

# Cooperative luminescence sensitisation and spontaneous Raman scattering in a borate glass doped with $\text{Pr}^{3+}$ and $\text{Nd}^{3+}$ ions

G.F. Chanturia, L.M. Kutaladze, R.A. Tatarashvili, A.N. Shchegolikhin

**Abstract.** Cooperative sensitisation of luminescence of  $\text{Nd}^{3+}$  ions at the  ${}^4F_{3/2} \rightarrow {}^4I_{13/2}$ ,  ${}^4I_{9/2}$  transitions by  $\text{Pr}^{3+}$  ions was observed in a borate glass doped with  $\text{Pr}^{3+} - \text{Nd}^{3+}$  ion pairs. The luminescence was excited by a 800-mW, 1.064- $\mu\text{m}$   $\text{Nd}^{3+}:\text{YAG}$  laser. Simultaneously, spontaneous Raman scattering was observed in glasses containing  $\text{Pr}^{3+} - \text{Nd}^{3+}$  ion pairs or only  $\text{Pr}^{3+}$  ions. The Stokes shift from the 9398- $\text{cm}^{-1}$  excitation line is 794  $\text{cm}^{-1}$ . The mechanism of nonradiative energy transfer is discussed.

**Keywords:** nonradiative energy transfer, cooperative luminescence sensitisation, Raman scattering.

The sensitisation and quenching of luminescence in inorganic glasses doped with donor–acceptor pairs of trivalent rare-earth ions occur due to nonradiative energy transfer between interacting rare-earth ions and between excited ions and a glass matrix. In the latter case, the excitation energy of a rare-earth ion transfers to a glass matrix due to multiphonon nonradiative relaxation, which is present in glasses of all types at any dopant concentrations [1].

The processes of energy transfer have been most extensively studied in oxygen-containing glasses, in particular, silicate glasses doped with the  $\text{Pr}^{3+} - \text{Nd}^{3+}$ ,  $\text{Tb}^{3+} - \text{Yb}^{3+}$ ,  $\text{Eu}^{3+} - \text{Yb}^{3+}$ , and  $\text{Tm}^{3+} - \text{Ho}^{3+}$  ion pairs [2–5]. Cooperative nonradiative energy transfer from excited  $\text{Pr}^{3+}$  ions to the ground-state  $\text{Nd}^{3+}$  ions in a silicate glass doped with  $\text{Pr}^{3+} - \text{Nd}^{3+}$  pairs accompanied by the cooperative sensitisation of luminescence at a wavelength of 1.35  $\mu\text{m}$  was studied in Ref. [6].

Because the efficiency of nonradiative energy transfer depends substantially on the glass base, modifiers, composition, and dopants, it is interesting, both from the scientific and practical points of view, to study this process in oxygen-containing glasses of other types, for example, in borate glasses, where the efficiency of multiphonon nonradiative relaxation is the highest.

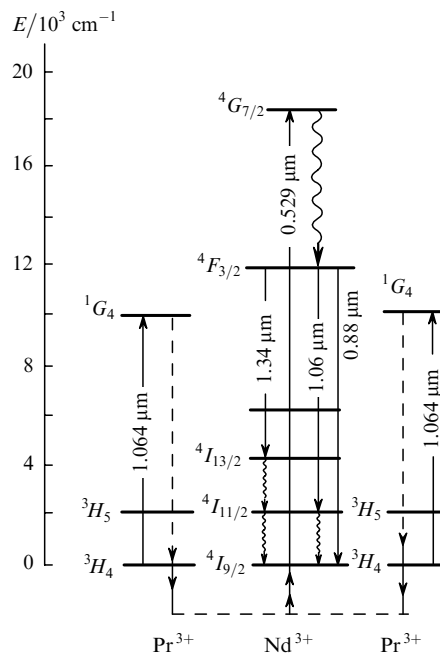
G.F. Chanturia, L.M. Kutaladze, R.A. Tatarashvili Institute of Cybernetics, Academy of Science of Georgia, ul. Sandro Euli 5, 380086 Tbilisi, Georgia; e-mail: chant@cyber.acnet.ge;  
A.N. Shchegolikhin Institute of Biochemical Physics, Russian Academy of Sciences, ul. Kosygina 4, 117977 Moscow, Russia;  
e-mail: Shchegol@deom.chph.ras.ru

Received 27 May 2003; revision received 26 November 2003  
Kvantovaya Elektronika 34 (4) 385–387 (2004)  
Translated by M.N. Sapozhnikov

In this paper, we have found for the first time, to our knowledge, that resonance Raman scattering is observed simultaneously with cooperative sensitised luminescence in a borate glass doped with donor–acceptor  $\text{Pr}^{3+} - \text{Nd}^{3+}$  ion pairs.

We studied glass samples containing components at the following weight concentrations: 65% of  $\text{B}_2\text{O}_3$ , 17% of  $\text{Al}_2\text{O}_3$ , 15% of  $\text{K}_2\text{O}$ , 1% of  $\text{Pr}_2\text{O}_3$ , and 2% of  $\text{Nd}_2\text{O}_3$ . The glasses were synthesised from chemically pure and extra chemically pure reagents and the samples were prepared in the form of rectangular plates of size  $1.5 \times 1.5 \times 0.3$  cm. The luminescence spectra were recorded using a setup consisting of a 1.064- $\mu\text{m}$ , 800-mW cw  $\text{Nd}^{3+}:\text{YAG}$  laser, MDR-23 monochromator, and a FEP-4 photoelectric detector. The experiments were performed at room temperature.

Luminescence was excited by a cw laser radiation at the  ${}^3H_4 \rightarrow {}^1G_4$  transition from the ground state of a  $\text{Pr}^{3+}$  ion (Fig. 1). It was established that two  $\text{Pr}^{3+}$  ions absorb separately one pump photon each and simultaneously

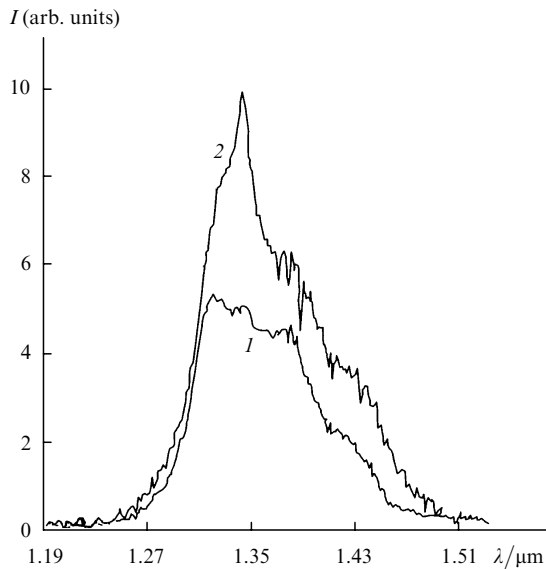


**Figure 1.** Simplified energy level diagram for the  $\text{Pr}^{3+}$  and  $\text{Nd}^{3+}$  ions demonstrating nonradiative energy transfer in a borate glass. The solid arrows directed upward and downward denote absorption and emission, respectively. The dashed and wavy arrows denote nonradiative energy transfer and multiphonon relaxation, respectively.

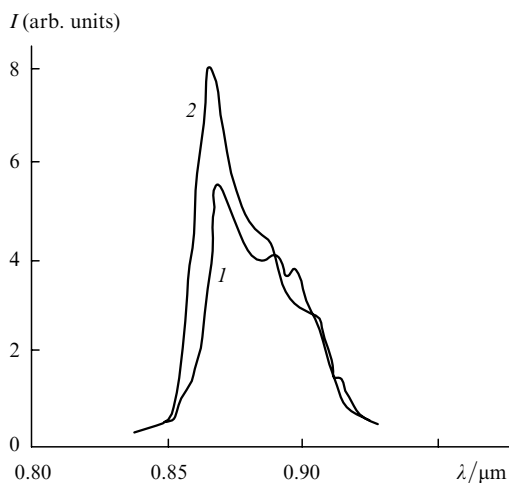
transfer their energy to a  $\text{Nd}^{3+}$  ion in the ground state. This ion is excited to the  ${}^4G_{7/2}$  level and then relaxes to the  ${}^4F_{3/2}$  metastable level, from which luminescence observed in our experiments occurs (see details in Ref. [6]). Absorption to the  ${}^1G_4$  level represents a broad band with a maximum at  $1.02\ \mu\text{m}$  and the optical density  $\sim 0.04$  at the maximum.

Silicate and borate glass samples doped with  $\text{Pr}^{3+} - \text{Nd}^{3+}$  ion pairs exhibited luminescence bands of  $\text{Nd}^{3+}$  ions at the  ${}^4F_{3/2} \rightarrow {}^4I_{13/2}, {}^4I_{9/2}$  transitions with maxima at  $1.35$  and  $0.88\ \mu\text{m}$ , respectively (Figs 2, 3).

The analysis of possible energy transfer processes performed in Ref. [6] suggests that these bands belong to cooperative sensitised luminescence of  $\text{Nd}^{3+}$  ion as well. However, the intensity of this luminescence in the borate glass is lower, while the bands are broader (Figs 2 and 3). Glasses doped separately only with  $\text{Pr}^{3+}$  or  $\text{Nd}^{3+}$  ions exhibit no luminescence when excited at the same wavelength.

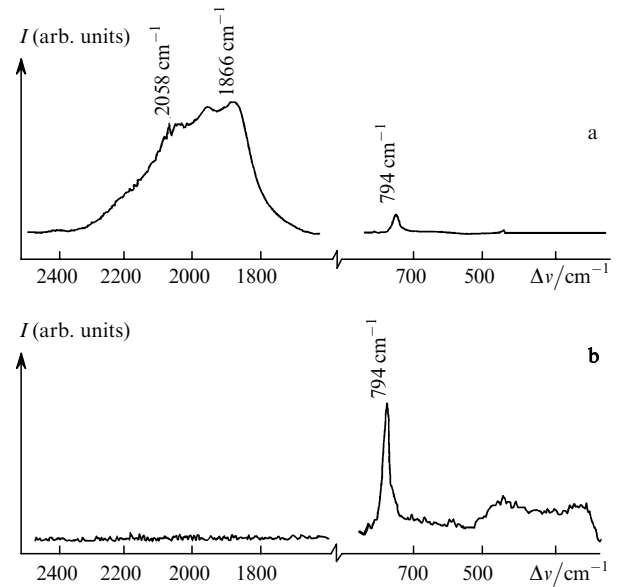


**Figure 2.** Spectra of cooperative sensitised luminescence of  $\text{Nd}^{3+}$  at  $1.35\ \mu\text{m}$  in borate (1) and silicate (2) glasses doped with  $\text{Pr}^{3+} - \text{Nd}^{3+}$  ion pairs.



**Figure 3.** Spectra of cooperative sensitised luminescence of  $\text{Nd}^{3+}$  at  $0.88\ \mu\text{m}$  in borate (1) and silicate (2) glasses doped with  $\text{Pr}^{3+} - \text{Nd}^{3+}$  ion pairs.

Glass samples doped with  $\text{Pr}^{3+} - \text{Nd}^{3+}$  pairs showed, along with cooperative sensitised luminescence bands, the  $1.162\text{-}\mu\text{m}$  band of small width  $\Delta\lambda \sim 30\ \text{\AA}$  (Fig. 4a). Emission at this wavelength was also found in samples doped only with  $\text{Pr}^{3+}$  ions, its intensity being almost five times higher than that in samples doped with  $\text{Pr}^{3+} - \text{Nd}^{3+}$  ion pairs (Fig. 4b). Glass samples of the same thickness that did not contain rare-earth ions exhibited emission at  $1.162\ \mu\text{m}$  upon the same excitation, the emission intensity being half the luminescence intensity of sample doped with  $\text{Pr}^{3+} - \text{Nd}^{3+}$  ion pairs.



**Figure 4.** Spectra of cooperative sensitised luminescence and the Raman line in a borate glass doped with  $\text{Pr}^{3+} - \text{Nd}^{3+}$  ion pairs (a) and only with  $\text{Pr}^{3+}$  ions (b). The line intensities are presented at the same scale.

It is obvious that this emission cannot be assigned to luminescence of  $\text{Nd}^{3+}$  or  $\text{Pr}^{3+}$  ions because they do not have the appropriate energy levels. The wavelength and width of this emission line corresponds to the spontaneous Raman line in a borate glass matrix [7]. According to Ref. [7], the frequency shift  $\Delta\nu$  of the Stokes component of a spontaneous Raman line in a single-phase  $\text{B}_2\text{O}_3$  glass is  $808\ \text{cm}^{-1}$ , while this shift in glasses studied here is  $794\ \text{cm}^{-1}$ . The discrepancy by  $14\ \text{cm}^{-1}$  is explained by a more complex composition of our samples, which contain along with the glass forming  $\text{B}_2\text{O}_3$  also  $\text{Al}_2\text{O}_3$  and  $\text{K}_2\text{O}$  modifiers. Unlike Ref. [7], we observed a variant of spontaneous Raman scattering – resonance Raman scattering whose intensity increases when excitation is performed into the electronic absorption band of matter [8]. We failed to observe the anti-Stokes component of spontaneous Raman scattering.

Cooperative sensitised luminescence and Raman scattering are observed simultaneously due to a competition between two types of nonradiative energy transfer: cooperative transfer, which is responsible for cooperative sensitisation of luminescence, and multiphonon nonradiative relaxation, which is responsible for Raman scattering.

Glass samples doped only with  $\text{Pr}^{3+}$  ions do not exhibit cooperative sensitised luminescence bands, but the Raman line intensity increases in them. Therefore, cooperative nonradiative energy transfer is absent in the absence of

$\text{Nd}^{3+}$  ions, and Raman scattering is determined by multiphonon nonradiative relaxation. Among oxygen-containing glasses, a borate glass has the most intense and broad spectrum of fundamental vibrations of the matrix (of the B–O bond) with the high-frequency boundary  $\nu_m$  achieving 1380–1480  $\text{cm}^{-1}$  [9]. The efficiency of multiphonon nonradiative relaxation strongly increases at such high values of  $\nu_m$ . This results in a low quantum yield of luminescence of rare-earth ions in borate glasses. In our case, the  $\text{Pr}^{3+}$  ion is excited to the  $^1G_4$  level by absorbing a laser photon at 1.064  $\mu\text{m}$ . Luminescence from this level in silicate and borate glasses is very weak [10] due to efficient multiphonon nonradiative relaxation. All the energy accumulated on this level transfers to a glass matrix due to multiphonon relaxation going successively through all the lower electronic states, resulting in the enhancement of the intensity of the B–O bond vibrations. These vibrations should be manifested in the spontaneous Raman spectrum.

Therefore, we have observed simultaneously cooperative sensitised luminescence in the regions at 0.88 and 1.35  $\mu\text{m}$  resonance Raman scattering at 1.162  $\mu\text{m}$  shifted by 794  $\text{cm}^{-1}$  and having a linewidth of 25  $\text{cm}^{-1}$  in a borate glass doped with  $\text{Pr}^{3+}$ – $\text{Nd}^{3+}$  donor–acceptor pairs. Glasses doped only with  $\text{Pr}^{3+}$  ions exhibited only resonance Raman scattering. These results stimulate further studies of resonance Raman scattering in optical fibres for the development of Raman fibre lasers and amplifiers. It is promising to use 1- $\mu\text{m}$  high-power laser diodes for pumping in these studies.

**Acknowledgements.** This work was supported by the Academy of Sciences of Georgia (Grant No. 2.1.02).

## References

1. Zhabotinskii M.E. (Ed.) *Lazernye fosfatnye stekla* (Laser Phosphate Glasses) (Moscow: Nauka, 1980) p. 99.
2. Makeeva G.A., Reishakhrit A.A., Lun'kin S.P. *Zh. Prikl. Spekt.*, **5**, 730 (1966).
3. Bilak V.I., Zverev G.M., Karapetyan G.O., Onishchenko A.M. *Pis'ma Zh. Eksp. Teor. Fiz.*, **14**, 301 (1971).
4. Antipenko B.M., Dmitruk A.V., Zubkova V.S., Karapetyan G.O., Mak A.A. *Izv. Akad. Nauk SSSR, Ser. Fiz.*, **37**, 466 (1973).
- doi> 5. Jacson S.D., King T.A. *IEEE J. Quantum Electron.*, **34**, 1578 (1988).
- doi> 6. Chanturia G.F., Blagidze Yu.M., Gvatusa Sh.Sh., Nakashidze G.A., Tatarashvili R.A., Gaprindashvili Kh.I. *Kvantovaya Elektron.*, **30**, 20 (2000) [*Quantum Electron.*, **30**, 20 (2000)].
- doi> 7. Galener F.L., Mikkelsen J.C., Geils R.H. Jr., Mosby W.J. *Appl. Phys. Lett.*, **32**, 34 (1978).
8. Sushchinskii M.M. *Kombinatsionnoe rasseyaniye sveta i stroenie veshchestva* (Raman Scattering of Light and the Structure of Matter) (Moscow: Nauka, 1981).
9. Mak A.A., Soms L.N., Fromzel' V.A., Yashin V.E. *Lazery na neodimovom stekle* (Neodymium Glass Lasers) Ed. by A.A. Mak (Moscow: Nauka, 1990).
10. Makeeva G.A., Lun'kin S.P., Feofilov P.P. *Zh. Prikl. Spekt.*, **4**, 245 (1966).