Dominant Cr^{3+} Centers in $LiNbO_3$ Under Hydrostatic Pressure

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Low temperature luminescence spectra of stoichiometric Cr : $LiNbO_3$ and of congruent Cr,Mg : $LiNbO_3$ were studied. Cr^{3+} impurity ions occupy preferentially Li^+ sites (Cr_{Li}) in the $LiNbO_3$ crystal lattice while Cr^{3+} substituting Nb^{5+} ions (Cr_{Nb}) occur in addition to Cr_{Li} centers in co-doped Cr,Mg : $LiNbO_3$ crystals. Application of high hydrostatic pressure leads to a transformation of dominant in concentration Cr^{3+} centers from low to high crystal field centers. Due to strong pressure induced blue shift of $^4T_2$ state resulting in the crossing with ^2E state, the replacement of broad band $^4T_2 \rightarrow {}^4A_2$ emission by narrow R-lines emission $^2E \rightarrow {}^4A_2$ occurs in luminescence spectra of the samples. This effect of level crossing was observed for the dominant Cr^{3+}_{Li} and Cr^{3+}_{Nb} centers at pressures well correlated with estimations based on $^4T_2$–^2E energy gap (230 and 1160 cm^{-1}) and on the rate of their pressure induced change (14.35 and 11.4 cm^{-1}/kbar respectively).

$LiNbO_3$ crystals doped with Cr^{3+} ions have being investigated intensively since 1968, and considerable progress was made recently in the understanding of the complicated optical spectra of the material [1–9]. In the rhombohedral (space group $R3c$) lattice of $LiNbO_3$ the cations Li^+ and Nb^{5+} are surrounded by 6 oxygen ions forming trigonally distorted octahedrons. Present interpretation (see for example [4]) based on ESR data [10–12 and references therein] assumes that the "main" (dominant in concentration) Cr^{3+} centers in $LiNbO_3$ crystals correspond to Cr^{3+} ions substituting regular Li^+ sites in the host lattice. The energy diagram of $Cr^{3+}_{Li}(3d^3)$ electronic states corresponds to the case of low octahedral crystal field where the energy of the electronic $^4T_2(t^2e)$ state is lower than that of $^2E(t^3)$. Therefore the broad band $^4T_2(t^2e) \rightarrow {}^4A_2(t^3)$ transition [2,4] dominates at low temperatures in photoluminescence spectrum of Cr^{3+} : $LiNbO_3$. The positions of two broad absorption bands $^4A_2 \rightarrow {}^4T_2$, $^4A_2 \rightarrow {}^4T_1$ provide the green color of Cr^{3+} : $LiNbO_3$ samples.

Most of studies of Cr^{3+} on congruent $LiNbO_3$ crystals co-doped with Mg (Mg concentration less than 4.5 mol.%) show that Cr^{3+} ions also occupy preferentially Li^+ sites (Cr^{3+}_{Li}). But with Mg concentration increasing (higher than 4.5 mol.% for congruent samples) a fraction of Cr^{3+} ions tends to occupy additionally Nb^{5+} sites (Cr^{3+}_{Nb}) in the $LiNbO_3$ lattice, which was confirmed by ESR and ENDOR studies [13–15]. Above that Mg concentration threshold the samples change their color from green to pink due to a strong red shift of broad band transitions $^4A_2 \rightarrow {}^4T_2$, $^4A_2 \rightarrow {}^4T_1$ of Cr^{3+}_{Nb} centers relative those of Cr^{3+}_{Li} centers. Cr^{3+} ions substituting Nb^{5+} are also in low octahedral crystal field sites and the emission of Cr^{3+}_{Nb} centers in Mg co-doped $LiNbO_3$ samples is characterized by an intense broad band $^4T_2 \rightarrow {}^4A_2$ transition which exhibits a red shift relative to the $^4T_2 \rightarrow {}^4A_2$ transition of Cr^{3+}_{Li} centers in $LiNbO_3$ [4,15].

As it was shown earlier [16] the effect of high hydrostatic pressure on spectroscopic properties of crystals with octahedrally coordinated impurity Cr^{3+} ions is a powerful tool for studying of the electronic structure of impurity centers. Indeed the hydrostatic pressure results in a decrease of the distance R between impurity ions and ligands and hence in an increase of the crystal field strength Dq ($\sim 1/R^5$). According to the crystal field theory for $Cr^{3+}(3d^3)$ ions in octahedral field the increase of Dq strongly shifts up energies of $^4T_2$ and $^4T_1$ states while energy of the ^2E state depends on the distance from ligands much less [17]. Therefore the applied pressure drastically changes the distance between low lying $^4T_2$ and ^2E levels of Cr^{3+} resulting in strong effects in luminescence properties of Cr^{3+} ions due to changes in the mixing and relative population of $^4T_2$ and ^2E states [16]. Of special interest is the behavior of low field sites of Cr^{3+} under pressure application when pressure induced crossing of the lower $^4T_2$ and the higher ^2E electronic levels can be achieved. This crossing leads to the inversion of the lowest (emitting) state of Cr^{3+} from $^4T_2$ (at ambient pressure) to ^2E (at higher pressure). That manifests itself in the drastic effects in spectral and kinetic properties of the Cr^{3+} luminescence at low temperatures. Such pressure induced $^4T_2, {}^2E$ crossing was recently discovered experimentally for low field dominant Cr^{3+}_{Li} centers in congruent $LiNbO_3$. At low temperatures the change from broad band $^4T_2 \rightarrow {}^4A_2$ luminescence at ambient pressure to sharp R-line emission $^2E \rightarrow {}^4A_2$ under high hydrostatic pressure application was observed [18,19]. As to low field Cr^{3+}_{Nb} centers in Mg co-doped congruent $LiNbO_3$ the large pressure induced shift of the $^4T_2 \rightarrow {}^4A_2$ band was observed but the highest pressure value ($\sim$ 100 kbar) used in [18,19] was insufficient to observe the crossing of $^4T_2$ and $^4A_2$ levels of $\mathrm{Cr}^{3+}_{\mathrm{Nb}}$ centers.

In the present paper the effect of high pressures up to 300 kbar on luminescence spectra of low field $\mathrm{Cr}^{3+}_{\mathrm{Li}}$ and $\mathrm{Cr}^{3+}_{\mathrm{Nb}}$ centers in $LiNbO_3$ was studied experimentally at 4 K. The appearance of R-lines emission due to pressure induced crossing of $^4T_2, {}^2E$ levels was observed for both types of Cr^{3+} centers. The energies determined for electronic levels $^4T_2$ and ^2E together with the data on pressure dependence of $^4T_2{-}^2E$ energy gap allowed us to estimate the values of pressures which correspond to $^4T_2{-}^2E$ crossing points for $\mathrm{Cr}^{3+}_{\mathrm{Li}}$ (16 kbar) and for $\mathrm{Cr}^{3+}_{\mathrm{Nb}}$ (102 kbar). These values coincide well with experimentally determined ones when $^4T_2, {}^2E$ level crossing of these centers occurs under pressure applied. The studies of photoexcitation (in the energy region of R-lines) spectra of the $^4T_2 \to {}^4A_2$ broad band luminescence of $\mathrm{Cr}^{3+}_{\mathrm{Li}}$ and $\mathrm{Cr}^{3+}_{\mathrm{Nb}}$ centers at ambient pressure reveal a strong homogeneous broadening of ^2E-states due to fast non-radiative relaxation to the lower ($^4T_2$) states of these low field sites.

Perfect, close to stoichiometric, "green" samples $Cr^{3+}:LiNbO_3$ were used to study $\mathrm{Cr}^{3+}_{\mathrm{Li}}$ centers. For the study of $\mathrm{Cr}^{3+}_{\mathrm{Nb}}$ centers congruent co-doped "red" Cr,Mg:$LiNbO_3$ samples were used (these samples contain both $\mathrm{Cr}^{3+}_{\mathrm{Li}}$ and $\mathrm{Cr}^{3+}_{\mathrm{Nb}}$ centers). High hydrostatic pressure measurements were performed using a diamond-anvil cell. A mixture of ethanol, methanol, and water was used as a pressure-transmitting medium. For pressure calibration and monitoring of hydrostatic conditions the R-line luminescence of ruby was used from small ruby crumbs ($\sim$ 20 μm size) which were loaded into the cell together with probe sample ($\sim$ 80 μm size). The 488 nm line of an Ar-ion laser was used as an excitation source for luminescence measurements of $Cr^{3+}:LiNbO_3$ and ruby. The high pressure cell was mounted in a bath helium cryostat for measurements at 4 K.

1. Effect of high pressure on luminescence spectra of low field $\mathrm{Cr}^{3+}_{\mathrm{Li}}$ centers in $Cr^{3+}:LiNbO_3$ crystals

The close to stoichiometric sample $Cr^{3+}:LiNbO_3$ ($\sim$ 0.25 mol.% Cr) was prepared by the vapor phase transport equilibration (VTE) technique [5]. At ambient pressure in luminescence of this sample at liquid helium temperatures only transitions from the lowest excited state $^4T_2$ of the low field Cr^{3+} centers are observed. The broad $^4T_2 \to {}^4A_2$ band emission with narrow zero-phonon line at 13540 cm^{-1} is associated with dominating in concentration "majority" low field $\mathrm{Cr}^{3+}_{\mathrm{Li}}$ sites [8]. Some contribution to the broad band emission $^4T_2 \to {}^4A_2$ is given also by the "minority" low field Cr^{3+} centers [8] with relatively small concentration. The microscopic nature of the minority centers is not completely clear yet (these centers were attributed to Cr^{3+} ions in intrinsic octahedral void in $LiNbO_3$ lattice [8]). The presence of minority low field centers in the sample directly follows from the luminescence spectrum at enhanced temperature when the appearance of $^2E \to {}^4A_2$ transitions (R-lines) is stimulated by thermal population of the upper doublet ^2E states. Indeed, at 65 K besides the doublet $R_1 = 13\,772$ and $R_2 = 13\,810$ cm^{-1} belonging to majority $\mathrm{Cr}^{3+}_{\mathrm{Li}}$ centers, additional lines $R'_1 = 13\,683$ and $R'_2 = 13\,747$ cm^{-1} of minority low field sites are observed in luminescence (see also Fig. 3 in [8]).

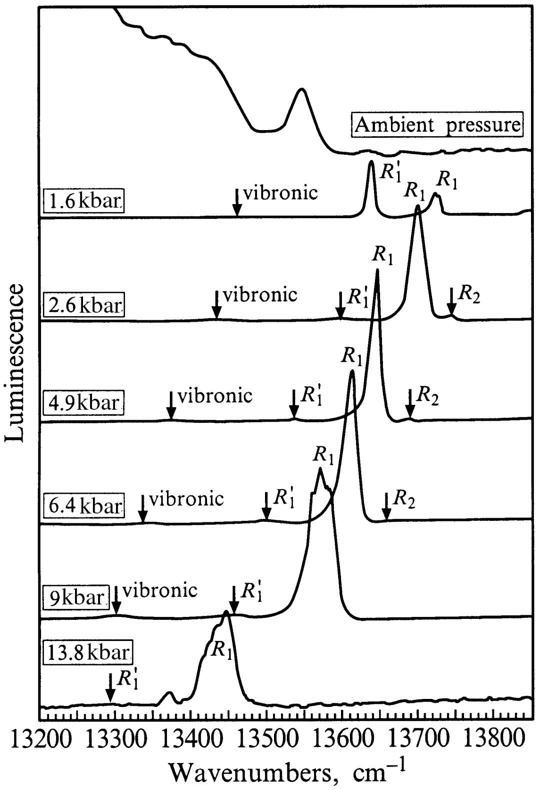

Figure 1. Luminescence spectra of VTE treated sample Cr:$LiNbO_3$ under hydrostatic pressure ($T = 4$ K, $\lambda_{\mathrm{exc}} = 488$ nm).

The luminescence spectra of the stoichiometric $Cr^{3+}:LiNbO_3$ at different hydrostatic pressures are presented in Fig. 1. At ambient pressure only the onset of $^4T_2 \to {}^4A_2$ broad band transition with the zero phonon line 13 540 cm^{-1} of dominant $\mathrm{Cr}^{3+}_{\mathrm{Li}}$ sites can be seen. The short wavelength region of $^2E \to {}^4A_2$ transitions is practically empty. But already at 16 kbar two lines R'_1 and R_1 in this spectral region are clearly seen. We may attribute them to $E(^2E) \to {}^4A_2$ transitions from populated at 4 K the lowest sublevel of doublet ^2E-state of minority and majority low field sites respectively. Proofs of this assignment are given below. While at 16 kbar the intensity of R'_1 exceeds the intensity of the R_1-line, at higher pressures the R_1-line of majority sites becomes dominant in the spectra. The pressure-induced appearance of $E(^2E) \to {}^4A_2$ lines is obviously due to the crossing of excited $^4T_2, {}^2E$ states when $E(^2E)$ state becomes the lowest emitting one. At some spectra in Fig. 1 the R_2-line related to $2A(^2E) \to {}^4A_2$ transitions from upper sublevel of doublet ^2E-state of majority centers also shows up in luminescence. The reason

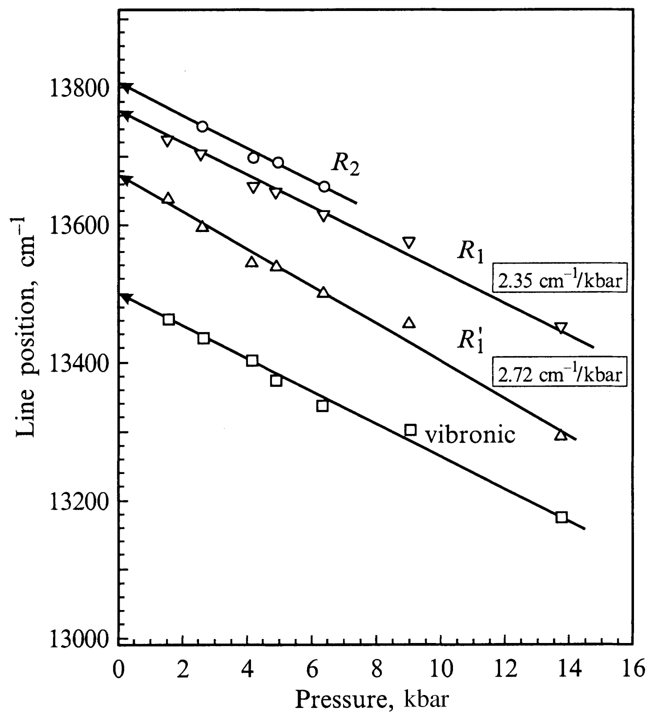

Figure 2. Pressure dependence of spectral position of R-lines of Cr : LiNbO$_3$.

is thermal population of the upper sublevel caused by local heating by the excitation laser beam of a very small piece of $\mathrm{Cr}^{3+}:\mathrm{LiNbO}_3$ in the high pressure cell. It should be noted also that at very high pressures > 140 kbar the luminescence spectrum changes drastically revealing the appearance of some additional structure of R-lines. The origin of such behavior is not completely clear. It may be caused by non-hydrostatic perturbation or by a formation of different crystalline phases of LiNbO$_3$ at very high pressures.

Fig. 2 displays frequencies of the luminescence lines detected at different hydrostatic pressures. With increase of pressure all R-lines exhibit a red shift. The linear extrapolation of experimental dependencies to zero pressure gives the positions of these lines at ambient pressure. The obtained values for R_1- and R_2-lines 13 772 and 13 810 cm^{-1} coincide with R_1 and R_2 frequencies $(E(^2E) \to {}^4A_2,\ 2A(^2E) \to {}^4A_2$ transitions$)$ of majority low field sites. These lines manifest themselves also in absorption and photoexcitation spectra of $\mathrm{Cr}^{3+}:\mathrm{LiNbO}_3$ at ambient pressure [2–4,20] and are interpreted as lines of dominant low field $\mathrm{Cr}_{\mathrm{Li}}^{3+}$ centers (γ-centers[4]). The frequency of R'_1-line extrapolated to zero pressure is equal to 13 683 cm^{-1} coinciding well with that for $E(^2E) \to {}^4A_2$ transition of minority low field sites [8]. It follows from Fig. 2 that energies of ^2E states of majority and of minority low field sites have slightly different sensitivity to pressure (linear shift coefficients 2.35 and 2.72 cm^{-1}/kbar respectively). The weak line at the low energy side of the spectra (Fig. 1) demonstrates the same pressure dependence of frequency as the R_1-line and probably can be associated with a vibronic satellite of the zero-phonon R_1-line of majority low field $\mathrm{Cr}_{\mathrm{Li}}^{3+}$ sites, the participating vibration frequency is ~ 270 cm^{-1}.

The above explanation of the origin of pressure induced R-line spectra of $\mathrm{Cr}^{3+}:\mathrm{LiNbO}_3$ as the result of $^4T_2, {}^2E$ level crossing of low field majority and minority Cr^{3+} sites is confirmed also by quantitative estimation of applied pressure values corresponding to $^4T_2, {}^2E$ levels crossing point for majority and minority Cr^{3+} sites. Evidently these pressure values depend on the $^4T_2 - {}^2E$ energy difference and on the rate of its change with applied hydrostatic pressure. The energy interval between electronic $^4T_2$ and ^2E states of low field centers is directly determined as the spectral distance between zero-phonon lines of $^4T_2 \to {}^4A_2$ broad band and of $E(^2E) \to {}^4A_2$ transition (R-lines). The energies of zero-phonon $^4T_2 \to {}^4A_2$ lines for majority and minority low field Cr^{3+} sites are 13 540 [8] and 13 560 cm^{-1} [20] respectively. Using the energies of R_1 (13 772 cm^{-1}) and R'_1 (13 683 cm^{-1}) for majority and minority sites we obtain the values of $^4T_2 - E(^2E)$ intervals for these sites as ~ 230 and 125 cm^{-1} respectively. The rate of pressure induced change of $^4T_2 - {}^2E$ interval is determined by the algebraic difference of rates for $^4T_2$ and ^2E levels. The rate of the pressure induced blue shift of $^4T_2$ level based on measurements of shift of $^4T_2 \to {}^4A_2$ emission band of $\mathrm{Cr}_{\mathrm{Li}}^{3+}$ centers is equal to 12 ± 3 cm^{-1}/kbar [18]. The observed blue direction of pressure induced shift of $^4T_2 \to {}^4A_2$ band is consistent with prediction of Sugano-Tanabe theory [17]. Using the rates for red shifts of R_1- and R'_1-lines (Fig. 2), 2.35 and 2.72 cm^{-1}/kbar, we obtain the rates of pressure induced shifts of $^4T_2 - {}^2E$ intervals for majority and minority sites as 14.35 and 14.72 cm^{-1}/kbar respectively. The ratio of the $^4T_2 - {}^2E$ interval to the above rate gives the value of pressure at which this interval becomes zero (crossing point): 16 kbar for majority and 8.5 kbar for minority low field Cr^{3+} sites. These estimations are in good agreement with the observed sequence of appearance of R_1-lines in the luminescence spectra of the crystal with increase of pressure. The R'_1-line of minority centers appears first and dominates at relatively small pressures below ~ 16 kbar, while the R_1-line of majority centers becomes dominant at higher pressures. Constant ratio of intensities of R'_1-, R_1-lines at pressures > 26 kbar is consistent with low concentration of minority low field Cr^{3+} centers in comparison with the concentration of dominating $\mathrm{Cr}_{\mathrm{Li}}^{3+}$ centers.

The R_1- and R_2-lines of the main $\mathrm{Cr}_{\mathrm{Li}}^{3+}$ centers observed in luminescence of $\mathrm{Cr}^{3+}:\mathrm{LiNbO}_3$ under hydrostatic pressure due to high concentration of these sites are easily observed at ambient pressure in absorption and photoexcitation spectra of broad band $^4T_2 \to {}^4A_2$ luminescence of $\mathrm{Cr}^{3+}:\mathrm{LiNbO}_3$ crystal [2–4,20]. In pioneering work [2] the anomalous large linewidth 50 cm^{-1} of absorption R_1-, R_2-lines of dominant low field Cr^{3+} centers in congruent LiNbO$_3$ was observed and explained by lifetime broadening of the ^2E state due to non-radiative relaxation from the ^2E to lower excited states of low field Cr^{3+} centers. Recently [20] the comparison of linewidth of R_1 and of R_2 transitions of dominant Cr^{3+}_{Li} centers in samples of different stoichiometry allowed to estimate the lifetime broadening of the ^2E state as $\sim 10\,cm^{-1}$ that corresponds to a decay time of $\sim 5 \cdot 10^{-13}$ s.

2. The effect of high pressure on the luminescence spectra of low field Cr^{3+}_{Nb} sites in Cr,Mg : $LiNbO_3$ congruent samples

Congruent $LiNbO_3$ co-doped with 0.25 mol% Cr and 6 mol% Mg was grown using Czochralskii method. The red color of the sample is typical for the $LiNbO_3$ samples with high (more than 4.5 mol%) concentration of Mg where Cr^{3+} ions occupy not only Li sites but also Nb sites of crystal lattice. At ambient pressure the low (liquid helium) temperature luminescence spectrum of such samples contains overlapping broad $^4T_2 \to {}^4A_2$ bands of both low field sites of Cr^{3+}_{Li} and of Cr^{3+}_{Nb} (maximum at 900 and at 1000 nm respectively[15]) centers. In the short wavelength region of the $^4T_2 \to {}^4A_2$ band the inhomogeneous broadened R-lines of high field perturbed Cr^{3+}_{Li} centers (α- and β-types [4]) are observed in our congruent Cr,Mg : $LiNbO_3$ sample.

Fig. 3 represents the low temperature ($T = 4$ K) luminescence spectra in the region of the $^2E \to {}^4A_2$ transitions at hydrostatic pressures starting from 55 kbar. In accordance with observations on stoichiometric sample (Fig. 1), the pressure induced R_1-line of the main Cr^{3+}_{Li} centers is dominating at 55 kbar. Further increasing of the pressure results in the appearance of the other intensive lines at the long wavelength region of the spectra which we attribute to R_1-lines of Cr^{3+} ions in Nb sites. The most intense new short wavelength line that dominates in spectra at high pressures above 140 kbar can be attributed to the R_1-line, $E(^2E) \to {}^4A_2$ transition, of the main Cr^{3+}_{Nb} centers which are responsible for the red shifted absorption $^4A_2 \to {}^4T_2, {}^4T_1$ and emission $^4T_2 \to {}^4A_2$ bands of red colored Cr,Mg : $LiNbO_3$ samples with Mg concentration above 4.5 mol% threshold. The second rather intense R'_1-line in the spectra indicates the presence of another Cr^{3+}_{Nb} center in the sample. As follows from Fig. 3 the relative intensity of R_1-line of the main Cr^{3+}_{Li} centers decreases significantly at pressures above 70 kbar. The observed drastic change of relative intensity of R_1-luminescence of Cr^{3+}_{Nb} and Cr^{3+}_{Li} centers with increase of the pressure (compare the spectra at pressures below and above 86 kbar) is caused by the difference of site selective excitation of these centers by Ar line 488 nm at low and high pressures. In Fig. 4 the excitation spectra of the broad band $^4T_2 \to {}^4A_2$ emission of congruent Cr,Mg : $LiNbO_3$ and of stoichiometric Cr : $LiNbO_3$ samples at ambient pressure are shown. Indeed, the excitation spectra are significantly different for the sample with only Cr^{3+}_{Li} centers and for the sample with both Cr^{3+}_{Li} and Cr^{3+}_{Nb} centers due to difference in energy of the $^4A_2 \to {}^4T_1$ absorption band of Cr^{3+} ions in Li and Nb sites. As one can see, at ambient pressure the 488 nm Ar-laser line is located near the maximum of $^4A_2 \to {}^4T_1$ band of Cr^{3+}_{Li} centers thus providing the preferential excitation of Cr^{3+}_{Li} centers at moderate hydrostatic pressures. Assuming the pressure induced shift of $^4T_1$ state to higher energy with approximate rate 12 cm^{-1}/kbar [18] we conclude that at hydrostatic pressures above 70 kbar the $^4A_2 \to {}^4T_1$ band shift to higher energies will reduce strongly the efficiency of 488 nm photoexcitation of Cr^{3+}_{Li} centers and increase this efficiency for Cr^{3+}_{Nb} centers.

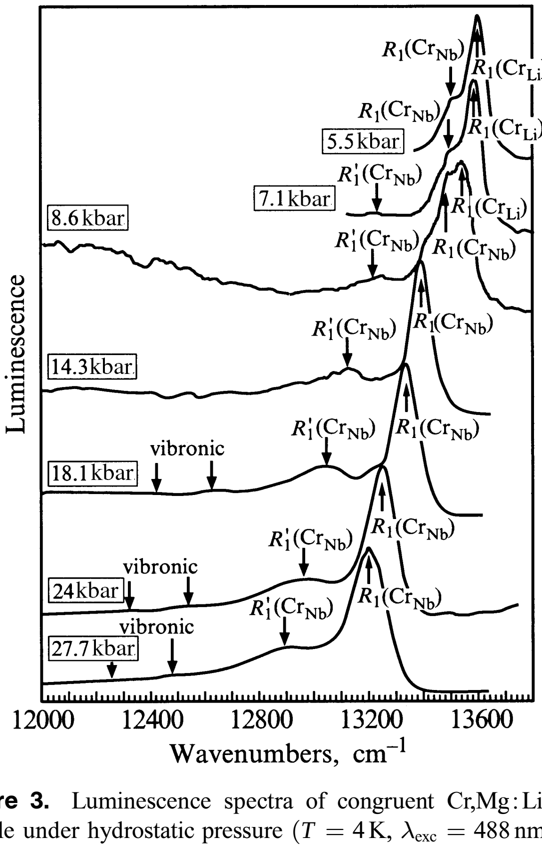

Figure 3. Luminescence spectra of congruent Cr,Mg : $LiNbO_3$ sample under hydrostatic pressure ($T = 4$ K, $\lambda_{exc} = 488$ nm).

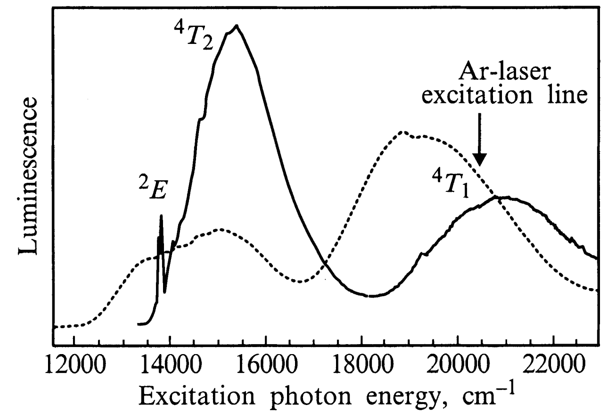

Figure 4. Photoexcitation spectra of $^4T_2 \to {}^4A_2$ emission in stoichiometric Cr : $LiNbO_3$ (solid line) and congruent Cr,Mg : $LiNbO_3$ (dashed line) samples ($T = 4$ K). Luminescence monitored at 11 200–8500 cm^{-1}.

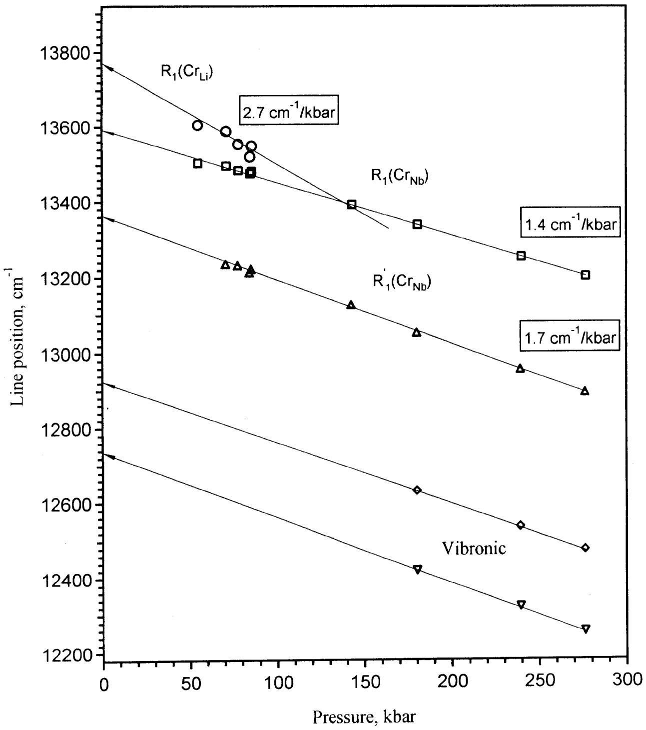

Figure 5. Pressure dependence of spectral position of *R*-lines of Cr,Mg : LiNbO$_3$ sample.

In Fig. 5 the energies of detected lines are plotted versus hydrostatic pressure. A linear pressure dependence of these energies is demonstrated. The slope of R_1 position of $\mathrm{Cr}_{\mathrm{Li}}^{3+}$ centers $\sim 2.7\,\mathrm{cm}^{-1}$/kbar coincides well with that for $\mathrm{Cr}_{\mathrm{Li}}^{3+}$ centers in stoichiometric samples (Fig. 2). R_1- and R_1'-lines of two $\mathrm{Cr}_{\mathrm{Nb}}^{3+}$ centers are much less sensitive to pressure (1.4 and $1.7\,\mathrm{cm}^{-1}$/kbar respectively). The linear extrapolation to ambient pressure gives frequencies 13 595 for R_1- and $13\,365\,\mathrm{cm}^{-1}$ for R_1'-line. The positions of two weak satellite lines detected at the low energy region of the spectra (Fig. 4) reveal the same pressure dependence ($1.7\,\mathrm{cm}^{-1}$/kbar) as the most intense R_1-line of $\mathrm{Cr}_{\mathrm{Nb}}^{3+}$ and probably can be associated with vibronic satellites of this line. The corresponding frequencies of vibrations are equal to 670 and $860\,\mathrm{cm}^{-1}$.

As was mentioned above, the most intense R_1-line that appears at high pressures only in Cr,Mg : LiNbO$_3$ should be attributed to dominant low field $\mathrm{Cr}_{\mathrm{Nb}}^{3+}$ centers responsible for the main spectroscopic features of red samples such as the absorption bands ${}^4A_2 \to {}^4T_2, {}^4T_1$ and the broad band ${}^4T_2 \to {}^4A_2$ emission centered at 1000 nm [15]. The hydrostatic pressure induces a blue shift of this emission band with a rate approximately $10\,\mathrm{cm}^{-1}$/kbar (Fig. 5 in ref. [18]). As it was observed in the present study the broad band ${}^4T_2 \to {}^4A_2$ is totally absent at a pressure of 140 kbar (Fig. 3) due to the crossing of ${}^4T_2, {}^2E$ states accompanied also by the appearance of a R_1-line ${}^2E \to {}^4A_2$ emission. This pressure strongly exceeds the pressure of 16 kbar required for the ${}^4T_2, {}^2E$ level crossing in the main $\mathrm{Cr}_{\mathrm{Li}}^{3+}$ centers (sec. 1). We assume that this difference is due to a much larger distance between ${}^4T_2$ and ${}^2E$ states of $\mathrm{Cr}_{\mathrm{Nb}}^{3+}$ centers in comparison with this distance ($230\,\mathrm{cm}^{-1}$) for $\mathrm{Cr}_{\mathrm{Li}}^{3+}$ sites. The absence of a detectable zero-phonon line ${}^4T_2 \to {}^4A_2$ in $\mathrm{Cr}_{\mathrm{Nb}}^{3+}$ centers does not allow to determine the position of electronic ${}^4T_2$ state of these centers directly and does not allow to find precisely the distance ${}^4T_2{-}{}^2E$ for $\mathrm{Cr}_{\mathrm{Nb}}^{3+}$ sites. However, the following estimation can be performed. Indeed, the red shift of broad band ${}^4T_2 \to {}^4A_2$ emission of dominant $\mathrm{Cr}_{\mathrm{Nb}}^{3+}$ sites (maximum at 1000 nm) relative to that of dominant $\mathrm{Cr}_{\mathrm{Li}}^{3+}$ sites (maximum at 900 nm) is equal to $\sim 1100\,\mathrm{cm}^{-1}$ [15]. Assuming the same red shift for the zero-phonon line of ${}^4T_2 \to {}^4A_2$ band and with known position of ${}^4T_2 \to {}^4A_2$ zero-phonon line of $\mathrm{Cr}_{\mathrm{Li}}^{3+}$ centers ($13\,540\,\mathrm{cm}^{-1}$), we obtain the position of this line of $\mathrm{Cr}_{\mathrm{Nb}}^{3+}$ centers: $12\,440\,\mathrm{cm}^{-1} = 13\,540{-}1100\,\mathrm{cm}^{-1}$ which is equal to the excitation energy of the electronic ${}^4T_2$ state. The value of $12\,440\,\mathrm{cm}^{-1}$ is in agreement with the position of the zero-phonon line ${}^4A_2{-}{}^4T_2$ estimated in [4] for $\mathrm{Cr}_{\mathrm{Nb}}^{3+}$ centers denoted as δ-centers. The energy distance $({}^4T_2{-}{}^2E) = 1160\,\mathrm{cm}^{-1}$ is determined as the difference of $13\,600$–$12\,440\,\mathrm{cm}^{-1}$ between this energy and the energy of the lowest sublevel of the ${}^2E$ doublet extrapolated to the ambient pressure position of the R_1-line — $13\,595\,\mathrm{cm}^{-1}$. Thus, the value of ${}^4T_2{-}{}^2E$ energy interval for $\mathrm{Cr}_{\mathrm{Nb}}^{3+}$ centers ($1160\,\mathrm{cm}^{-1}$) exceeds by factor of 5 this interval for $\mathrm{Cr}_{\mathrm{Li}}^{3+}$ centers ($230\,\mathrm{cm}^{-1}$) and correspondingly the pressure needed for crossing of ${}^4T_2$ and ${}^2E$ levels for $\mathrm{Cr}_{\mathrm{Nb}}^{3+}$ centers should be much higher than that for $\mathrm{Cr}_{\mathrm{Li}}^{3+}$.

In order to estimate the pressure that corresponds to the crossing point of ${}^4T_2, {}^2E$ levels we used the data [18] on the pressure induced shift of broad ${}^4T_2 \to {}^4A_2$ emission band of $\mathrm{Cr}_{\mathrm{Nb}}^{3+}$ centers in Cr,Mg : LiNbO$_3$ crystal with Mg concentration $\sim 5.5\%$ (Fig. 5 in ref. [18]). At Fig. 5 of [18] we compared the spectra at 24 kbar (at this pressure the ${}^4T_2, {}^2E$ crossing in $\mathrm{Cr}_{\mathrm{Li}}^{3+}$ centers did already occurr and only ${}^4T_2 \to {}^4A_2$ band of $\mathrm{Cr}_{\mathrm{Nb}}^{3+}$ centers should be seen) and at 93 kbar. From the observed shift of ${}^4T_2 \to {}^4A_2$ band we determined the linear rate of its pressure-induced blue shift as $\sim 10\,\mathrm{cm}^{-1}$/kbar. Adding to this value the rate $1.4\,\mathrm{cm}^{-1}$/kbar of red shift of the R_1-line of the ${}^2E \to {}^4A_2$ transition frequency (R_1-line, Fig. 5), we obtain the coefficient of the linear pressure induced change of the ${}^4T_2{-}{}^2E$ energy interval as $11.4\,\mathrm{cm}^{-1}$/kbar. This rate provides a decrease of the ${}^4T_2{-}{}^2E$ distance from $1160\,\mathrm{cm}^{-1}$ to zero (crossing point) at the pressure 102 kbar ($= 1160/11.4\,\mathrm{cm}^{-1}$/kbar). This estimation is in a good agreement with the observed (Fig. 5) value of the pressure between 86 and 143 kbar needed for the disappearance of the broad ${}^4T_2 \to {}^4A_2$ band.

The optical transitions ${}^4A_2 \to {}^2E$ of $\mathrm{Cr}_{\mathrm{Nb}}^{3+}$ centers found in the above high pressure experiments located at ambient pressure at $13\,595\,\mathrm{cm}^{-1}$ should in principle reveal themselves in observations of corresponding resonant *R*-transitions in absorption spectra and in ${}^4T_2 \to {}^4A_2$ photoexcitation spectrum of Cr,Mg : LiNbO$_3$ samples — similar to these transitions of $\mathrm{Cr}_{\mathrm{Li}}^{3+}$ centers (sect. 1 and [2–4,20]). Fig. 6 shows the broad

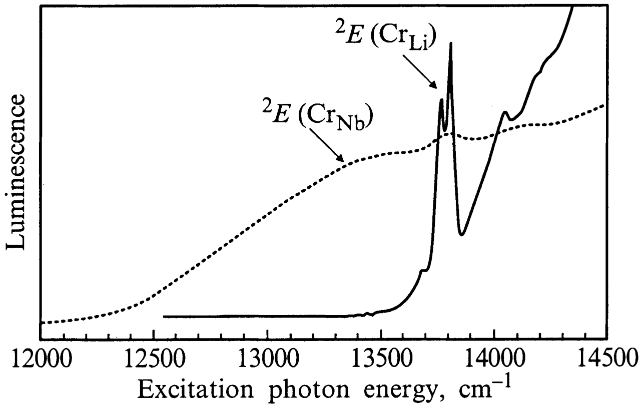

Figure 6. Detailed photoexcitation spectra of the $^4T_2 \to {}^4A_2$ emission in Cr:$LiNbO_3$ (solid line) and in Cr,Mg:$LiNbO_3$ (dashed line) samples in the region of $^4A_2 \to {}^2E$ transitions ($T = 4$ K). Luminescence monitored at 11 200–8500 cm^{-1}.

band $^4T_2 \to {}^4A_2$ luminescence photo-excitation spectrum of congruent Cr,Mg:$LiNbO_3$ red sample used in high pressure measurements in the low energy region of the $^4A_2 \to {}^4T_2$ absorption including also the region of $^4A_2 \to {}^2E$ transitions. In contrast to the case of Cr^{3+}_{Li} centers in $LiNbO_3$ where R_1, R_2 peaks were clearly observed in the photoexcitation spectrum (Fig. 6 and also [20]), no structure in the vicinity of the position ($\sim 13\,600\,cm^{-1}$) of $^4A_2 \to {}^2E$ transitions of Cr^{3+}_{Nb} centers is observed in the spectrum of congruent Cr,Mg:$LiNbO_3$ sample. We assume that the lack of resonant $^4A_2 \to {}^2E$ structure in photoexcitation spectrum of Cr^{3+}_{Nb} sites is caused by a very large broadening of these transitions due to lifetime homogeneous broadening of the ^2E state together with a very large inhomogeneous broadening of R-transitions in congruent co-doped Cr,Mg:$LiNbO_3$ sample. The latter is clearly seen in luminescence spectra of the sample at high pressure when these transitions appear in luminescence due to $^4T_2, {}^2E$ level crossing (Fig. 3). The observed spectral width of R_1-line of Cr^{3+}_{Nb} sites $\sim 80\,cm^{-1}$ not only strongly exceeds the width of the corresponding line of Cr^{3+}_{Li} sites (Fig. 1) observed at high pressure in near to stoichiometry VTE treated samples but also exceeds the inhomogeneous R-line spectral width of perturbed high field Cr^{3+} sites in congruent Cr:$LiNbO_3$ samples at ambient pressure [21,22]. This very large inhomogeneous broadening of R-lines of Cr^{3+}_{Nb} centers can be explained by a strong disorder in the lattice of co-doped Cr,Mg:$LiNbO_3$ due to the very high (~ 6 mol.%) concentration of Mg ions. Fig. 3 demonstrates also a prominent increase of inhomogeneous width of R_1-line of Cr^{3+}_{Nb} sites with increase of pressure. This effect possibly can be attributed to different pressure induced shifts of transition frequencies inside the inhomogeneous shape of the zero-phonon line of the impurity ion [23,25].

3. Discussion

The experimental results of Section 1 on the pressure induced crossing of $^4T_2$ and ^2E states of majority Cr^{3+}_{Li} centers in VTE treated samples Cr:$LiNbO_3$ are in a good agreement with results of earlier study made on congruent samples (Cr:$LiNbO_3$ co-doped with small 2% concentration of Mg) [18,19]. The measured coefficient of pressure induced R_1-line linear shift of majority Cr^{3+}_{Li} centers is close to the value 3 cm^{-1}/kbar given in [18]. At the same time our experimental results show that the pressure induced luminescence line that appears in the low energy region of R_1-line of majority centers should be attributed to R'_1-line of minority Cr^{3+} centers [8] but not to perturbed defect β-centers [4] as it was supposed in [18,19]. Indeed, the β-centers whose R_1 frequency at ambient pressure coincides accidentally with that of low field minority Cr^{3+} centers [8] are practically absent in our close to stoichiometry Cr^{3+}:$LiNbO_3$ sample. Furthermore, quantitative estimations of the pressure value that corresponds to $^4T_2, {}^2E$ level crossing point based on spectroscopic data on $^4T_2{-}E(^2E)$ energy intervals at ambient pressure for majority ($230\,cm^{-1}$) and minority ($125\,cm^{-1}$) low field centers as well as on measured linear pressure induced shifts of spectral $^4T_2 \to {}^4A_2$, $^2E \to {}^4A_2$ transitions, give a good agreement with experimental data for both low field sites that confirms validity of our interpretation. Generally it should be noted that at high pressures when inversion of $^4T_2, {}^2E$ levels of the main Cr^{3+} sites already occurred, the relative intensity of R-lines of high field perturbed Cr^{3+}_{Li} sites (α, β) always must be negligible compared to R-lines of main centers — even in congruent samples, where integrated intensity of R-line emission of perturbed centers does not exceed $\sim 1/1000$ of integrated emission intensity of main Cr^{3+} centers.

The results of Section 2, concerning the pressure induced $^4T_2, {}^2E$ level crossing in Cr^{3+}_{Nb} centers in congruent Cr,Mg:$LiNbO_3$ samples allowed us to get a detailed information about energy diagram of excited electronic $^4T_2$ and ^2E states of these low field centers, which are studied much less than the Cr^{3+}_{Li} centers. The centers of Cr^{3+} on Nb^{5+} sites were discussed recently in [24]. It becomes clear now that the large broadening of ^2E level due to fast decay into lower excited states together with the large inhomogeneous broadening of R-lines caused by a strong disorder of co-doped congruent Cr,Mg:$LiNbO_3$ crystals hampers any direct manifestation of narrow R-lines of low field Cr^{3+}_{Nb} centers in absorption and photoexcitation spectra at ambient pressure. Only the pressure induced inversion of $^4T_2, {}^2E$ levels that results in cancellation of lifetime broadening of the ^2E state allows us to observe directly the resonant $^2E \to {}^4A_2$ transitions in luminescence of congruent Cr,Mg:$LiNbO_3$ crystals. In a paper just published [26] the appearance of R-line in luminescence of Cr^{3+}_{Nb} centers under hydrostatic pressure was detected in "near-stoichiometric" Cr,Mg:$LiNbO_3$ samples which reveal reduced inhomogeneous broadening of R-lines. The determined values of the

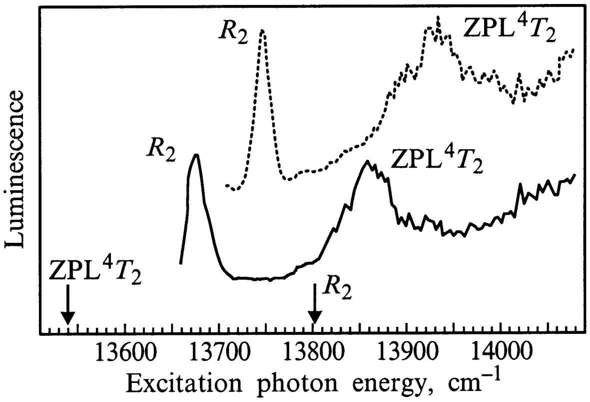

Figure 7. Photoexcitation spectra of $2A(^2E) \to {}^4A_2$ emission of α-centers (solid line) and β-centers (dashed line) in congruent $LiNbO_3$ sample at ambient pressure ($T = 4\,K$). Luminescence monitored at $R_1(\alpha)$- and $R_1(\beta)$-lines respectively. The arrows indicate the positions of R_2-line and of zero-phonon $^4T_2 \to {}^4A_2$ line of unperturbed trigonal Cr^{3+}_{Li} centers.

$^4T_2-{}^2E$ energy gaps for Cr^{3+}_{Nb} centers in the present paper ($1160\,cm^{-1}$) and in [26] ($> 1000\,cm^{-1}$) are consistent.

It is interesting to note that while the pressure induced linear blue shifts of the $^4T_2 \to {}^4A_2$ optical transitions differ slightly ($\sim 20\%$) for Cr^{3+}_{Li} and Cr^{3+}_{Nb} centers, the pressure induced red shifts of R-lines ($^2E \to {}^4A_2$ transitions) for these centers differ almost by factor of 2. As is known [17,21], the $^2E-{}^4A_2$ energy interval in $Cr^{3+}(3d^3)$ ions is determined mainly by the Racah parameters B, C, which describe the Coulomb electron-electron interaction in $3d$ shell in Cr^{3+} ions, and less by crystal field strength $10Dq$. The Racah parameters of $3d$ ions in crystals are reduced from their free ion values by covalency between the $3d$ and ligand electrons, a phenomenon known as nephelauxetic effect [21]. Similarly to the case of ruby, the pressure induced red shift of R-lines of Cr^{3+} centers in $LiNbO_3$ may be due to the decrease of distance Cr–O and increase of the overlap between $3d$ and ligand electrons, thus resulting in reduction of Racah B parameter and, hence, in reduction of the $^4A_2 \to {}^2E$ excitation energy. As is seen, the pressure induced reduction of Racah parameter is essentially different for Cr^{3+} ions occupying the Li^+ or Nb^{5+} sites in $LiNbO_3$ lattice. We can add that it is this change in Racah parameter that is responsible not only for the pressure induced red shift of R-lines of Cr^{3+} centers in $LiNbO_3$ but also for the small energy shifts of R-line frequencies in random fields of intrinsic defects (inhomogeneous broadening of R-lines of Cr^{3+} ions in $LiNbO_3$ [21,22]).

The existing model of the microstructure of main low field Cr^{3+}_{Li} and Cr^{3+}_{Nb} centers assumes that both centers have simple structure when Cr^{3+} ions substitute regular Li^+ or Nb^{5+} ions in $LiNbO_3$ lattice and are located in the trigonal (group C_3) crystal field. The perturbed Cr^{3+}_{Li} sites (α, β) which exhibit at low temperatures relatively weak R-lines in luminescence spectra, belong to high field Cr^{3+} centers formed by Cr^{3+}_{Li} ions with nearby intrinsic defect in the nearest cation coordination sphere [4,22]. Hence, these are nearby point defects, which are responsible for the transformation of low field Cr^{3+}_{Li} site into high field complex center. It is important to note that this defect induced transformation of trigonal Cr^{3+}_{Li} centers from low field to high field site has some common spectroscopic features with similar transformation of these trigonal main centers under high pressure. Indeed, the frequencies of $^4A_2 \to {}^2E$ and $^4A_2 \to {}^4T_2$ electronic transitions of both α- and β-centers are shifted to low energy and high energy sides respectively relative to these transitions of trigonal Cr^{3+}_{Li} centers. The same behavior of corresponding transitions of Cr^{3+}_{Li} centers was observed under application of hydrostatic pressure. This is clearly seen in photoexcitation spectra of $2A(^2E) \to {}^4A_2$ emission of α- and β-centers where corresponding R_2-lines and zero-phonon lines of the $^4A_2 \to {}^4T_2$ transition are shown (Fig. 7). The above mentioned similarity indicates the role of the lattice compression around Cr^{3+}_{Li} ion produced by nearby defects.

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References

[1] G. Burns, D.F. O'Kane, R.S. Title. Phys. Rev. **167**, *2*, 314 (1968).
[2] A.M. Glass. J. Chem. Phys. **50**, *4*, 1501 (1969).
[3] W. Jia, H. Liu, R. Knutson, W.M. Yen. Phys. Rev. **B41**, **16**, 10 906 (1990).
[4] P.I. Macfarlane, K. Holliday, J.F.H. Nicholls, B. Henderson. J. Phys.: Condens. Matter **7**, 9657 (1995).
[5] C. Fisher, S. Kapphan, Xi-qi Feng, Ning Cheng. Radiation Effects and Defects in Solids **135**, *1–4*, 199 (1995).
[6] V. Trepakov, A. Skvortsov, S. Kapphan, L. Jastrabik, V. Vorlichek. Ferroelectrics **239**, 297 (2000).
[7] F. Lhomme, P. Bourson, M.D. Fontana, G. Malovichko, M. Aillerie, E. Kokanyan. J. Phys.: Condens. Matter **10**, 1137 (1998).
[8] G.M. Salley, S.A. Basun, G.F. Imbusch, A.A. Kaplyanskii, S. Kapphan, R.S. Meltzer, U. Happek. J. Lumin. **83–84**, 423 (1999).
[9] G.M. Salley, S.A. Basun, A.A. Kaplyanskii, R.S. Meltzer, K. Polgar, U. Happek. J. Lumin. **87–89**, 1133 (2000).
[10] G.I. Malovichko, V.G. Grachev, S.N. Lukin. Sov. Phys. Solid State **28**, 553 (1986).
[11] G. Corradi, A.V. Chadwick, A.R. West, K. Cruickshank, M. Paul. Radiation Effects and Defects in Solids **134**, *1–4*, 219 (1995).

[12] G. Malovichko, V. Grachev, E. Kokanyan, O. Schirmer. Phys. Rev. **B59**, *14*, 9113 (1999) see references therein.
[13] J. Diaz-Caro, J. Garcia-Sole, D. Bravo, J.A. Sanz-Garcia, F.J. Lopez, F. Jaque. Phys. Rev. **B54**, *18*, 13042. (1996).
[14] G. Corradi, G. Sothe, J.-M. Spaeth, K. Polgar. J. Phys. Condens. Matter **3**, 1901 (1991).
[15] J. Diaz-Caro, J. Garcia-Sole, J.L. Martinez, B. Henderson, F. Jaque, T.P.J. Han. Optical Materials **10**, 69 (1998).
[16] V. Hömmerich, K.L. Bray. Phys. Rev. **B51**, *13*, 8595 (1995).
[17] B. Henderson, G.F. Imbusch. Optical Spectroscopy of Inorganic Solids. Oxford University Press. Clarendon, Oxford (1989).
[18] A. Kaminska, J.E. Dmochowski, A. Suchocki, J. Garcia-Sole, F. Jaque, L. Arizmendi. Phys. Rev. **B60**, *11*, 7707 (1999).
[19] A. Kaminska, A. Suchocki, M. Grinberg, J. Garcia-Sole, F. Jacue, L. Arizmendi. J. Lumin. **87–89** (2000).
[20] G.M. Salley, S.A. Basun, A.A. Kaplyanskii, A.B. Kutsenko, Th. Tröster, G.F. Imbusch, S. Kapphan, K. Polgar, R.S. Meltzer, U. Happek (to be published).
[21] P.I. Macfarlane, K. Holliday, B. Henderson. Chem. Phys. Lett. **252**, 311 (1995).
[22] V. Dierolf, A.A. Kaplyanskii, S. Kapphan, A.B. Kutsenko. Proceedings of the ICDIM'2000. Radiation Effects and Defects in Solids in print (2001).
[23] B.B. Laird, J.L. Skinner. J. Chem. Phys. **90**, *6*, 3274 (1989).
[24] V. Grachev, G. Malovichko. Phys. Rev. **B62**, *12*, 7779 (2000).
[25] P. Shellenberg, J. Friedrich, J. Kikas. J. Chem. Phys. **100**, *8*, 5501 (1994).
[26] A. Kaminska, A. Suchocki, L. Arizmendi, D. Callejo, F. Jaque, M. Grinberg. Phys. Rev. **B62**, *16*, 10 802 (2000).