Optical spectra and luminescence dynamics of Pr^{3+} and Nd^{3+} in SrLaAlO₄ single crystals

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Abstract. Single crystals of $SrLaAlO_4: Pr^{3+}$ and $SrLaAlO_4: Nd^{3+}$ have been grown by the Czochralski method and their optical properties have been studied for different activator concentrations. The absorption and emission spectra of the activators are inhomogeneously broadened because the Sr^{2+} and La^{3+} ions are distributed randomly on the sites of C_{4v} symmetry, however, the symmetry selection rules are still obeyed. Strong self-quenching of the praseodymium luminescence occurs by cross relaxation which is supposed to be assisted by phonon emission in the case of the $^3P_0$ level. Self-quenching of Nd^{3+} luminescence disappears at low temperature indicating that the condition of resonance in the cross-relaxation process is fulfilled only for higher components of the ground state.

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Availability of powerful laser diodes has stimulated the search for new laser crystals better suited for laser-diode pumping than those developed for broad-band pumping. Some interest has been directed recently to so called disordered crystals because inhomogeneous broadening of pump band matches better the pumping radiation, also the control of laser-diode temperature becomes less stringent. On the other hand, the inhomogeneous broadening may influence adversely the laser efficiency [1]. Therefore, knowledge of number and nature of activator sites as well as their mutual interaction is fundamental for the development of all solid-state lasers.

In this work, we present the results of investigation of a new disordered SrLaAlO₄ crystal which may be a promising host for the design of transition-metal or rare-earth-doped laser materials. SrLaAlO₄ belongs to a wide family of compounds of general chemical formula ABCO₄ where A denotes Sr or Ca, B denotes Y or rare-earth element, C denotes Al, Ga or transition-metal element. Considerable efforts have been made recently to understand the crystal growth of these compounds [2–4]. Some physical properties of several crystals belonging to the ABCO₄ family have been reported [5, 6], but little is known about their optical properties. Unpolarized absorption and emission spectra of CaYAlO₄ crystals doped with neodymium and erbium have been measured in the past [7]. More recently, the crystal structure and optical properties of CaNdAlO₄ have been investigated [8]. It has been found also that the majority of Cr^{3+} ions in chromium-doped SrLaAlO₄ are situated in the low crystal field [9], thus the crystal may be of interest as a tunable laser material. Preliminary investigation of neodymium-doped SrLaAlO₄ crystal has been reported in our–previous work [10], and the laser action in this activator–host combination has been achieved with laser-diode pumping [11].

Intention of this work is to get a better knowledge of the nature of the activator site and the activator–activator interactions relevant for laser behaviour of the crystal. Structural study showed that SrLaAlO₄ crystal is built up from translationally equivalent AlO₆ layers formed in the *ab*-plane of tetragonal structure belonging to the space group I4/*mmm* [8]. Between the layers, the Sr^{2+} and La^{3+} are distributed randomly in the nine-coordinated sites of C_{4v} symmetry. Rare-earth ions substitute lanthanum ions and transition-metal ions substitute aluminum ions and they are exposed to a strongly distorted crystal field. At least two non-equivalent Cr^{3+} sites have been observed in SrLaAlO₄ [9], however-extremely high density of point defects in the crystal prevented a meaningful interpretation of data.

In this study, praseodymium has been chosen for several reasons. First, its energy level scheme is relatively simple and easy to deal with. Second, the praseodymium-doped crystals are of interest as laser-active material emitting in the visible. Also, the ionic radius of Pr^{3+} is close to that of La^{3+}, and the doping does not introduce an additional distortion to the crystal structure.

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1 Experimental

Strontium lanthanum aluminate $SrLaAlO_4$ melts congruently at $1650°C$ and the crystals may be grown by the Czochralski method from stoichiometric melts. However, the process of crystallization of compounds belonging to the $ABCO_4$ family is not fully understood. It has been reported that the crystal growth was unstable [2] and that the obtained crystals were frequently opaque. Undoped crystals may look green, yellow and brown [3]. It has been concluded that the colour of the crystal is related to oxygen stoichiometry which is strongly influenced by the purity of chemicals, stability of the crystal growth, and the temperature gradient on the crystal–melt interface [4]. Therefore, we will describe in greater detail the preparation of our samples.

La_2O_3 and Al_2O_3 of 4 and 5 N purity respectively and $SrCO_3$ of 99.95 purity were used and all of them were checked by chemical analysis and by a trace analysis using a Perkin Elmer 430 atomic absorption spectrophotometer. The chemicals were annealed in standard conditions before weighting. $SrLaAlO_4$ was synthesised at $1200°C$ in an oxygen flow during 10 h. Crystal growth was performed by the Czochralski method using an rf induction heating with a passive afterheater. An iridium crucible 50 mm high and 50 mm in diameter with the walls 1.5 mm thick was used and the crystals were pulled in an atmosphere of nitrogen containing about 1% of oxygen. All crystal were grown using seeds with orientation (1 0 0). Four crystals containing 0.5, 1, 2 and 6 at. % of Pr^{3+} and two crystals containing 1 and 5 at. % of Nd^{3+} were grown for this study. X-ray analysis showed that the unit cell parameters $a = 3.757$ nm and $c = 12.636$ nm recorded for undoped crystals are not influenced by activators at the doping levels studied. The density of colour centres in neodymium-doped samples was considerably higher than in those doped with praseodymium, probably because the ionic radius of Nd^{3+} is smaller than that of Pr^{3+} and the crystal structure was strongly distorted.

For spectroscopic measurements, the samples in the form of plates of $1 \times 5 \times 5$ mm^3 were prepared with the optical axis (c-axis) in the plane of the plates, and the optical spectra were measured with the light polarized perpendicular (σ-polarization) and parallel (π-polarization) to the optical axis. Absorption spectra were measured with a Varian Model 2300 spectrophotometer whose spectral bandwidth was set to 0.2 nm. Luminescence was excited by a tunable dye laser which delivered the train of pulses of duration inferior to 10 ns. The luminescence was analyzed through a 1 m Hilger & Watts monochromator. Luminescence decay curves were recorded using a Canberra 35 + multichannel analyzer and the luminescence spectra were recorded using a photon-counting system. For low-temperature measurements the samples were placed in a liquid-helium cryostat equipped with a temperature controller.

2. Results

2.1 Praseodymium

In Fig. 1, we present the absorption spectra of $SrLaAlO_4 : Pr^{3+}$ in the visible region recorded at 7 K for

σ- and π-polarization. Splitting and energies of excited states may be determined directly from these spectra, since at such a low temperature solely the lowest component of the ground $^3H_4$ multiplet is populated. Apparently, the symmetry selection rules are obeyed, and there are no lines appearing in both polarizations. According to the results of structural investigation [8] we will assume that the rare-earth ions in $SrLaAlO_4$ are situated in the field of C_{4v} symmetry. Number and types of levels split out of a given J-multiplet by a crystal field of C_{4v} symmetry are recalled in Table 1. It should be noted that the $2J + 1$ degeneracy is not lifted completely for J integer. Selection rules for electric-dipole transitions are given in Table 2. With these data we may check the consistency of the absorption spectra in Fig. 1 with the site symmetry inferred from a structural study. According to Table 1, the unsplit $^3P_0$ multiplet is designed as A_1. The $^3H_4(1)-^3P_0$ transition is π-polarized therefore the lowest crystal-field component of the ground $^3H_4$ multiplet should be one of the two existing A_1 levels. The $^3P_1$ multiplet has one A_1 and one E component. Table 2 predicts only one transition to be allowed, with σ-polarization. Consistently, there is no absorption corresponding to a $^3H_4(A_1)-^3P_1$ transition in π-polarization. The $^3P_2$ multiplet has four crystal field components but only two transitions from the $^3H_4(1)$ are allowed: One σ-polarized and one π-polarized. These predictions agree well with the observed experimental results. One line peaking at
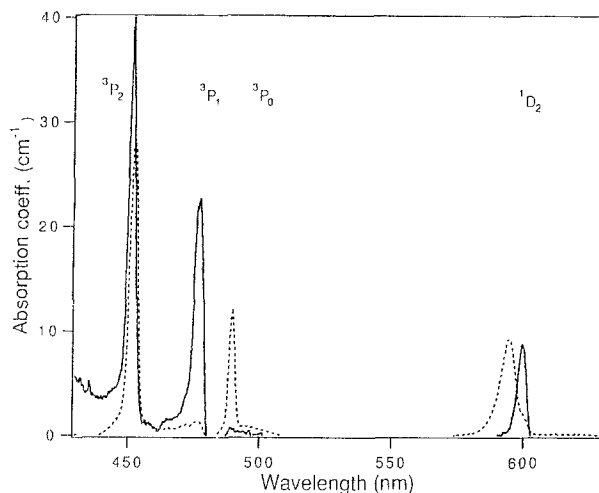
Fig. 1. Absorption spectra of Pr^{3+} in $SrLaAlO_4$ recorded at 7 K. *Dashed line*: polarization π; *solid line*: polarization σ. Pr^{3+} concentration was 2 at. %. All transitions from the ground $^3H_4(1)$ level to the levels indicated

Table 1. Types and number of energy levels for J integer in the crystal field of C_{4v} symmetry

J	0	1	2	3	4	5	6
A_1	1	0	1	0	2	1	2
A_2	0	1	0	1	1	2	1
B_1	0	0	1	1	1	1	2
B_2	0	0	1	1	1	1	2
E	0	1	1	2	2	3	3

451.5 nm is visible in the σ-polarized spectrum and one line peaking at 452 nm appears in the π-polarized spectrum. Similarly, two lines with different polarizations are seen in the spectra associated with the $^3H_4(A_1)$–$^1D_2$ transition. The π-polarized band is centered at 594.2 nm whereas the σ-polarized band is centred at 599.6 nm. We could not locate the $^1I_6$ multiplet since the $^3H_4$–$^1I_6$ transition does not appear in the absorption spectra. The particularly strong inhomogeneous broadening of the spectral lines of Pr^{3+} in $SrLaAlO_4$ is evidenced by the band associated with the $^3H_4(1)$–$^3P_0$ transition peaking at 489.6 nm (20 450 cm^{-1}). At 7 K, the bandwidth of this transition is 105 cm^{-1}. Excitation into the $^3P_2$, $^3P_1$ or $^3P_2$ multiplets leads to luminescence originating from the $^3P_0$ and from the thermally populated $^3P_1$ multiplet at higher temperatures. In Fig. 2, we present the complete luminescence spectrum excited at 450 nm and recorded at 8 K. The spectrum is dominated by a strong band corresponding to the $^3P_0$–$^3H_4$ transition centred at about 500 nm. A considerably weaker band associated with the $^3P_0$–$^3H_5$ transition appears at about 550 nm and the broad $^3P_0$–$^3H_6$ band is centred at about 635 nm. Two bands peaking at 656 and 745 nm have been assigned to the $^3P_0$–$^3F_2$ and $^3P_0$–$^3F_4$ transitions, respectively. Examination of the polarized luminescence spectra indicates that the symmetry selection rules are not obeyed as strictly as in absorption, and the number of the band components exceeds the number predicted for almost all transitions originating in the $^3P_0$. It should be noted that the emission band peaking at 497 nm is particularly intense and the terminal level for this transition is 400 cm^{-1} above the lowest crystal field component of the
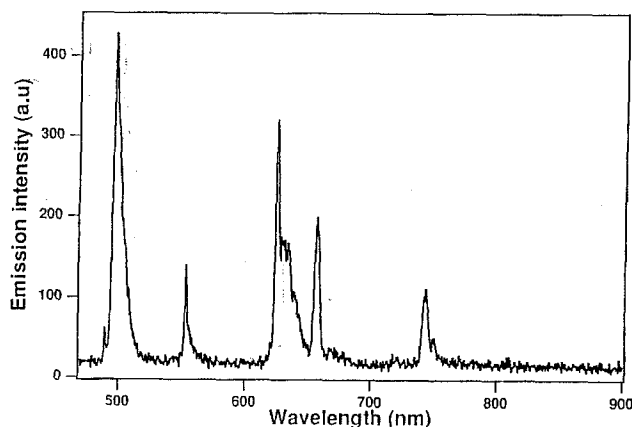
$^3H_4$ ground state. At low temperature, laser action associated with this transition may be feasible in a four-level laser scheme. Decay curves of luminescence originating from the $^3P_0$ level for samples containing 0.5, 2 and 6 at.% of praseodymium are shown in Fig. 3. For the lowest Pr^{3+} concentration the decay follows a single exponential time dependence, whereas a slight deviation from an exponential decay is seen during initial period of several microseconds for 2 and 6 at.% of praseodymium. At 7 K the luminescence decay curves were essentially the same as at room temperature. In Fig. 4 the decay curves of the luminescence originating from the $^1D_2$ multiplet are compared for the same concentrations of Pr^{3+}. In this measurement the $^1D_2$ multiplet was excited directly since the excitation via the $^3P_0$ was inefficient. It can be seen in Fig. 4 that in this case the decay does not follow an exponential time dependence even for the lowest content of praseodymium. At 7 K the decays become considerably slower: for 0.5 at.% of Pr^{3+} the room temperature decay time of 64 μs increases to 80 μs, but for all samples the decay curves are still nonexponential. The luminescence

Fig. 2. Complete luminescence spectrum excited at 451 nm. $T = 7$ K

Table 2. Symmetry selection rules for electric dipole transitions in the crystal field of C_{4v} symmetry

	A_1	A_2	B_1	B_2	E
A_1	π				σ
A_2		π			σ
B_1			π		σ
B_2				π	σ
E	σ	σ	σ	σ	σ

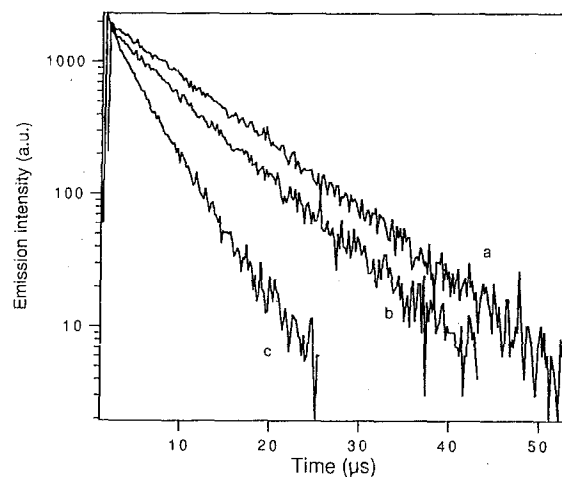**Fig. 3.** Decay curves of the $^3P_0$ luminescence for different Pr^{3+} concentrations: 0.5 at. % (a), 2 at.% (b) and 6 at. % (c), $T = 300$ K

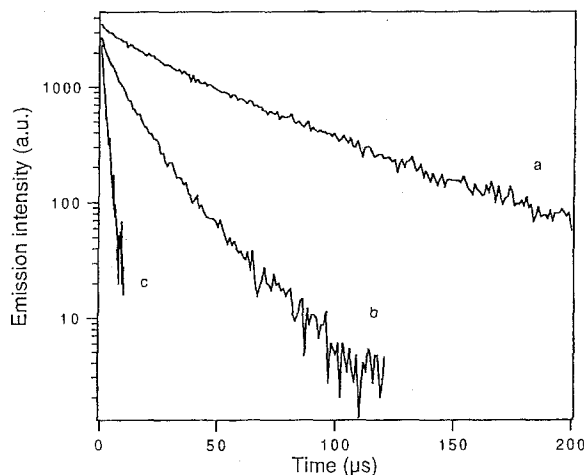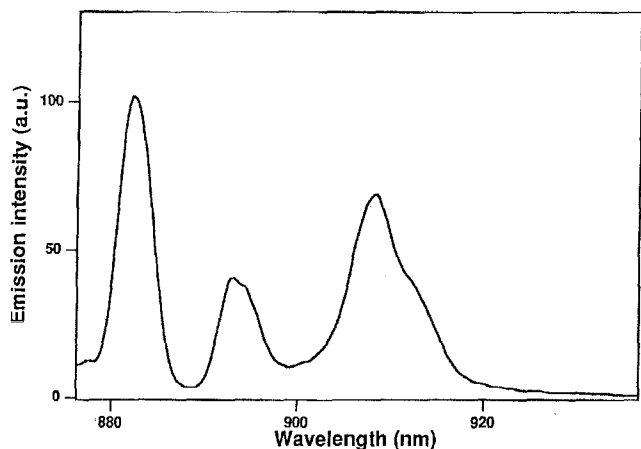**Fig. 4.** Decay curves of the $^1D_2$ luminescence for different Pr^{3+} concentrations: 0.5 at. % (a), 2 at. % (b) and 6 at. % (c), $T = 300$ K

Table 3. Luminescence lifetimes of the $^3P_0$ and $^1D_2$ levels recorded at room temperature for several Pr^{3+} concentrations

| Pr^{3+} concentration [at. %]	$^3P_0$ lifetime [μs]	$^1D_2$ lifetime [μs]
0.5	9.1	63.2
1	9.0	40.5
2	8.3	20.7
6	4.5	3.6

Fig. 5. $^4F_{3/2}-^4I_{9/2}$ emission band recorded at 7 K

lifetimes of the $^3P_0$ and $^1D_2$ levels for several concentration of Pr^{3+} in $SrLaAlO_4$ are compared in Table 3.

2.2 Neodymium

The luminescence spectrum corresponding to the $^4F_{3/2}(1) - ^4I_{9/2}$ transition recorded at 7 K is shown in Fig. 5. In this measurement, the luminescence was excited directly into the higher crystal field component of the $^4F_{3/2}$ multiplet by a pulsed dye laser equipped with a Raman shifter. Only three crystal field components of the $^4I_{9/2}$ state may be located unambiguously at 0, 113 and at 237 cm^{-1}. In Fig. 6 we present the excitation spectrum of the luminescence associated with the $^4F_{3/2}(1) - ^4I_{9/2}(1)$ transition recorded at 7 K. The $^4F_{3/2}(2)$ level centred at 871 nm was excited by a laser beam having a spectral bandwidth of 0.04 cm^{-1} and the resulting luminescence was sampled through a 10 μs gate delayed by 10 μs. The high resolution of this measurement never attainable in classical absorption spectroscopy would show nonequivalent and weakly coupled Nd^{3+} sites in the crystal. In our case, the excitation spectrum reproduces the absorption spectrum recorded at the same temperature.

The decay curves of the luminescence of the sample containing 5 at. % of Nd^{3+} recorded at 300, 150 and 7 K are compared in Fig. 6. The room temperature decay time of 48 μs increases to 57 μs at 150 K and attains 108 μs at 7 K. Deviation from an exponential time dependence occurs during the initial 20 μs of decay at room temperature and at 150 K. At 7 K, the decay curve follows a single exponential time dependence. The decay times recorded with the sample containing 1 at. % of Nd^{3+} were indepen-
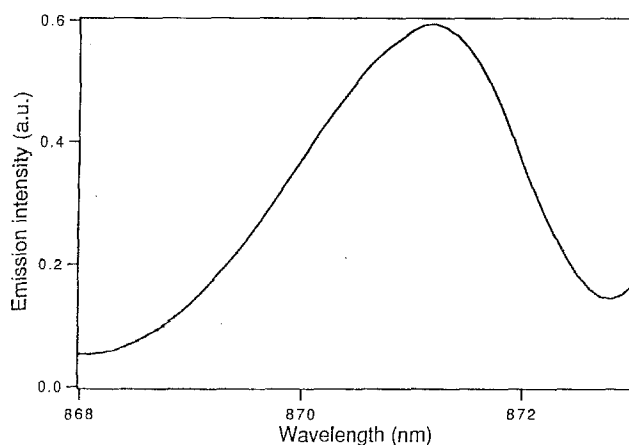
Fig. 6. Excitation spectrum of the $^4F_{3/2}(1)-^4I_{9/2}(1)$ emission of Nd^{3+} recorded a a7 K
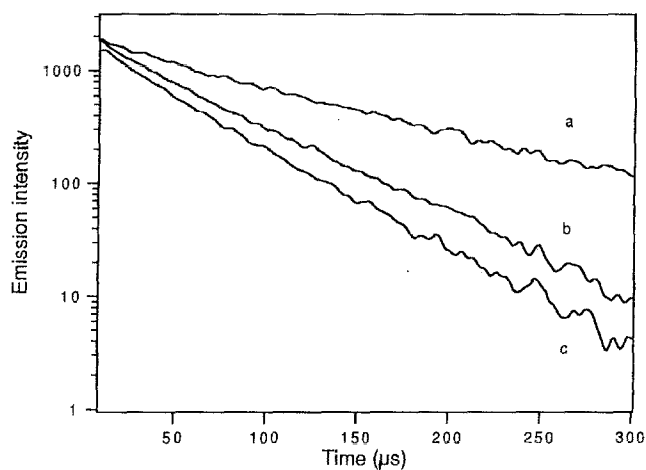
Fig. 7. Decay curves of ND^{3+} luminescence recorded at 7 K (a), 150 K (b) and at 300 K (c). Nd^{3+} concentration was 5 at. %

dent of the temperature in the 7–300 K temperature region and amounted to 110 μs. The decay curves followed an exponential time dependence.

3 Discussion

The low temperature optical spectra of Pr^{3+} and Nd^{3+} presented above give an evidence that $SrLaAlO_4$ forms a structure with an important disorder in the sites occupied by the rare earth ions. In the majority of the so-called disordered crystals the inhomogeneous broadening of the spectral bands of the rare earth ions results from a superposition of lines originating from slightly nonequivalent sites and weakly coupled ions. The number of different sites may be easily determined by low-temperature fluorescence line narrowing. In this way four sites have been found in neodymium doped $LaMgAl_{11}O_{19}$ single crystals [12] and three different ones have been observed in neodymium doped $LiNbO_3$ [13]. In contrast to these structures the rare earth ions in $SrLaAlO_4$ seem to be distributed in numerous sites in which the strength of the crystal field deviates statistically from a certain mean value. As

a result large and symmetric bands appear in the optical spectra. The polarized absorption spectra indicate that the structural disorder influences the strength but not the symmetry of the crystal field in the sites occupied by rare earth ions.

The relaxation dynamics for the three luminescent levels investigated in this work is not the same indicating contribution of different decay processes. Several processes may contribute to the decay, however in the limit of weak excitation the decay rate for an excited state of a rare earth ion in a solid may be approximated by the sum of radiative transition rates, the multiphonon transition rate, and the rate of nonradiative energy transfer between active ions. At relatively low concentration of activators, so as to minimize the ion–ion interaction, the excited levels are depopulated by radiative transitions, which are independent of temperature and by the temperature-dependent multiphonon relaxation. At higher concentrations of the rare earth ions the process of nonradiative energy transfer may contribute to the decay, too. In singly doped matrices activator ions act simultaneously as donors and acceptors giving rise to self-quenching of the luminescence. The time dependence of the donor luminescence following pulsed excitation is determined by the relative importance of the excitation energy migration over the donors and the self-quenching of the donor luminescence. If the energy migration over the donors may be neglected the decay is nonexponential because of nonuniform distribution of acceptors around the donors. If energy migration is important, the averaging over the donor–acceptor interactions occurs and the decay approaches an exponential time dependence. For diluted samples the decay curves of the luminescence originating from the $^3P_0$ multiplet of Pr^{3+} and from the $^4F_{3/2}$ multiplet of Nd^{3+} are exponential and temperature independent, indicating that the contributions of multiphonon relaxation and self-quenching of the luminescence are negligible. For Pr^{3+} the energy gap between the $^3P_0$ and the next lower $^1D_2$ levels is about 3400 cm^{-1} and for Nd^{3+} the energy gap between the $^4F_{3/2}$ and $^4I_{15/2}$ levels is about 4700 cm^{-1}. Since the phonon cut-off frequency in this matrix is situated at 750 cm^{-1}, at least seven phonons are needed to cover the energy gap in the case of neodymium, and four phonons in the case of praseodymium. The empirical energy gap law determined recently during the study of erbium doped $CaYAlO_4$ [14] gives for the $^3P_0$ a multiphonon relaxation rate of $3–4 \times 10^3$ s^{-1}. This value is roughly two orders of magnitude lower than the inverse of the observed $^3P_0$ lifetime. Consistently, there are not luminescence emissions from the $^1D_2$ level if the $^3P_0$ level is excited. Assuming that the decays of the $^3P_0$ level of Pr^{3+} and of the $^4F_{3/2}$ level of Nd^{3+} in diluted samples are purely radiative and taking the inverse of luminescence lifetimes we obtain radiative transition rates of 1.1×10^5 and 9.1×10^3 s^{-1}, respectively. The reduction of the luminescence lifetime of the $^3P_0$ level with increasing praseodymium concentration seems to be only slight, although the actual cross relaxation rate is quite high in this host: for 6 at.% of Pr^{3+} it is of the order of 10^5 s^{-1}, a value comparable to the radiative transition rate. The self-quenching seems to be resonant or assisted by phonon emission since the luminescence lifetimes of the concen-

trated samples do not depend on temperature. There is only one energy conserving cross-relaxation scheme in which an excited ion makes the $^3P_0–^1G_4$ downward transition and its unexcited neighbour makes the $^3H_4–^1G_4$ upward transition. Only three crystal field components of the $^1G_4$ multiplet can be located at 9680, 9872 and 10080 cm^{-1} from the low-temperature absorption, and these energies do not fulfill the condition of resonance. However, two of these levels may be involved in the process assisted by an emission of phonons with energies between 250 and 750 cm^{-1}. The self-quenching of the Nd^{3+} luminescence proceeds through a cross-relaxation process in which an excited ion makes the $^4F_{3/2}–^4I_{15/2}$ transition and its unexcited neighbour makes the $^4I_{9/2}–^4I_{15/2}$ transition. The strong temperature dependence of the luminescence lifetime of the concentrated sample indicates that the cross-relaxation process is assisted by phonon absorption or that the condition of resonance is fulfilled for higher crystal field components of the $^4I_{9/2}$ ground state. The low-temperature absorption allows to locate seven crystal field components of the $^4I_{15/2}$ level at 5805, 5900, 6035, 6106, 6228, 6385, and 6503 cm^{-1}. It can be seen that the crystal field component of the ground state at 237 cm^{-1} fulfills the condition for resonance in the cross relaxation via the crystal field level at 5805 cm^{-1}. At least two energy conserving cross-relaxation schemes may be involved in the self-quenching of the $^1D_2$ level. The self-quenching persists at low temperature even in the diluted sample. It may be resonant or assisted by phonon emission, however the operative scheme cannot be identified. The decay curves of the $^1D_2$ luminescence are non-exponential for all concentrations and on the whole time scale investigated. There is no migration of the $^1D_2$ excitation energy. It is obviously negligible because it involves the spin forbidden transition to and from the ground multiplet.

4 Conclusions

Random distribution of the divalent strontium and the trivalent lanthanum ions with a distribution ratio of 1 : 1 in the sites of C_{4v} symmetry results in a strong inhomogeneous broadening of the spectral lines of the activators which substitute the La^{3+} ions. Obtained results indicate that the activator ions in this matrix can be characterized by a definite probability of radiative transitions. The crystal allows the important ion–ion interaction as evidenced by an efficient self-quenching of praseodymium and neodymium luminescence.

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