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Comparative study of spectroscopic behaviour of Nd^{3+} in magnetoplumbite type laser crystals

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A comparative analysis of the spectroscopic behaviour of Nd^{3+} doped in $Sr_{1-x}Nd_yLa_{x-y}Mg_xAl_{12-x}O_{19}$ (ASL: Nd) crystals, with an extended compositional parameter $0.05 \le x \le 0.8$ and $x = 1$ ($La_{1-y}Nd_yMgAl_{11}O_{19}$ - LMA: Nd) is presented. The crystals were grown by the Czochralski method from iridium crucibles under nitrogen atmosphere. The optical absorption spectra revealed that Nd^{3+} ions are distributed over at least two (for $x \le 0.5$) or three (for $x \ge 0.8$) sites. The absorption spectra in polarized light were analyzed in order to obtain information on the local symmetry of the Nd^{3+} centers in ASL: Nd and LMA: Nd crystals.

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1. Introduction

Extensive development of diode-pumped solid state lasers continuously triggers the search for new laser active materials. In particular, diode-pumped solid state lasers operating in the blue range are of interest for various applications. Such a device can be realized using a Nd - doped laser material operating on the $^4F_{3/2} \rightarrow {}^4I_{9/2}$ transition and an appropriate doubling crystal.

Strontium hexa-aluminates ($SrAl_{12}O_{19}$-SAO) crystals have magnetoplumbite - type structure, with space group $P6_3/mmc$ [1]. The Sr^{2+} ions are situated in mirror planes perpendicular on optical axis *c*, the large cationic *2d* sites with D_{3h} local symmetry. In SAO crystals structure, the Sr^{2+} ions could be replaced by the trivalent Ln^{3+} (La^{3+} and Nd^{3+}) ions. The charge compensation can be accomplished by a partial substitution of Al^{3+} with Mg^{2+} ions [2 - 5] and the Nd^{3+} content can be diluted within the limits imposed by the concentration self-quenching by the optical inert La^{3+} ions [6 -8], obtaining the disordered $Sr_{1-x}Nd_yLa_{x-y}Mg_xAl_{12-x}O_{19}$ (ASL) crystals. The 12-fold O^{2-} coordination of the *2d* sites determines low covalence for the metal-ligand bonds and low nephelauxetic effects [9, 10] for the doping rare earth ions as well as moderate crystal field effects. This makes the ASL: Nd crystals attractive for short wavelength Nd^{3+} $^4F_{3/2} \rightarrow {}^4I_{9/2}$ laser emission, i.e. ~ 900 nm, [11, 12].

Initially the Nd^{3+} optical spectra in ASL have been interpreted in terms of a single center, with composition dependent spectral characteristics [3, 4]. Recently, it was demonstrated that in ASL: Nd crystals with $x \le 0.5$ two families of Nd^{3+} centers exist, C_1 and C_2, with distinct spectral characteristics, dependent mainly by the compositional parameter x and structural models were proposed [13]. At the end of the series $x = 1$ ($La_{1-y}Nd_yMgAl_{11}O_{19}$ - LMA: Nd^{3+}), the spectroscopic investigations [14, 15] have revealed three main Nd^{3+} centers (I, II and III); the first two Nd^{3+} centers (I and II) have been associated to Nd^{3+} ions situated in similar sites of nearly D_{3h} symmetry and the center III to the Nd^{3+} ions in a lower symmetry, probably C_{2v}, but with no definite structural models. Structural X- ray investigations on LMA: Nd^{3+} crystals [16] revealed that the structure of LMA crystals is close to magnetoplumbite - type (with space group $P6_3/mmc$), the Ln^{3+} (La and Nd) cations could occupy beside the theoretical *2d* sites (fixed coordinates) the *6h* sites (close to the *2d* ones) with 1/3 occupation ratio each. This lowers the Ln^{3+} point symmetry from D_{3h} (C_3 - axis $\parallel$ c) in the ideal magnetoplumbite structure to C_{2v} (C_2 -axis $\perp$ c).

In this work a comparative study of the spectroscopic behaviour of Nd^{3+} ions in $Sr_{1-x}Nd_yLa_{x-y}Mg_xAl_{12-x}O_{19}$ crystals over an extended range of compositional parameter x toward smaller and larger values ($0.05 \le x \le 1$) is presented. An analysis of the non-equivalent Nd^{3+} centers based on high resolution optical spectroscopy data (including polarization) was performed.

2. Experiment

Single crystals of $Sr_{1-x}Nd_yLa_{x-y}Mg_xAl_{12-x}O_{19}$ with $x = 0.05 - 0.5$, $y = 0.05$ and $x = 0.8, 1.0$ with the same $y = 0.1$, were grown by Czochralski method from stoichiometric compositions using iridium crucibles under nitrogen atmosphere. The absorption spectra at 15 K and 300 K were measured with a set-up consisting of a tungsten halogen lamp, a GDM 1m monochromator with resolution of ~0.3 cm^{-1}, a photon counting photomultiplier, a Turbo-MCS multichannel analyzer and a helium closed cycle system for low temperatures.

3. Results and discussion

The optical spectroscopic measurements of Nd^{3+} in ASL crystals were performed on an extended spectral range up to ~ 24000 cm^{-1}. The absorption spectra of Nd^{3+}: ASL crystals in unpolarized light were measured with propagation along the *c* axis. In order to obtain information on the local symmetry of a specific center the measurements in polarized light, with light propagation in the mirror (***a***, ***b***) plane along ***a*** crystallographic axis (which is perpendicular on ***c*** axis) were recorded.

a). Composition dependence of the Nd^{3+} spectra in $Sr_{1-x}La_{x-y}Nd_yMg_xAl_{12-x}O_{19}$ at small x (x ≤ 0.5).

Recent high-resolution optical spectroscopy [13, 17, 18] of ASL: Nd^{3+} for $0.05 \le x \le 0.5$ revealed clearly the presence of at least two types of structural centers, labelled C_1 and C_2, whose proportion and spectroscopic properties (the lines positions, shapes and widths) are determined especially by the compositional parameter x having a very small dependence on the y parameter (the Nd^{3+} content). The most important difference between the two Nd^{3+} structural centers was found in the $^4I_{9/2} \rightarrow {}^4F_{3/2}$ absorption spectra as illustrated in Fig. 1. The spectra show the predominance of C_2 centers at low x ($x \le 0.05$), and the strong growth of the C_1 center intensity with x: at x = 0.5 its relative intensity is larger than 95%. The effective crystal field splitting of the $^4F_{3/2}$ manifold, estimated from the peaks in the low temperature absorption bands, depends on the composition parameters *x* for both centers, being ~ 110cm^{-1} about twice larger for C_1 center (x=0.5) than ~ 50 cm^{-1} for C_2 (x=0.05), but with similar barycenters (within ~ 2-3 cm^{-1}). In Nd^{3+} $^4I_{9/2} \rightarrow {}^2P_{1/2}$ transition the absorption lines of C_1 and C_2 centers are overlapping. An additional splitting of C_2 lines was observed at very low x (x < 0.2), suggesting the existence of two distinct C_2 type centers C_2' and C_2'' [18].

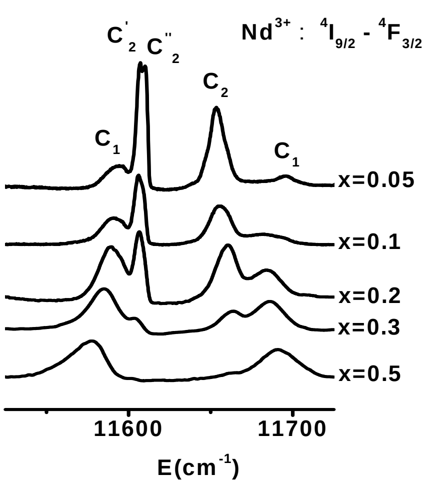

Fig. 1. The $^4I_{9/2} \rightarrow {}^4F_{3/2}$ absorption spectra at 15 K of Nd^{3+}: ASL with $0.05 \le x \le 0.5$ and y=0.05.

b). Absorption spectra in polarized light of $Sr_{1-x}La_{x-y}Nd_yMg_xAl_{12-x}O_{19}$ crystals with x ≤ 0.5

In order to obtain information on the local symmetry of a specific center from polarization data, the measurements in polarized light were concentrated on samples with x = 0.05, sample where C_2 center is prevailing, and x = 0.5 sample where C_1 is dominant. The polarization data at small x=0.05 for Nd^{3+} C_2 center satisfy the selection rules of D_{3h} while the interpretation of the polarization data for C_1 (x=0.5) is more difficult and indicates an obvious lowering in symmetry from the ideal D_{3h} [19]. This behaviour is consistent with the considerably larger effects of crystal field perturbations on the energy levels of these centers and the deviations of the D_{3h} symmetry at Nd^{3+} ions for large x that has been remarked in X - ray analysis [6].

c). Composition dependence of the Nd^{3+} spectra in $Sr_{1-x}La_{x-y}Nd_yMg_xAl_{12-x}O_{19}$ at high x (x = 0.8 and 1)

In the $^4I_{9/2} \rightarrow {}^4F_{3/2}$ absorption spectra at 15 K of ASL: Nd crystal with x=0.8 (Fig. 2) two broad and asymmetric lines are observed. For the same transition the absorption spectra for x = 1 (LMA: Nd) crystal the two centers (I and II) lines are structurally better resolved. The low temperature absorptions spectra of Nd^{3+} $^4I_{9/2} \rightarrow {}^2P_{1/2}$ transition (Fig. 3) for x = 0.8 and x = 1 show three lines, a doublet at 23414 cm^{-1} - 23444 cm^{-1} and one isolated line at 23243 cm^{-1}, indicating that Nd^{3+} ions are distributed over at least three crystallographic sites (two of them being structurally similar) unlike in the crystals with small x where only two structural centers are present.

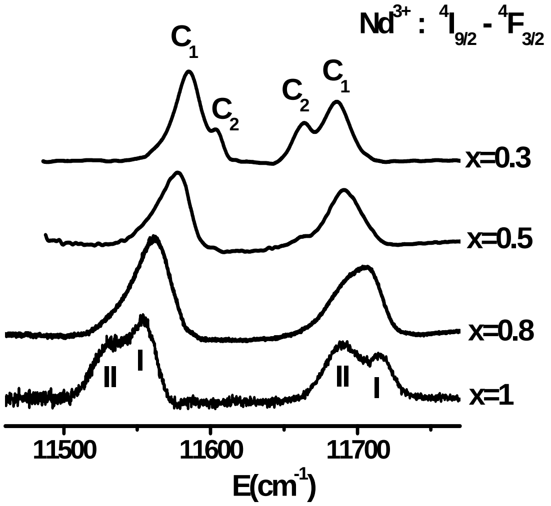

Fig. 2. The $^4I_{9/2} \rightarrow {}^4F_{3/2}$ absorption spectra at 15 K of ASL: Nd for x=0.3, 0.5, y=0.05, and x=0.8, 1 y=0.1.

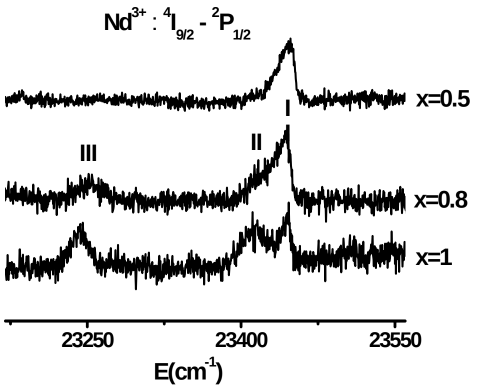

Fig. 3. The $^4I_{9/2} \rightarrow {}^2P_{1/2}$ absorption spectra at 15K of ASL: Nd for x=0.5, y= 0.05 and x=0.8, 1, y=0.1.

The most of the lines have asymmetric shape and are inhomogeneously broadened (10-15 cm^{-1} for center I, 25-30 cm^{-1} for center II, and 15-25 for center III) indicating a large structural disorder in the environment of the Nd^{3+} ions. The relative intensity of II/I lines decreases with x and the spectral shapes of the bands are independent on y (the Nd^{3+} content).

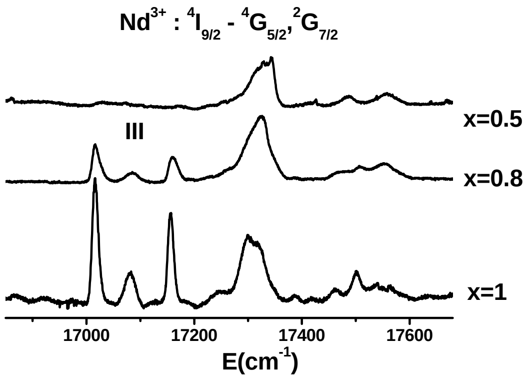

Fig. 4. The $^4I_{9/2} \rightarrow {}^4G_{5/2}$, $^2G_{7/2}$ absorption spectra at 15 K of ASL: Nd for x=0.5, y= 0.05 and x=0.8, 1 with y=0.1.

The intensities of the center III lines are very small in $^4I_{9/2} \rightarrow {}^4F_{3/2}$ absorption, but are clearly observed in the hypersensitive Nd^{3+} $^4I_{9/2} \rightarrow {}^4G_{5/2}$, $^2G_{7/2}$ transition (x = 0.8 and 1) (Fig. 4), and is not observed in samples with small x (x < 0.5). They are shifted with ~ 220 cm^{-1} from the group of other lines and their intensity increases with x.

d). Absorption spectra in polarized light of $Sr_{1-x}La_{x-y}Nd_yMg_xAl_{12-x}O_{19}$ crystals with x = 0.8.

The $^4I_{9/2} \rightarrow {}^4F_{3/2}$ absorption spectra at 300 K and 15 K with σ and π polarizations show clear and strong polarization effects (Figs. 5 and 6) for the absorption lines associated to the I and II centers of ASL: Nd sample with x = 0.8. In the π polarization the $^4I_{9/2}$ (Z_1)$\rightarrow$ $^4F_{3/2}$ (R_1) line at 15 K has week intensity, while the $^4I_{9/2}$ (Z_1)$\rightarrow$ $^4F_{3/2}$ (R_2) absorption lines disappear completely.

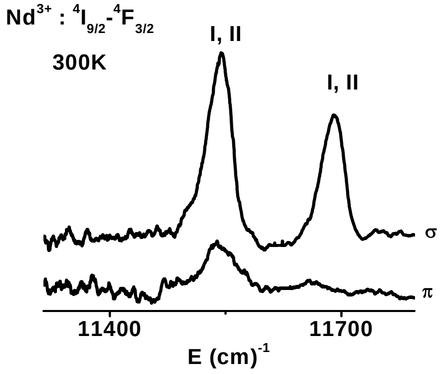

Fig. 5. The $^4I_{9/2} \rightarrow {}^4F_{3/2}$ polarized absorption spectra at 300K of ASL: Nd of x = 0.8 with y=0.1.

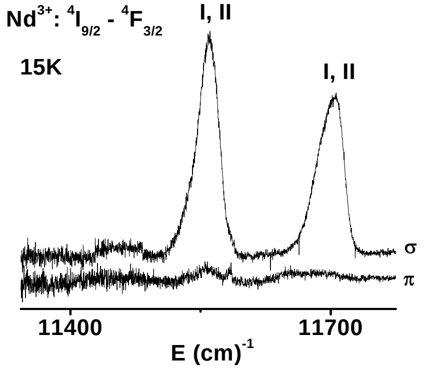

Fig. 6. The $^4I_{9/2} \rightarrow {}^4F_{3/2}$ polarized absorption spectra at 15K of ASL: Nd of x = 0.8 with y=0.1.

In the Nd^{3+} $^4I_{9/2} \rightarrow {}^2P_{1/2}$ absorption spectra at 15K, the lines assigned to the centers (I, II) lines at 15 K are observed in both σ and π polarizations (Fig. 7) and as well as that associated to center III.

As shown in Fig. 8 in the hypersensitive Nd^{3+} $^4I_{9/2} \rightarrow {}^4G_{5/2}$, $^2G_{7/2}$ transition, the absorption lines assigned to the center III are present in both σ and π polarizations, one line of this group being more intense in π polarization.

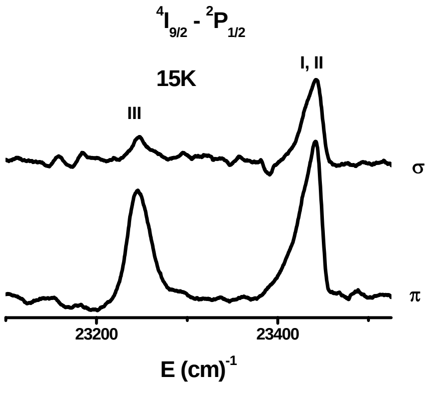

Fig. 7. The $^4I_{9/2} \rightarrow {}^2P_{1/2}$ polarized absorption spectra at 15K of ASL: Nd of x = 0.8 with y=0.1.

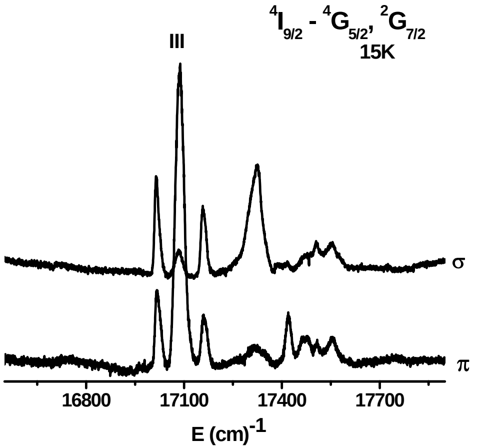

Fig. 8. The $^4I_{9/2} \rightarrow ^4G_{5/2}$, $^2G_{7/2}$ polarized absorption spectra at 15K of ASL: Nd of x = 0.8 with y=0.1.

In the case of centers I and II, the observed polarization effects in the 15 and 300 K absorption spectra of analysed transitions satisfy the selection rules of D_{3h} group [20] presented in table 1, with Γ_8 being ground state [18]. The crystal field levels of some *J* manifolds are $D^{1/2} \rightarrow \Gamma_7$, $D^{3/2} \rightarrow \Gamma_7 + \Gamma_9$, $D^{5/2} \rightarrow \Gamma_7 + \Gamma_8 + \Gamma_9$, $D^{9/2} \rightarrow \Gamma_7 + 2\Gamma_8 + 2\Gamma_9$. For lower symmetries the selection rules relax, and for groups with symmetries lower than C_{2v} all the transitions are electric - dipole allowed. Since for center III in $^4I_{9/2} \rightarrow ^4G_{5/2}$ transition one observe three lines (not two in σ spectrum and one in π as expected for D_{3h} local symmetry) one could conclude that center III has a lower symmetry than D_{3h}, probably C_{2v} symmetry.

Table 1. Electric - dipole selection rules for Kramers ions in D_{3h} symmetry [20] , with σ ($\vec{E} \perp c$) and π ($\vec{E} \parallel c$), and $\vec{E}$ - the electric field direction.

	Γ_7	Γ_8	Γ_9
Γ_7	-	σ, π	σ
Γ_8	σ, π	-	σ
Γ_9	σ	σ	π

In order to elucidate the structure of I, II, and III centers in $Sr_{1-x}La_{x-y}Nd_yMg_xAl_{12-x}O_{19}$ crystals with high compositional parameter x, the obtained spectroscopic results were analyzed in correlation with previous X- ray data [6], which suggest a deviation from the ideal magnetoplumbite structure and the possibility that the local symmetry of Nd^{3+} sites is lower than D_{3h}. Important data could be obtained from the barycenters position of $^{2S+1}L_J$ manifold, defined as ΔE ($^{2S+1}L_J$) = $E(^{2S+1}L_J)-E(^4I_{9/2})$, of different centers (Fig. 9). The barycenters position [10] depends on: the nature of surrounding ions, the coordination number (increase with it), and the size of the ion to be replaced by Nd^{3+} in the lattice host (increase with it La^{3+}- 1.32 Å, Sr^{2+} - 1.4 Å). Because the barycenters of centers I and II are close to those of C_1 and C_2 centers, and the barycenter of center III is much lower, we can suppose that centers I, II, C_1 and C_2 could have the same anionic vicinity with 12 O^{2-}, and center III could have a lower than 12 O^2 in the anionic vicinity, (oxygen vacancies), but larger than 8 as for Nd in YAG or GGG.

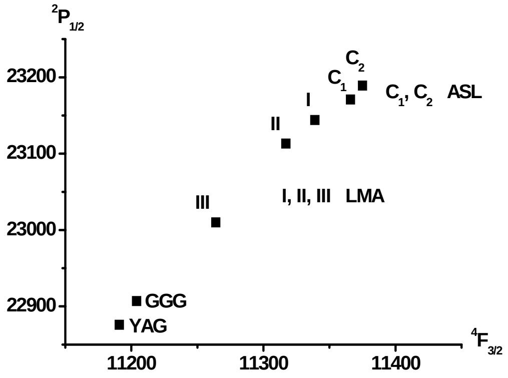

Fig. 9. The barycenters position of the $^4F_{3/2}$ and $^2P_{1/2}$ manifolds, defined as ΔE ($^{2S+1}L_J$) = $E(^{2S+1}L_J)-E(^4I_{9/2})$ for Nd^{3+} doped in different crystals.

4. Conclusions

The spectroscopic investigations of Nd^{3+} in $Sr_{1-x}La_{x-y}Nd_yMg_xAl_{12-x}O_{19}$ magnetoplumbite type laser crystals over an extended range of compositional parameter x toward smaller and larger values ($0.05 \leq x \leq 1$) shows different behaviour for low and high x parameter.

In the $Sr_{1-x}La_{x-y}Nd_yMg_xAl_{12-x}O_{19}$ crystals with $x \leq 0.5$ the presence of at least two types of structural centers, C_1 and C_2, whose proportion and spectroscopic properties are determined especially by the compositional parameter x was demonstrated. An additional splitting of the C_2 center in two components, $C_2^{'}$ and $C_2^{''}$, was evidenced for x < 0.2. Models for the main Nd^{3+} centers have been proposed in our previous investigations [18]. The Nd^{3+} ions for both centers is assumed to have the same ionic environment 12 O^{2-}, the differences coming from the electric charge differences of nearby cations (Sr^{2+}, Ln^{3+}) in the nearby six *2d* sites. The C_2 centers could correspond to Nd^{3+} in a Sr^{2+} *2d* site with no nearby Ln^{3+} (Nd^{3+}, La^{3+}) ions, while C_1 lines are composite lines of various structural centers of Nd^{3+} in a *2d* site with one up to six *2d* nearest neighbour sites occupied by Ln^{3+}. The charge compensator Mg^{2+} effects are assumed to contribute mainly to linewidths. According to [21] Mg^{2+} ions substitute preferentially Al^{3+} situated in the tetrahedral sites (Al_{tetr}^{3+}) but the closest coordination sphere of Al_{tetr}^{3+} sites (at 5.85Å) is slightly farther than the first *2d* coordination sphere (5.56 Å).

Our data demonstrate that at high x (x = 0.8) in $Sr_{1-x}La_{x-y}Nd_yMg_xAl_{12-x}O_{19}$ crystals the spectral composition is changed and reveals the same types of centers (I, II, III) as previously reported for x=1 LMA crystals [14, 15]. The most of the absorption lines have asymmetric shape and are inhomogeneously broadened indicating a large structural disorder in the environment of the Nd^{3+} ions. The crystal field splitting of $^4F_{3/2}$ is center and composition dependent and present larger values (I, II ~ 160 cm^{-1}, III ~ 200 cm^{-1}) than for low x centers (C_1 ~ 100 cm^{-1}, C_2 ~ 50 cm^{-1}). The polarization data indicate a clear lowering in symmetry from D_{3h} for center III.

For large x the *2d* or *6h* sites are preponderantly occupied with trivalent Ln^{3+} cations and in order to conserve the local neutral charge, more Mg^{2+} ions substituting Al^{3+} ions, are required, and probably enter in Al^{3+} sites closer to Nd^{3+}. There are many Al^{3+} sites close to a given *2d* Nd^{3+} site: three bypiramidal Al^{3+} sites at ~3.2 Å in the mirror plane and 24 Al^{3+} octahedral sites out of this plane (six at 3.46 Å, six at 3.47 Å and twelve at 5.26 Å), we can assume that Mg^{2+} could substitute Al_{tetr}^{3+} sites as well as other Al^{3+} sites situated inside of the nearby *2d* cationic sphere of Nd^{3+} ions. The crystal field perturbations that lead to centers I and II could be given by $12O^{2-}$ coordination, Ln^{3+} or Mg^{2+} in nearby sites. The center III correspond to Nd^{3+} in a site of lower symmetry than D_{3h}, probably C_{2v} symmetry, as is sustained by the polarized absorption and the barycenter position.

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