

## Luminescence of $\text{LiNbO}_3\text{:MgO,Cr}$ crystals under high pressure

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The results of high-pressure studies of  $\text{LiNbO}_3\text{:Cr}(0.2\%)$ , Mg crystals doped with two concentrations of magnesium (2% and 5.5%) are reported. The results reveal information about the electronic structure of different  $\text{Cr}^{3+}$  centers in lithium niobate crystals. There are three major  $\text{Cr}^{3+}$  centers (denoted by  $\alpha$ ,  $\beta$ , and  $\gamma$ ) in the crystal with 2% of magnesium. These centers correspond to  $\text{Cr}^{3+}$  ions in  $\text{Li}^+$  sites with different crystal field. At ambient pressure the  $\alpha$  center experiences strong crystal field and the  $\beta$  and  $\gamma$  centers are the intermediate crystal-field centers. The energy differences between the  ${}^4T_2$  and  ${}^2E$  levels are positive and negative for the  $\beta$  and the  $\gamma$  centers, respectively. Additional broadband luminescence observed in the sample with 5.5% of magnesium even at pressure of almost 100 kbar testifies that another very weak crystal-field center exists in this crystal. This center (denoted by  $\delta$ ) corresponds to  $\text{Cr}^{3+}$  ions located in  $\text{Nb}^{5+}$  sites. The  $R$  lines of the  $\text{Cr}^{3+}$  centers exhibit very large redshift with pressure of about  $3\text{ cm}^{-1}/\text{kbar}$ .

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Lithium niobate is an important material for application in nonlinear optics. Its importance grows since it could be used as a laser material for tunable laser action and for self-frequency doubling.<sup>1</sup> Optical properties of  $\text{LiNbO}_3\text{:Cr}$  crystals have been a subject of numerous studies.<sup>2-14</sup> Lithium niobate could be grown as stoichiometric crystal but it is easier to grow it with the congruent composition (lithium deficient). The structural defects present in the congruent crystals are responsible for formation of several luminescent centers in the crystals doped with transition-metal and/or rare-earth ions. Recent optical studies revealed at least six different luminescent  $\text{Cr}^{3+}$  centers in  $\text{LiNbO}_3$  crystals<sup>12</sup> and a similar number of different centers for trivalent rare-earth ions.<sup>15</sup>  $\text{LiNbO}_3$  crystals exhibit strong photorefractive effect, known also as optical damage. In order to prevent it the crystals are doped with Mg or Zn with large concentrations up to a few percent.<sup>13,14,16</sup> In spite of many studies there are still some ambiguities related to detailed electronic structure of the  $\text{Cr}^{3+}$  ions in  $\text{LiNbO}_3$  crystals. Most studies show that in crystals codoped with magnesium up to concentration of about 4.5% the  $\text{Cr}^{3+}$  ions occupy only  $\text{Li}^+$  sites  $\text{Cr}_{\text{Li}}$ . Such crystals are green in color. In crystals codoped with magnesium with concentration higher than 4.5% a fraction of  $\text{Cr}^{3+}$  ions tends to occupy  $\text{Nb}^{5+}$  sites in the lithium niobate host. Above that Mg concentration threshold lithium niobate crystals change color from green to pink. This effect has been related to the transfer of part of chromium ions into the Nb sites.<sup>5,6,10,12-14</sup>

We used a diamond-anvil cell high-pressure technique to study the spectroscopic properties of  $\text{Cr}^{3+}$  ions in  $\text{LiNbO}_3$  crystals. This is a powerful tool for obtaining information about the electronic structure of luminescent centers. The application of high pressure reduces the distances between a dopant ion and the ligands. Thus pressure increases the

crystal-field strength applied to the dopant ion, since its strength is approximately proportional to the inverse of the fifth power of the dopant ion–ligand distance. Some of the  $\text{Cr}^{3+}$  ions in lithium niobate crystals are located in sites with so-called intermediate crystal field, that is the  ${}^2E$  level is located close to the  ${}^4T_2$  level. Using high pressure it is possible to transform these centers into the high-crystal field ones. Information about the crystal field experienced by different chromium centers in this material can be obtained this way.

Two samples of congruent  $\text{LiNbO}_3\text{:Cr, Mg}$  with a concentration of chromium ions of 0.2% and concentration of magnesium equal to 2% (a green one) and 5.5% (a pink one) have been studied. The samples were grown using the Czochralski method. Continuous wave emission spectra were obtained using a 514.5-nm line of an argon-ion laser as the excitation source. The spectra were measured with use of GDM-1000 double grating monochromator equipped with a cooled photomultiplier (EMI 9684B) with S1-type cathode and an SR530 lock-in amplifier. The high-pressure measurements were performed using a low-temperature diamond-anvil cell (Diacell Products MCDAC-1). The argon was used as a pressure transmitting medium. The diamond-anvil cell was mounted into an Oxford 1204 cryostat equipped with temperature controller for low-temperature measurements. The  $R_1$  line ruby luminescence was used for pressure calibration. The polished samples of thickness about  $30\ \mu\text{m}$  were loaded into the cell along with a small ruby ball. To measure the luminescence the argon-ion laser line was focused either on the measured  $\text{LiNbO}_3$  sample or on ruby. The changes of pressure were done at room temperature in order to minimize nonhydrostatic effects that are known to exist in diamond-anvil cells especially at higher pressure. The hydrostatic conditions could be partially monitored by recording

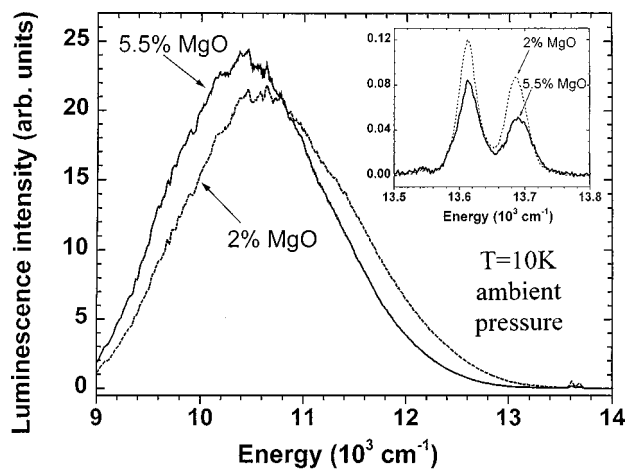


FIG. 1. The luminescence spectra of  $\text{LiNbO}_3:\text{Cr}(0.2\%)$ , Mg crystals with 2% and 5.5% of magnesium at temperature  $T=10\text{ K}$  at ambient pressure, excited by the 514.5-nm argon-ion laser line. The expanded region of  $R$  lines is shown in the inset.

the half-width of the ruby emission. In our measurements we observed increase of the half-width of ruby luminescence with increasing pressure. The half-width of the  $R_1$  ruby luminescence did not exceed  $6\text{ cm}^{-1}$  at high pressures ( $2.5\text{ cm}^{-1}$  at ambient pressure). This means that the nonhydrostatic effects were rather weak. Additionally, possible weak nonhydrostatic effects should not affect our results since important changes of luminescence occurred at relatively low pressures, when the nonhydrostatic effects were negligible.

The luminescence spectra of  $\text{LiNbO}_3:\text{Cr}^{3+}$ , Mg crystals with magnesium concentration of 2% and 5.5% at ambient pressure at temperature 10 K are presented in Fig. 1. The spectra consist of a very broad band peaked at about  $10\,600\text{ cm}^{-1}$  (943 nm) for the sample doped with 2% of Mg and about  $10\,400\text{ cm}^{-1}$  (961 nm) for the crystal with 5.5% of Mg. This means that at ambient pressure the luminescence spectra are dominated by the  ${}^4T_2 \rightarrow {}^4A_2$  transitions. Very weak (as compared with the broadband luminescence) sharp lines are visible, with maxima at  $13\,614\text{ cm}^{-1}$  (734.5 nm) and  $13\,686\text{ cm}^{-1}$  (730.7 nm), which are associated with  ${}^2E \rightarrow {}^4A_2$  transitions (see the inset in Fig. 1). Due to low-temperature measurements, we detect only emission from lower components of the  ${}^2E$  levels ( $R_1$  lines).

The low-temperature luminescence spectra at ambient pressure are similar to those previously observed by several authors. The line with a maximum at  $(13\,614 \pm 2)\text{ cm}^{-1}$  we recognize as a  $R_1$  line of center  $\alpha$  (using notation of Macfarlane *et al.*<sup>9</sup>) or the same  $L_2$  center (using notation of Lhomme *et al.*<sup>12</sup>). Spectral position of this line depends slightly on the chromium concentration<sup>12</sup> and this is the most probable reason for observed small differences in the position of this line reported by different authors.

The pressure application drastically changes the luminescence spectra. The examples of the luminescence spectra recorded at higher pressures of the crystal doped with 2% of magnesium are shown in Figs. 2 and 3. At relatively low pressures we observe a strong increase of the sharp luminescence in a part of the region of the  $R$  lines at the broadband luminescence expense. The broadband luminescence is practically absent at pressures above 40 kbar. The peak position

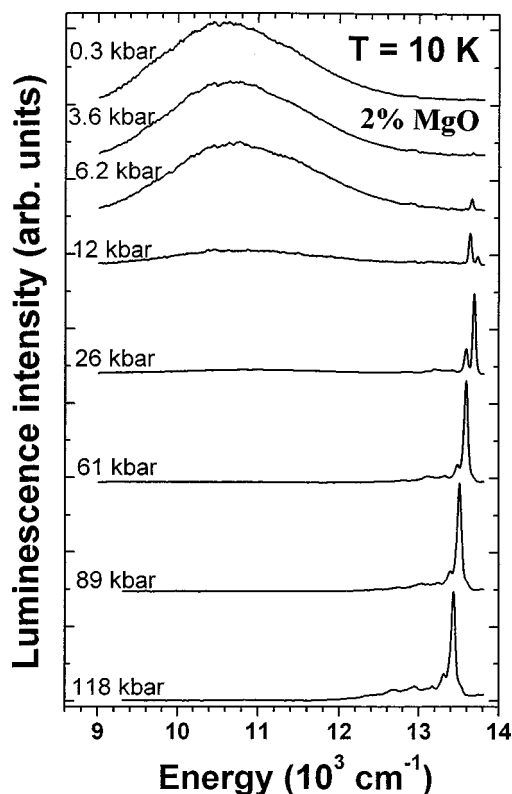


FIG. 2. The pressure dependence of the  $\text{Cr}^{3+}$  luminescence in  $\text{LiNbO}_3:\text{Cr}$ , Mg(2%) crystal at temperature  $T=10\text{ K}$ .

of the broadband luminescence, associated with  ${}^4T_2 \rightarrow {}^4A_2$  transitions, is shifted to shorter wavelengths with increasing pressure with an approximate rate of  $(12 \pm 3)\text{ cm}^{-1}/\text{kbar}$ . The positions of the  $R$ -line shift almost linearly with pressure increase towards longer wavelength with an approximate rate between 2 and  $3\text{ cm}^{-1}/\text{kbar}$ .

The intensity of the  $R$  line associated with a peak at  $13\,614\text{ cm}^{-1}$  at 1 bar practically does not depend on the pressure. Eventually this line is not discernible at higher pressures above 20 kbar since it overlaps with much stronger luminescence at these pressures coming from the other centers. It confirms that the  $\alpha$  center corresponds to  $\text{Cr}^{3+}$  ions in  $\text{Li}^+$  sites having a high-crystal field also at ambient pressure, as was proposed previously.<sup>9</sup>

The line peaking at  $(13\,687 \pm 2)\text{ cm}^{-1}$  at ambient pressure was marked as a  $\beta$  line (Macfarlane *et al.*<sup>9</sup>) or  $L_1$  (Lhomme *et al.*<sup>12</sup>). The intensity of this line, almost the same at ambient pressure as the intensity of the  $\alpha$  line increases with pressure up to about 20 kbar and remains practically unchanged at higher pressures. Intensity of this line grows at the expense of the broad band observed at longer wavelengths, associated with the  ${}^4T_2 \rightarrow {}^4A_2$  transitions. Thus we associate the  $\beta$  center with an intermediate crystal field at ambient pressure  $\text{Cr}_{\text{Li}}^{3+}$  center. Additional studies are necessary to estimate the exact value of the energy difference  $\Delta_\beta$  between the  ${}^4T_2$  and  ${}^2E$  levels for this center at ambient pressure. Most probably it is positive since we do not observe any anticrossing behavior in this line luminescence, observed by Hömmerich and Bray in the luminescence of  $\text{Cr}^{3+}$  ions in  $\text{Gd}_3\text{Sc}_2\text{Ga}_3\text{O}_{12}$  and  $\text{Gd}_3\text{Ga}_5\text{O}_{12}$  garnet crystals.<sup>17</sup> The intensity ratio between the broadband  ${}^4T_2$  and sharp  ${}^2E$  luminescence depends on the value of  $\Delta$ , since

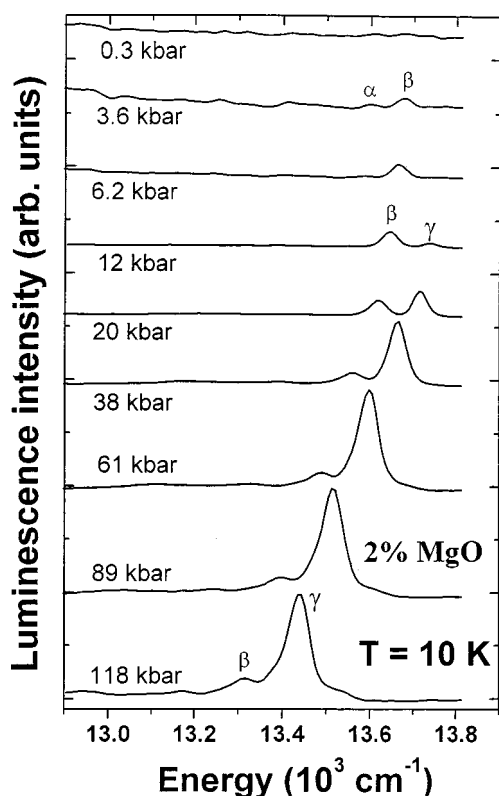


FIG. 3. The pressure dependence of the  $\text{Cr}^{3+}$  luminescence in  $\text{LiNbO}_3:\text{Cr}, \text{Mg}(2\%)$  crystal at temperature  $T=10\text{ K}$  in the region of the  $R$  lines.

the forbidden  ${}^2E \rightarrow {}^4A_2$  transition occurs due to the spin-orbit interaction induced admixture of the  ${}^4T_2$  quartet state into the  ${}^2E$  doublet electronic wave function.<sup>18</sup> It is expected to be large for small values of  $\Delta$ .<sup>19</sup> We estimate that the  $\Delta_\beta$  value at ambient pressure is in the order of few tens of  $\text{cm}^{-1}$  since this ratio is large at this pressure for the  $\beta$  center luminescence.

At pressures above 7 kbar another line is observed on the high-energy side of the line associated with the  $\beta$  center. Intensity of this line grows strongly with increase of pressure and eventually this line dominates the spectrum at pressure of about 40 kbar. Spectral position of this line as a function of pressure is presented in Fig. 4. An extrapolation of the position to the ambient pressure gives a value  $(13\,771 \pm 3)\text{ cm}^{-1}$ . It agrees very well with the position of a  $R_1$  line, which is observed only in absorption spectrum at ambient pressure.<sup>6,9</sup> This line has been associated with a dominating  $\text{Cr}^{3+}$  center, emitting only broad-band luminescence at ambient pressure, denoted as center  $\gamma$  by Macfarlane *et al.*<sup>9</sup> The position of the  $R_1(\gamma)$  line, as observed in the absorption spectrum, is also shown in Fig. 4. Lack of sharp luminescence at ambient pressure and a strong increase of the  $R$ -line emission at relatively low pressures strongly supports that the  $\text{Cr}^{3+}$  ions in the  $\gamma$  centers are experiencing an intermediate crystal field with the  ${}^4T_2$  level located just below the  ${}^2E$  one. Knowing the combined value of the shift rates of the  ${}^4T_2 \rightarrow {}^4A_2$  broad band luminescence and the sharp line  ${}^2E \rightarrow {}^4A_2$  emission ( $12\text{ cm}^{-1}$  and  $-3\text{ cm}^{-1}$ , respectively) one can estimate the value of the energy difference  $\Delta_\gamma$  between the  ${}^4T_2$  and  ${}^2E$  levels for this center at ambient pressure, which is equal to at least  $\Delta_\gamma = -100\text{ cm}^{-1}$ .

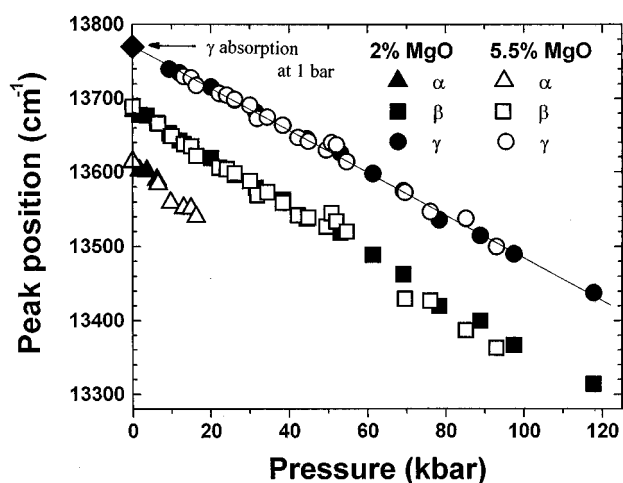


FIG. 4. Spectral positions of the  $R_1$  lines of the  $\alpha$ ,  $\beta$ , and  $\gamma$  centers of  $\text{Cr}^{3+}$  luminescence of  $\text{LiNbO}_3:\text{Cr}, \text{Mg}(2\%)$  and  $\text{LiNbO}_3:\text{Cr}, \text{Mg}(5.5\%)$  crystals at temperature  $T=10\text{ K}$  as a function of pressure. The position of the  $R_1(\gamma)$  observed in the absorption spectrum (Refs. 6 and 9) is marked by  $\blacklozenge$  on the vertical axis of the graph.

Additional estimates of the  $\Delta_\beta$  and  $\Delta_\gamma$  values could be obtained from analysis of the pressure dependence of the luminescence decay times of various chromium centers. This will be a subject of the forthcoming paper.

Other small intensity sharp lines are discernible but only in strongly expanded luminescence spectra. They are probably related to low concentration chromium centers, other than those previously described ( $\alpha$ ,  $\beta$ , and  $\gamma$ ) and they will not be discussed further in this paper since the  $\gamma$  center dominates the luminescence spectrum at any pressure by the broad-band luminescence at low pressure or by the sharp one at pressure higher than 40 kbar (see Figs. 2 and 3). The  $\beta$  center constitutes about 10% of total emission when excited by the 514.5-nm line of argon-ion laser at higher than 60-kbar pressure. The remaining centers, including the  $\alpha$  center, contribute only very little to the total luminescence intensity. This means that their concentration is very low in spite of the  $\alpha$  center luminescence which is clearly observed at ambient pressure.

There are some ambiguities related to the nature of the different  $\text{Cr}^{3+}$  centers in the  $\text{LiNbO}_3$  crystals. Macfarlane *et al.* in the previous work<sup>9</sup> identified the  $\gamma$  center as undistorted  $\text{Cr}_{\text{Li}}$  site in the  $\text{LiNbO}_3$  host. The possible candidates for the  $\alpha$  and  $\beta$  centers were proposed by Macfarlane *et al.*<sup>9</sup> as  $\text{Cr}_{\text{Li}}^{3+}$  perturbed by nearby  $\text{Nb}^{5+}$  vacancies or antisites ( $\text{Nb}^{5+}$  ions in  $\text{Li}^+$  sites). Lhomme *et al.*<sup>12</sup> has linked these centers, which are likely to exist in nonstoichiometric crystals, to  $\text{Cr}^{3+}$  ions having niobium antisites ( $\text{Nb}_{\text{Li}}$ ) and cationic vacancies ( $V_{\text{Nb}}$  or  $V_{\text{Li}}$ ) in their nearest surrounding.

The crystal doped with 5.5% of Mg (above the 4.5% Mg threshold) exhibits different pressure dependence of the luminescence spectra. Luminescence spectra of this crystal under different pressure are shown in Fig. 5. The pressure evolution of the sharp  ${}^2E \rightarrow {}^4A_2$  luminescence in this sample resembles very much this evolution in the crystal with 2% of Mg. The spectral positions of the major sharp  $\text{Cr}^{3+}$  luminescence lines at various pressures are the same in both crystals (see Fig. 4). This indicates that the  $\text{Cr}_{\text{Li}}^{3+}$  centers existing in

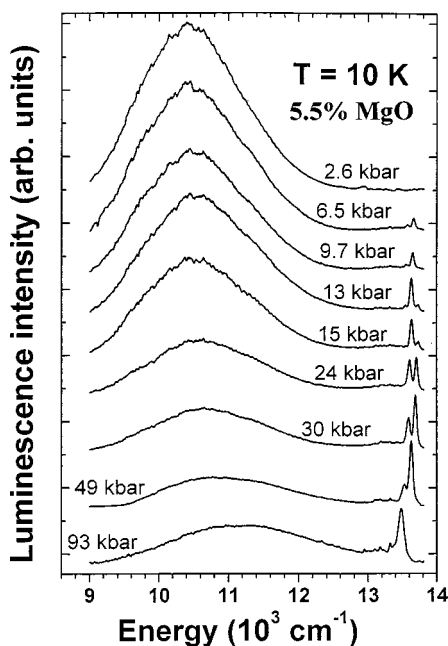


FIG. 5. The pressure dependence of the  $\text{Cr}^{3+}$  luminescence in  $\text{LiNbO}_3:\text{Cr}, \text{Mg}(5.5\%)$  crystal at temperature  $T = 10 \text{ K}$ .

the 2% Mg codoped sample are also present in the 5.5% Mg codoped crystal. However, the  $R$ -lines are slightly broader than in the crystal codoped with 2% of Mg, which is related to the larger disorder in the 5.5% Mg doped sample.

The most relevant difference is observed in the broad band luminescence. An additional broadband luminescence is observed in the crystal with 5.5% of magnesium at ambient pressure that has been associated with the chromium ions in niobium sites ( $\text{Cr}_{\text{Nb}}^{3+}$ ).<sup>5,6,9,10,12-14</sup> Results of electron paramagnetic resonance (EPR) (Ref. 10) and electron-nuclear double resonance (ENDOR) (Refs. 20 and 21) experiments strongly support this conclusion. It has been denoted as center  $\delta$  by Macfarlane *et al.*<sup>9</sup> The broadband luminescence of this center overlaps strongly with the broadband luminescence of the center  $\gamma$  at ambient pressure. The broadband luminescence of the center  $\delta$  have similar pressure coefficient as the broadband luminescence of center  $\gamma$  [i.e., (12

$\pm 3$ )  $\text{cm}^{-1}/\text{kbar}$ ]. The  $\delta$  center luminescence does not disappear at pressures of almost 100 kbar in contrast to the sample with 2% of Mg where the broadband luminescence disappears at pressure below 40 kbar. Therefore at pressures above 40 kbar the broad-band luminescence of sample with 5.5% of Mg is associated only with luminescence of center  $\delta$ . We do not observe any new additional sharp lines associated with this center, even at pressure of 93 kbar. It means that the center  $\delta$  is a very low crystal-field center since even shift of the  ${}^4T_2$  level larger than  $1200 \text{ cm}^{-1}$  does not transform it into a high-crystal field center. However, additional studies are necessary to reveal the exact electronic structure of this center.

All  $\text{Cr}_{\text{Li}}^{3+}$  centers exhibit very large redshift rates of the  ${}^2E \rightarrow {}^4A_2$  transitions with pressure of about  $3 \text{ cm}^{-1}/\text{kbar}$ . The shifts observed in other oxide materials, as ruby or garnets, are usually smaller than  $1 \text{ cm}^{-1}/\text{kbar}$ . This shift is usually attributed to a decrease of interelectronic crystal field repulsion parameters  $B$  and  $C$  with pressure. The low symmetry of the  $\text{Cr}^{3+}$  ion environment may contribute to this behavior.

In summary, the results of the high-pressure luminescence studies of  $\text{LiNbO}_3:\text{Cr}, \text{Mg}$  crystals reveal information about the crystal-field strength that affects the  $\text{Cr}^{3+}$  ions in the various  $\text{Cr}^{3+}$  centers formed in  $\text{LiNbO}_3$ . The pressure dependencies of the luminescence of  $\text{Cr}_{\text{Li}}^{3+}$  ions in the  $\beta$  and  $\gamma$  centers show that both of them are rather intermediate crystal-field centers, although the values of the  ${}^4T_2$ - ${}^2E$  energy differences  $\Delta$  have different signs ( $\Delta_\beta > 0$  and  $\Delta_\gamma < 0$ , for the  $\beta$  and  $\gamma$  centers, respectively). On the other hand the  $\text{Cr}_{\text{Li}}^{3+}$   $\alpha$  center is a high-crystal field center. Concentration of the  $\alpha$  center is very low as compared with the concentrations of the  $\gamma$  and  $\beta$  centers. The experimental results also unambiguously show that an additional  $\text{Cr}^{3+}$  center  $\delta$  in crystals codoped with magnesium above the 4.5% Mg concentration threshold, that corresponds to the  $\text{Cr}^{3+}$  ions in  $\text{Nb}^{5+}$  sites, is a very low crystal-field center.

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