Excitation energy transfer between Pr³⁺ and Nd³⁺ rare-earth ions in silicate glass

G F Chanturiya, Yu M Blagidze, Sh Sh Gvatua,
G A Nakashidze, R A Tatarashvili, Kh I Gaprindashvili

Abstract. Nonradiative excitation transfer (NET) was observed between trivalent Pr³⁺ and Nd³⁺ ions in silicate glass. Cooperative sensitisation of the luminescence of Nd³⁺ ions by Pr³⁺ ions in the $^4F_{3/2} \to {}^4I_{13/2}$ transition was observed as a result of NET. The luminescence was excited by the cw radiation of an Nd³⁺ : YAG laser with a power of ~ 800 W ($\lambda = 1.064$ μm) operating on the basis of the $^3H_4 \to {}^1G_4$ transition at the wavelength corresponding to the Pr³⁺ absorption band. The NET mechanism, responsible for the luminescence of the Nd³⁺ ion at the wavelength corresponding to the band with a maximum at $\lambda = 1.34$ μm, is discussed.

Since the majority of modern optical communication systems operate in the wavelength range of about 1.3 μm, the search for and study of new laser media for fibre-optic lasers and amplifiers operating in this range are of considerable scientific and practical interest.

At present, optical fibres based on Pr³⁺-ion-activated fluoride [1] and sulfide [2] glasses, luminescing at $\lambda = 1.3$ μm (the $^1G_4 \to {}^3H_5$ transition), are believed to be the most promising. Fibres made of oxide glasses, for example silicate glasses, are suitable for this purpose, since the luminescence efficiency of the Pr³⁺ ion in such fibres is exceptionally low at $\lambda = 1.3$ μm [3]. However, silicate fibres have the best optomechanical characteristics and can be easily joined (by welding) to standard optical fibres. Furthermore, silicate glass is a good laser matrix for the Nd³⁺ ion and undergoes three radiative transitions in the spectral ranges with $\lambda = 0.88$, 1.06, and 1.35 μm.

The intensities of the optical transitions in the absorption and luminescence spectra of Nd³⁺ in glass have been investigated before [4]. The band in which we are interested, with a maximum at the wavelength $\lambda \sim 1.35$ μm, is of low intensity in neodymium-doped laser media. Less than 20% of the total energy accumulated at the $^4F_{3/2}$ metastable level is emitted in this band. Silicate glasses and Nd³⁺-ion-activated optical fibres based on them can be used as laser media in the range of about 1.3 μm if the luminescence with $\lambda = 1.06$ μm in the main laser transition $^4F_{3/2} \to {}^4I_{11/2}$

G F Chanturiya, **Yu M Blagidze**, **Sh Sh Gvatua**, **G A Nakashidze**,
R A Tatarashvili, **Kh I Gaprindashvili** Institute of Cybernetics of the
Academy of Sciences of Georgia, u. Sandro Éuli 5, 380086 Tbilisi, Georgia

is 'suppressed' and the efficiency of the luminescence at $\lambda = 1.35$ μm, resulting from the additional transition $^4F_{3/2} \to {}^4I_{13/2}$, is increased.

This communication describes a study of nonradiative excitation transfer (NET) from excited Pr³⁺ ions to unexcited Nd³⁺ ions in silicate glass activated by the Pr³⁺ – Nd³⁺ donor – acceptor pair, which is accompanied by the cooperative sensitisation of the luminescence [5]. The NET process had been investigated earlier in silicate glasses activated by the Pr³⁺ – Nd³⁺, Tb³⁺ – Yb³⁺, Eu³⁺ – Yb³⁺ pairs [6 – 8] and quite recently in silicate fibres activated by the Tm³⁺ – Ho³⁺ pair [9].

Our study was made on samples of silicate glass activated by the oxides Pr₂O₃ and Nd₂O₃ with mass concentrations of 4% and 2%, respectively, and on samples containing only Pr₂O₃ with a mass concentration of 4%.

The absorption spectra were recorded on Specord UV VIS and SF-26 spectrophotometers, whereas the luminescence spectra were in a setup consisting of an excitation source in the form of a cw Nd³⁺ : YAG laser with an output power of ~ 800 mW ($\lambda = 1.064$ μm) and MDR-23 monochromator, and a recording photodetection system comprising a germanium photodetector and an FÉP-4 photoelectric attachment. The experiments were carried out at room temperature.

In glass samples activated by the Pr³⁺ – Nd³⁺ ion pair, we observed IR luminescence at wavelengths of the band having

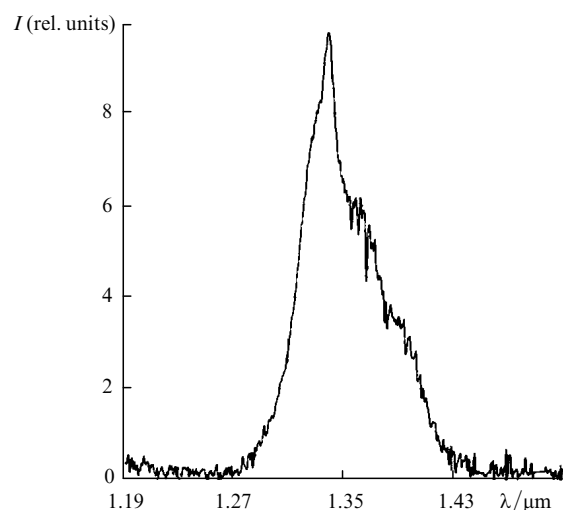**Figure 1.** Cooperative sensitised luminescence spectrum of Nd³⁺ ions in a silicate glass activated by the Pr³⁺ – Nd³⁺ ion pair.
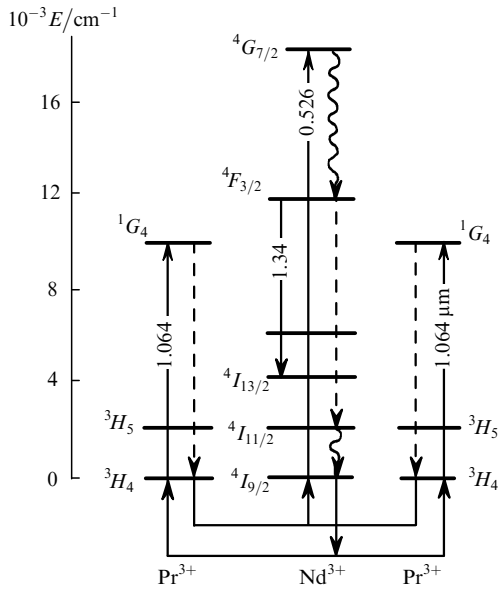
Figure 2. Simplified energy level diagrams of the Pr^{3+} and Nd^{3+} ions and the NET scheme of silicate glass. Continuous lines — absorption and emission; dashed lines — NET; wavy lines — multiphoton relaxation.

a maximum at $\lambda = 1.34 \ \mu m$ (Fig. 1). The luminescence was excited by laser radiation with $\lambda = 1.064 \ \mu m$ making use of the absorptive transition $^3H_4 \rightarrow {}^1G_4$ from the ground state of the Pr^{3+} ion (Fig. 2). The $^1G_4$ energy level is represented by a broad absorption band with a maximum at $\lambda \approx 1.02 \ \mu m$ and a low optical density of ~ 0.03. The wavelength $1.064 \ \mu m$ does not correspond exactly to resonance. This luminescence band is entirely absent under the same excitation conditions in glass samples containing separately only Pr^{3+} or only Nd^{3+} ions.

We identified the observed luminescence band as the cooperative sensitised luminescence of the Nd^{3+} ion corresponding to the $^4F_{3/2} \rightarrow {}^4I_{13/2}$ transition. The NET process between the excited Pr^{3+} ions (donors) and the unexcited Nd^{3+} ions (acceptors) is responsible for the appearance of this band. In our case, cooperative NET appears the most probable among all the varieties of NET [5]. This claim is based on the fact that the energy-level schemes of the Pr^{3+} and Nd^{3+} ions enable us to carry out the same analysis of the NET mechanism as in Ref. [5] for the $Yb^{3+} - Tm^{3+}$ pair.

Following Ovsyankin and Feofilov [5], one may claim that simultaneous excitation energy transfer takes place from two Pr^{3+} ions at the $^1G_4$ level to one unexcited Nd^{3+} ion ($^4I_{9/2}$) with summation of the energy quanta and subsequent transition to the $^4G_{7/2}$ level. This is promoted by the $2E_1 \approx E_2$ condition, where E_1 is the energy of the $^1G_4$ level of the Pr^{3+} ion and E_2 is the energy of the $^4G_{7/2}$ level of the Nd^{3+} ion (Fig. 2). This NET process is supported also by the quadratic dependence of the luminescence intensity on the excitation intensity.

Another type of NET — consecutive summation of the energies of two excitation quanta on a single Pr^{3+} ion in the $^1G_4$ level with subsequent transfer of this energy to an unexcited Nd^{3+} ion in order to effect its transition to the $^4G_{7/2}$ level — is unlikely, since the Pr^{3+} ion has no real levels with an energy approximately equal to twice the energy of the $^1G_4$ level. However, this mechanism may operate at higher laser excitation powers [7].

NET in nonresonant sensitisation of the luminescence is just as unlikely, since in this case nonresonant excitation energy transfer should take place from the Pr^{3+} to the Nd^{3+} ion with an energy deficit $\Delta E \approx 2000 \ cm^{-1}$ corresponding to the energy difference between the levels of the interacting transitions, i.e. the $^4F_{3/2}$ and $^1G_4$ levels. This deficit may be made good only by the energy of a matrix phonon, which requires the fulfillment of the condition $\Delta E \leqslant \nu_m$, where ν_m is the maximum limiting frequency of the fundamental vibration spectrum of the matrix [10]. This condition does not hold for silicate, phosphate, and borate glasses, because $\nu \approx 1000 - 1400 \ cm^{-1}$. Furthermore, a linear dependence of the luminescence intensity on the excitation intensity corresponds to the usual sensitisation of the luminescence.

NET is absolutely ruled out in nonlinear two-photon absorption owing to the smallness of the pump power. The efficiency of the luminescence transitions from the high-energy levels of the Nd^{3+} ion to the ground level is exceptionally low in silicate glasses. Most of the energy accumulated at these levels relaxes to the metastable level $^4F_{3/2}$. The energy emitted from the level $^4F_{3/2}$ by the $^4F_{3/2} \rightarrow {}^4I_{11/2}$, and $^4F_{3/2} \rightarrow {}^4I_{9/2}$ luminescent transitions is $\sim 80\%$.

The mechanisms of the nonradiative losses in the transitions from the level $^4F_{3/2}$, associated with the multipolar interaction of Nd^{3+} ions in crystals and glasses, have been investigated [11]. Furthermore, it is known [6, 12] that the Pr^{3+} ion quenches strongly the luminescence of the Nd^{3+} ion at $\lambda = 1.06 \ \mu m$. Part of the energy corresponding to the $^4F_{3/2} \rightarrow {}^4I_{11/2}$ transition is therefore transferred nonradiatively to unexcited Pr^{3+} ions, effecting their transition to the $^1G_4$ level (Fig. 2). This leads to the inverse NET process from the excited Nd^{3+} ions to the unexcited Pr^{3+} ions. Feedback, i.e. return of part of the energy to the system, promotes optimisation of the pump conditions at $\lambda = 1.06 \ \mu m$ and an increase in the luminescence efficiency in the $^4F_{3/2} \rightarrow {}^4I_{13/2}$ transition at $\lambda \approx 1.34 \ \mu m$, in which we are interested.

The present study thus demonstrates the possibility, in principle, of observing cooperative sensitised luminescence in the range of about $1.34 \ \mu m$ in silicate glass activated by the $Pr^{3+} - Nd^{3+}$ pair on irradiation of glass samples by $\lambda = 1.06 \ \mu m$ laser radiation and establishes the NET mechanism responsible for the luminescence. The results obtained have stimulated further investigations of this phenomenon in optical fibres in order to devise a laser medium for the $\sim 1.3 \ \mu m$ range. Powerful semiconductor laser diodes, emitting in the region of $\lambda \approx 1 \ \mu m$, may find a future application as excitation sources.

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