text{ cm}^{-1} \) (an increase of \( \sim 50\% \)) and \( B_0^e = 1041 \text{ cm}^{-1} \), resulting in an overall crystal-field strength \( S = 994 \text{ cm}^{-1} \) and \( t_4 \) in Pt cubic Stark levels at 0 (\( \Gamma_8 \)), 281 (\( \Gamma_8 \)), and 976 (\( \Gamma_6 \)) cm\(^{-1}\). The energy shifts of the \( t_4 \) cubic Stark levels with pressure can be followed from ambient pressure up to 23 GPa as a function of the overall CF strength in Fig. 4(left, solid lines).

The relevant results of this pressure simulation in the energy range of the \( t_4 \) splitting in garnet under study can be directly compared with the pressure dependence of the \( Z_5 \) Stark energy positions obtained from the emission spectra in the Nd\(^{3+}\):CGGG garnet under pressure. Inside the depicted overall CF strength range (700–1000 cm\(^{-1}\)), the similar behaviour of the \( \Gamma_6 \) Stark level energy position versus \( S \) with those of the pressure dependence of \( Z_5 \) energy position becomes evident. Obviously, because the non-cubic distortion has not been taken into account, which contributes with around 100 cm\(^{-1}\) (the R lines total splitting), the calculated values of the overall cubic CF strength, and hence the calculated \( t_4 \) cubic splitting, must be overestimated in some way (\( \sim 5\%–10\% \) appears reasonable value). In fact, assuming a fixed orthorhombic splitting of around 100 cm\(^{-1}\) added to both \( \Gamma_8 \) cubic levels in Fig. 4(right), the obtained pressure dependence of \( t_4 \) level positions is properly reproduced.

With the selected power law values (\( t_4 = 12 \), \( t_6 = 6 \)), the variation range of the overall CF strength obtained for cubic calculations (700–1000 cm\(^{-1}\)) corresponds to a distance reduction of 3% and a relative volume reduction of \( \Delta V/V = 8.5\% \). Taking into account the overestimation related to the non-cubic distortion, we can estimate a more reliable and reasonable distance reduction of 2.2%, entailing a relative volume reduction of \( \Delta V/V = 6.5\% \).

In summary, under compression, the overall strength of the crystal-field increases, the second-order parameters (and the R-lines splitting) decrease and the ratios of CF parameters become more cubic. Moreover, the cubic \( B_0^c \) parameter appears to be mainly responsible for the pressure increase of the energy gap between the \( Z_5 \) Stark level and the other \( Z_{1,4} \) levels.

### C. Optical pressure calibration

To use the energy positions of the \( R_1R_2 \rightarrow Z_5 \) peaks of the Nd\(^{3+}\) ion in the CGGG garnet as an indirect measurement of the pressure in the hydrostatic chamber, linear and quadratics fits were carried out in order to obtain a scale in the range of pressures achieved in this work. The results are shown in Table I and, although the quadratic equation provides better fits than linear fits, the latter is used to compare the results of this garnet with the Nd\(^{3+}\) ion in YAG and GSGG garnets, and with the Cr\(^{3+}\) ion in ruby.\(^{6,9,10}\) The \( R_1 \rightarrow Z_5 \) peak in all the garnets is the most sensitive to pressure, with a coefficient of \( -10.8 \text{ cm}^{-1}/\text{GPa} \) for the CGGG garnet under study, a slightly smaller value than that found for GSGG, but clearly larger than those of YAG and ruby. The pressure coefficient for the \( R_1 \rightarrow Z_5 \) peak in CGGG is smaller, similar to other garnets, but larger than ruby.

However, due to the broadening of the \( R_1R_2 \rightarrow Z_5 \) peaks observed above 15 GPa, more evident in the latter transition, it seems that for the range of pressure analysed the \( R_1 \rightarrow Z_5 \) line is more suitable for pressure sensor purposes and, due to their low temperature sensitivity,\(^9\) can be used in a wider range of temperatures, if it is wished to introduce this variable into the experiment.

The energies of the \( R_1R_2 \rightarrow Z_5 \) peaks of the Nd\(^{3+}\) ion in YAG, GSGG, and CGGG garnets are compared in Fig. 5. Analysis of these transitions at different pressures, ranging from ambient pressure up to around 12 GPa, which are the experimental values available in the literature,\(^9,10\) finds different transition energies and \( R_1R_2 \) energy gaps for the three

### Table I. Linear fit coefficients of the \( 4F_{2}(R_2) \rightarrow 4I_{2}(Z_5) \) peak positions as a function of pressure for three different Nd\(^{3+}\)-doped garnets and the R-lines of the Cr\(^{3+}\):Al\(_2\)O\(_3\) (Ruby). Quadratic coefficient fits are also included for the Nd\(^{3+}\):CGGG garnet.

<table>
<thead>
<tr>
<th>Transition</th>
<th>Linear fit cm(^{-1})(GPa)</th>
<th>Quadratic fit ( E_0 ) cm(^{-1}) + A P(GPa) + B P(^2)(GPa)(^2)</th>
<th>Composition</th>
</tr>
</thead>
<tbody>
<tr>
<td>( 4F_{2}(R_2) \rightarrow 4I_{2}(Z_5) )</td>
<td>-11.3</td>
<td>10743.3–12.3P–6.0 × 10(^{-4})P(^2)</td>
<td>Nd(^{3+}):GSGG(^9)</td>
</tr>
<tr>
<td>( 4F_{2}(R_2) \rightarrow 4I_{2}(Z_5) )</td>
<td>-10.8</td>
<td></td>
<td>Nd(^{3+}):CGGG (this work)</td>
</tr>
<tr>
<td>( 4F_{2}(R_2) \rightarrow 4I_{2}(Z_5) )</td>
<td>-9.9</td>
<td></td>
<td>Nd(^{3+}):YAG(^{10})</td>
</tr>
<tr>
<td>( 2E(R_2) \rightarrow A_2 )</td>
<td>-7.56</td>
<td></td>
<td>Cr(^{3+}):Al(_2)O(_3) Ruby(^6)</td>
</tr>
<tr>
<td>( 4F_{2}(R_1) \rightarrow 4I_{2}(Z_5) )</td>
<td>-8.8</td>
<td>10641.0–8.4P–3.7 × 10(^{-4})P(^2)</td>
<td>Nd(^{3+}):CGGG (this work)</td>
</tr>
<tr>
<td>( 4F_{2}(R_1) \rightarrow 4I_{2}(Z_5) )</td>
<td>-7.5</td>
<td></td>
<td>Nd(^{3+}):YAG(^{10})</td>
</tr>
<tr>
<td>( 2E(R_1) \rightarrow A_2 )</td>
<td>-7.56</td>
<td></td>
<td>Cr(^{3+}):Al(_2)O(_3) Ruby(^6)</td>
</tr>
</tbody>
</table>
garnets. However, a better comparison can be done if the energy gap between the emission peaks is the main variable taken into account. That is why the graphs corresponding to the YAG and GSGG garnets are superimposed and shifted in energy and pressure with respect to that of the CGGG garnets under study, in such a way that the transition energies of the different garnets can be directly compared. Of course, the XY scales are exactly the same for the three graphs.

Two main facts can be inferred from this comparison; first, at ambient conditions, the CGGG garnets has the largest energy gap between the R₁ and R₂ Stark levels, and only at around 1.5 GPa does it have a similar splitting as YAG at ambient pressure. However, the pressure must be increased to around 18.5 GPa to be comparable to the splitting in the GSGG garnet at ambient pressure. Second, the splitting shown in the latter garnet allows us to assume that the energy gap in the CGGG under study is still nonzero up to pressures around 30 GPa, if the hydrostatic conditions are kept using a different pressure transmitting medium. Thus it seems that the CGGG garnet gives the largest dynamic pressure range from ambient pressure up to 30 GPa, if the energies of the R₁R₂ → Z₅ emissions peaks of the Nd³⁺ ion are wanted to be used as a pressure measurement inside the DAC.

The key physical factor responsible for this feature has to be found in the local structure of the Nd³⁺ ions in the CGGG garnet at ambient conditions. The initial degree of orthorhombic distortion of the dodecahedral sites is larger when occupied by the Ca²⁺ ions than when occupied by the Gd³⁺ or the Y³⁺ ions, since the ionic radius of the Ca²⁺ ion is larger. In addition, the Nd³⁺ ion could be incorporated as a modifier replacing the Ca²⁺ ion, since both have similar ionic radii, obtaining from the crystalline network a stabilized 8-coordinated site with Ge⁴⁺ ions in the second sphere of coordination to achieve charge neutrality.

**IV. CONCLUSIONS**

The luminescence spectra as a function of pressure of the {⁴}F₃/₂ → {⁴}I₀/₂ transition of an Nd³⁺-doped CGGG garnet, obtained by exciting either by the 488 nm line of an Ar⁺ laser or with a 532 nm diode-pumped solid state laser were analysed. At ambient pressure, nine lines were identified according to the conventional notation of the {⁴}F₃/₂ and {⁴}I₀/₂ manifolds. The energy position of these lines is related to a small orthorhombic distortion of a main cubic crystal-field. The behaviour of the energy position of these lines as pressure increases is associated with a reduction in the non-cubic distortion and an increase in the main cubic field, mainly governed by the medium distance B₄c cubic parameter. This parameter appears to be mainly responsible for the pressure increase of the energy gap between the Z₅ Stark level and the other Z₁–₄ levels.

Two intense and isolated lines corresponding to R₁,R₂ → Z₅ transitions centred in the NIR in the interval from 10 600 to 10 800 cm⁻¹ are the most sensitive to pressure with linear coefficients of −10.8 cm⁻¹/GPa and −8.8 cm⁻¹/GPa, respectively, both with line shifts higher than that found for the most widely used pressure calibrated standard, the R₁ line of Cr³⁺ in ruby (−7.56 cm⁻¹/GPa), The initial orthorhombic distortions of the Nd³⁺ site seem to be the key factor in having a larger dynamic pressure scale, and the CGGG crystal shows the largest one among garnets studied. These facts, together with the advantages of excitation with a conventional Ar⁺ or laser diode and available detectors in this spectral range, make the Nd³⁺:CGGG garnet a potential candidate to be used as a NIR pressure sensor at room temperature in a diamond anvil cell from ambient to around 30 GPa pressure range.

**ACKNOWLEDGMENTS**

This work has been partially supported by MICINN (MAT2010-21270-C04-02, The MALTA Consolider CSD2007-0045 and the National Program of Infrastructure), and by EU-FEDER funds. S. F. León-Luis also wishes to thank MICINN for the FPI Grant (BES-2008-00353).

---

*2W. B. Holzapfel and N. S. Isaacs, High-pressure Techniques in Chemistry and Physics (Oxford University Press, 1997).