

Luminescence of gallium-containing complex oxide crystals

V.N.Shevchuk

I.Franko Lviv National University,
50 Dragomanov St., 79005 Lviv, Ukraine

Luminescence spectra of garnet $\text{Nd}_3\text{Ga}_5\text{O}_{12}$ and of acentric Ca-gallogermanate $\text{Ca}_3\text{Ga}_2\text{Ge}_4\text{O}_{14}:\text{Nd}^{3+}$ crystals under pulsed X-ray excitation (~1.5 ns) in 200–500 nm range are considered. The luminescence measurements carried out at 80 K and 295 K. Time characteristics of fast (~1 ns) emission components of the crystals are evaluated. The narrow luminescence bands (slow components) are ascribed to transitions from the ${}^2F_{5/2}$ level of Nd^{3+} ion.

Рассматриваются спектры люминесценции кристаллов граната $\text{Nd}_3\text{Ga}_5\text{O}_{12}$ и ацентрического Ca-галлогерманата $\text{Ca}_3\text{Ga}_2\text{Ge}_4\text{O}_{14}:\text{Nd}^{3+}$ при возбуждении короткими импульсами (~1.5 ns) рентгеновского излучения в области 200–500 нм. Измерения проведены при 80 К и 295 К соответственно. Оценены временные характеристики быстрых (~1 нс) компонент излучения кристаллов. Узкие полосы люминесценции (медленные компоненты) приписываются переходам с уровня ${}^2F_{5/2}$ иона Nd^{3+} .

The crystals of rare-earth (RE) gallium garnets (GG) $\text{R}_3\text{A}_2\text{Ga}_3\text{O}_{12}$ (R = Nd, Sm, Gd; A = Ga or Sc) are known to be promising luminescence materials, in particular, for UV region. The UV luminescence of REGG crystals is observed under excitation with X-rays [1, 2], cathode rays [3], and other high-energy radiation kinds [4, 5]. The wide-band components thereof are characterized by ultra-short decay times of nanosecond range [1, 2]. The narrow luminescence bands according to $4f^n-4f^n$ transitions of the RE ions show characteristics decay constants of microsecond range being typical of intra-ion electron transitions in the $4f^n$ shell of trivalent RE ions. However, the nature of wide bands of UV luminescence in REGG is not established unambiguously and its main regularities are still insufficiently studied.

The luminescence spectra of $\text{Ca}_3\text{Ga}_2\text{Ge}_4\text{O}_{14}:\text{Nd}^{3+}$ crystals of the Ca gallogermanate (CGG) structure type were studied before [6, 7] only in the IR region in connection with the potential laser emission from the corresponding transitions of Nd^{3+} ions. It is to note that the acentric crystals

of the CGG type are under constant attention of researchers in connection with the unique piezoelectric properties thereof and with anomalous behavior of some characteristics under temperature variations [8]. Of considerable interest are also the spectroscopic characteristics of Nd^{3+} in those compounds [6, 9].

In this work are considered the luminescence spectra of complex oxide crystals belonging to the structure type of garnet and Nd^{3+} doped CGG in the 200–500 nm region under excitation with short X-ray pulses. The crystals of Nd–Ga garnet (NGG) $\text{Nd}_3\text{Ga}_5\text{O}_{12}$ and Nd activated CGG $\text{Ca}_3\text{Ga}_2\text{Ge}_4\text{O}_{14}:\text{Nd}$ grown from the melt by Czochralski technique were studied. The luminescence was excited by short X-ray pulses of 1.5 ns duration at 100 kHz frequency. The luminescence spectra were recorded using a MDR-4 monochromator. The slot spectral width did not exceed 8 nm. The measurements were done at 80 K and 295 K. The experimental procedure and the estimation of the fast luminescence constants have been described before [2, 3] in more detail.

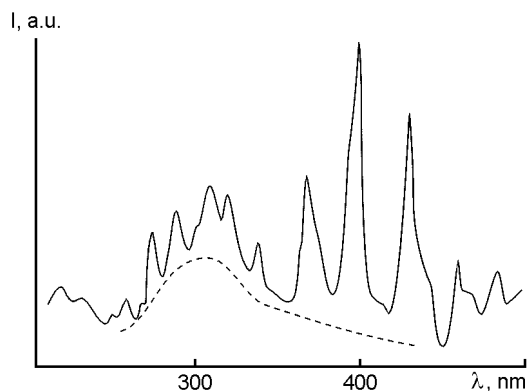


Fig. 1. Luminescence spectrum of $\text{Nd}_3\text{Ga}_5\text{O}_{12}$ crystal at 80 K. The dashed line denotes conventionally the fast component.

Fig. 1 presents the NGG luminescence spectrum at 80 K. A series of narrow bands both in UV and visible range are observed in the spectrum. Those bands can be interpreted as transitions between the corresponding levels of $4f^3$ configuration of Nd^{3+} ions in NGG. Those may be mainly emissive electron transitions from the ${}^2F_{5/2}$ level that are forbidden in the dipole approximation. The energy distance from the ground level (${}^4I_{9/2}$) to the mentioned excited one is about 4.7 eV [10]. The probable identification of the observed transition is given in the Table. The UV emissive transitions of Nd^{3+} ions in yttrium-aluminum garnet (YAG) are identified also as those from the high-energy ${}^2F_{5/2}$ level to the ground one [10–12]. It is to emphasize that the Nd^{3+} ions in NGG are located in the oxygen-coordinated dodecahedral positions of the crystal cubic structure as a major component and form the RE ion sublattice. Such crystals are classified as concentrated systems relatively to R^{3+} ions. The spacing thereof in REGG is about 0.4 nm. These features of REGG are a reason for considerable interaction between the R^{3+} ions, that, in turn, is reflected in the luminescence spectra thereof. So it is why the intensity of the REGG UV luminescence is low (the probable concentration quenching) and increases at low temperatures.

The evaluation of the NGG luminescence decay constant τ for the fast component gives a value of $\tau < 1$ ns. This value is close to the corresponding decay time of the wide-band UV luminescence in Gd–Ga garnet [1, 2]. Similarly, the wide band shown conventionally as the dashed line in Fig. 1 peaked near 300 nm may be due to that fast luminescence. The energetically lowest ob-

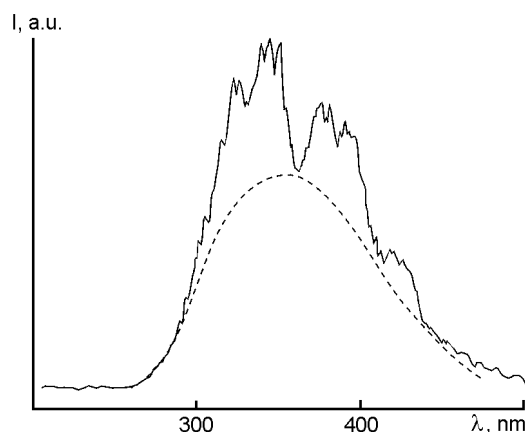


Fig. 2. Luminescence spectrum of $\text{Ca}_3\text{Ga}_2\text{Ge}_4\text{O}_{14}:\text{Nd}^{3+}$ crystal at 295 K. The dashed line denotes conventionally the fast component.

served luminescence band peaked at 225 nm is ascribed to the charge-transfer transition of $4f^25d$ configuration of Nd ion in YAG activated with Nd^{3+} [12].

The UV luminescence spectrum of CGG:Nd (Nd concentration about 0.1 at.%) is shown in Fig. 2. As in the NGG, the luminescence is observed in a wide region (270 to 500 nm). The spectrum is taken at 300 K along the main optical axis z . The luminescence intensity in the CGG:Nd crystal exceeds that of Gd–Ga garnet [1–3] by a factor of 1.3, the recording conditions of the fast UV components being the same. The maximum intensity in NGG is one decimal order lower than that in Gd–Ga garnet. In the latter case, the fast UV component contains overlapped peaks with maxima at 330, 297, and 265 nm [3].

A series of narrow luminescence bands against the background of the wide band (shown conventionally as the dashed line in Fig. 2) corresponds, as in the case of NGG, to transitions of Nd^{3+} ion from the high-energy ${}^2F_{5/2}$ level (see Table). The wide luminescence band (the fast component) is peaked near 350 nm.

The decay time estimation of the fast luminescence component in CGG:Nd has been resulted in $\tau \sim 1.9$ ns. This fast component corresponds to the "background" luminescence (dashed line in Fig. 2). When attempting to select the optimum conditions for CGG:Nd luminescence recording by varying the registration "time window" [13], it was revealed that the intensity of slow components decreases as the registration "time window" is shortened, the fast

Table. Emission lines of $\text{Nd}_3\text{Ga}_5\text{O}_{12}$ (I) and $\text{Ca}_3\text{Ga}_2\text{Ge}_4\text{O}_{14}:\text{Nd}^{3+}$ (II) crystals from the $2F_{5/2}$ level of Nd^{3+} ions. The maxima correspond to Figs. 1 and 2.

λ , nm	Transition
(I) 220	–
232	–
260	${}^4I_{9/2}$
275	${}^4I_{9/2}$
290	?
310	${}^4I_{15/2}$
320	${}^4I_{15/2}$
337	?
367	${}^4F_{3/2}$
398	${}^4F_{5/2} + {}^2H_{29/2}$
430	${}^4F_{9/2}$
458	${}^2H_{211/2}$
485	${}^2G_{7/2}$
(II) 307	${}^4I_{15/2} + {}^4I_{13/2}$
320	${}^4I_{15/2}$
345	?
375	${}^4F_{3/2}$
395	${}^4F_{15/2} + {}^2H_{29/2}$
425	${}^4F_{9/2}$

component remaining essentially unchanged.

When comparing the luminescence spectra of NGG and CGG:Nd, it is to note the similarity of the spectral shapes. Similar series of emissive transitions in Nd^{3+} ions are observed in both cases. A common feature consists also in that at least two luminescence components are registered both in NGG and CGG:Nd, namely, the fast wide-band one (peaked at 300 and 350 nm, respectively) and slow one ($4f^n-4f^n$ transitions). The latter was reported to be due to transitions of the $4f^3$ configuration of Nd^{3+} ions.

As to CGG:Nd, somewhat broadened bands of the $4f^3$ transitions of Nd^{3+} ions are observed. That broadening may be due to features of the CGG matrix structure where Nd^{3+} substitutes for Ca^{2+} . It is known [6] that CGG crystals are characterized by a partial composition disordering due to statistical occupation of the corresponding cationic sites $1a$ and $3f$ with Ga and Ge atoms in the ratio of 1:4 and 3:2, respectively. Thus, the local positions of Nd^{3+} centers in the CGG lattice may have different surroundings. The defect formation processes under activation occur according to the

scheme $\text{Ca}^{2+} + \text{Ge}^{4+} \rightarrow \text{Nd}^{3+} + \text{Ga}^{3+}$ and are caused by an uncompensated positive charge when an Nd^{3+} ion enters the CGG crystal. Simultaneously, the redistribution of Ga and Ge ions over $1a$ and $3f$ positions. These features cause the mentioned broadening of the Nd^{3+} narrow lines in CGG:Nd. The fast, wide-band luminescence is more pronounced in CGG:Nd as compared to NGG, as is seen in Figs. 1 and 2.

The wide bands of fast luminescence of the studied crystals are located in the UV region. The broad non-elementary bands of the intrinsic emission at about 300 nm are observed also in some garnet crystals [10] of various cationic composition, both in undoped and Nd^{3+} -doped ones. In particular, a broad intrinsic luminescence band peaked at about 320 nm is observed in Ca–Ga germanate [1, 2]. The τ values of the wide-band UV luminescence in NGG and CGG:Nd crystals are similar for both crystals as well as close to time characteristics of the intrinsic UV luminescence for other garnets mentioned [1, 2, 10]. This may evidence that the fast luminescence nature in the crystals studied herein and in the garnets investigated before is of the same type.

The author thanks sincerely Prof. A.S.Voloshinovskiy for the support and interest in this work.

This work is supported financially by the Ministry for Education and Science of Ukraine within the frame of the Subject No.FL-135F under the State Budget.

References

1. A.E.Nosenko, V.N.Shevchuk, A.S.Voloshynovskii, in: Proc. Int. Conf. SCINT'95. Delft, The Netherlands, Delft University Press (1996), p.220.
2. A.E.Nosenko, V.N.Shevchuk, A.S.Voloshynovskii, *Functional Materials*, **7**, 778 (2000).
3. V.N.Shevchuk, *Functional Materials*, **10**, 161 (2003).
4. O.A.Keda, M.V.Vasilenko, L.V.Viktorov et al., *Zh. Prikl. Spekt.*, **41**, 867 (1984).
5. V.A.Andriyuk, L.G.Volzhenskaya, Ya.M.Zakharko et al., *Fiz. Tverd. Tela*, **29**, 232 (1987).
6. A.A.Kaminsky, L.K.Aminov, V.L.Ermolaev et al., *Physics and Spectroscopy of Laser Crystals*, Nauka, Moscow (1986) [in Russian].
7. J.Azkargorta, I.Iparraguirre, R.Balda et al., *J. de Phys.*, **4**, C4-353 (1994).
8. B.V.Mill, B.A.Maksimov, Yu.V.Pisarevsky et al., *Kristallografiya*, **49**, 65 (2004).
9. A.V.Butashin, L.E.Li, A.F.Konstantinova et al., *Kristallografiya*, **49**, 524 (2004).
10. S.Kh.Batygov, Yu.K.Voron'ko, N.G.Margiani et al., in: *Spectroscopy of Oxide Crystals for*

- Quantum Electronics (Coll. of IOFAN, v.29) Nauka, Moscow (1991), p.101 [in Russian].
11. A.Niklas, W.Elenski, *Phys.Stat.Sol.(a)*, **77**, 393 (1983).
12. I.S.Gorban', A.F.Gumenyuk, V.Ya.Degoda, *Optika i Spekr.*, **58**, 705 (1985).
13. A.S.Voloshinovsky, S.V.Myagkota, A.V.Gloskovsky, *Zh.Fiz.Doslidzh.*, **4**, 335 (2000).

Люмінесценція кристалів галійвмісних складних оксидів

В.Н.Шевчук

Розглядаються спектри люмінесценції кристалів гранату $\text{Nd}_3\text{Ga}_5\text{O}_{12}$ та ацентричного Са-галогерманату $\text{Ca}_3\text{Ga}_2\text{Ge}_4\text{O}_{14}:\text{Nd}^{3+}$ при збудженні короткими імпульсами (~1.5 ns) рентгенівського випромінювання в області 200–500 нм. Вимірювання проведено при 80 К та 295 К відповідно. Оцінено часові характеристики швидких (~1 нс) компонент випромінювання кристалів. Вузькі смуги люмінесценції (повільні компоненти) приписуються переходам з рівня $2F_{5/2}$ іона Nd^{3+} .