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Fast VUV emission of rare earth ions (Nd^{3+}, Er^{3+}, Tm^{3+}) in wide bandgap crystals

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Abstract

The VUV emission of several wide bandgap crystals (BaY_2F_8, $LiYF_4$, SrF_2, BaF_2) doped with Er^{3+} and Tm^{3+}, stoichiometric ErF_3 and TmF_3, and (YPO_4, $LuPO_4$) doped with Nd^{3+}, has been studied using time-resolved spectroscopy under pulsed synchrotron radiation excitation. For Nd^{3+}, only fast (nanosecond) VUV emission due to allowed $4f^2 5d \rightarrow 4f^3$ interconfiguration transitions is observed in the studied spectral range (150–200 nm), while for Er^{3+} and Tm^{3+} both fast and slow (microsecond) emissions were detected. The efficiency of energy transfer from the matrix to the rare earth ion is very low in all fluoride crystals studied, while in YPO_4 and $LuPO_4$ doped with Nd^{3+} a very efficient energy transfer mechanism exists leading to a high quantum yield of the VUV emission for these compounds. On high-energy excitation the decay kinetics of the $5d \rightarrow 4f$ emission become non-exponential and both the acceleration and delay of the decay can be observed for the particular material. © 1998 Elsevier Science S.A.

Keywords: Energy transfer; 5d–4f luminescence; Rare earth ions; Scintillators; Time-resolved spectroscopy; Wide bandgap crystals

1. Introduction

Many fluoride crystals doped with Nd^{3+} show vacuum ultraviolet (VUV) emission with a decay time of the order of 10 ns [1–5]. The emission is due to parity-allowed radiative transitions from the lowest level of the excited $4f^2 5d$ configuration to various levels of the ground $4f^3$ configuration of Nd^{3+}. Nd-doped crystals are considered as promising VUV scintillators for radiation detectors which employ photosensitive gases (such as TMAE or TEA) or photocathodes sensitive to VUV photons only.

It is well known that in addition to Nd^{3+} other trivalent rare earth (RE) ions, namely Er^{3+} and Tm^{3+}, doped into different matrices possess fast VUV emission [1,6], but the decay kinetics of the emission is rather complicated. In the present paper the VUV emission of Er^{3+} and Tm^{3+} in several fluoride crystals and that of Nd^{3+} in two wide-bandgap matrices YPO_4 and $LuPO_4$ has been studied with time-resolved VUV spectroscopy under pulsed synchrotron radiation excitation.

2. Experimental

The time-resolved measurements were performed at the SUPERLUMI station of HASYLAB at DESY under the excitation from synchrotron radiation from the DORIS storage ring operated with a reduced number of bunches. The spectral range of the excitation was 7–30 eV and the temperature range 10–300 K. Some measurements were also performed at the S-60 electron synchrotron of LPI in Moscow (light yields and emission spectra on X-ray excitation). The setups used for the measurements are described elsewhere [6,7].

$LiYF_4$ single crystals were grown by the Czochralski method as described in Ref. [8]. BaY_2F_8 single crystals (as well as BaF_2 and SrF_2) were grown using the vertical Bridgeman method similar to that described in Ref. [9]. Powder samples of YPO_4:Nd^{3+} and $LuPO_4$:Nd^{3+} were

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obtained by the high temperature diffusion technique. ErF_3 and TmF_3 were high-purity powders with a concentration of other metal admixtures of less than 0.001% and mostly contaminated with oxygen (~0.02%).

3. Results and discussion

Fig. 1 shows the emission spectra of Er^{3+} and Tm^{3+} in different fluoride matrices. Both ''integral'' and time-resolved (measured with a time gate of 10 ns adjusted for the detection of the fast emission component) spectra are shown. In most cases two kinds of emission bands are observed in the range 150–190 nm. The band with the shortest wavelength has a decay constant in the nanosecond range (from a few to tens of nanoseconds for different crystals), while the neighbouring band has a slow decay (the decay constant is in the microsecond range). At longer wavelengths other fast and rather weak emission bands are observed. However, in some cases only the slow component is available (SrF_2–Er^{3+}, BaF_2–Er^{3+}), while in other cases (ErF_3) all VUV emission bands are fast.

We propose a model which explains the co-existence of the slow and fast components by competition between the parity-allowed interconfiguration $4f^{n-1}5d \rightarrow 4f^n$ radiative transitions (fast emission) and parity-forbidden intraconfiguration $4f^n \rightarrow 4f^n$ transitions (slow emission). The subbands of the fast emission are due to transitions from the same excited level (the lowest level of the $4f^{n-1}5d$ configuration) to various terms of the ground state of the $4f^n$ configuration. The competition of the bands depends on the relative energy position of the lowest level of the $4f^{n-1}5d$ configuration and the closest excited level of the $4f^n$ configuration. If the energy position of the former level is higher and well separated from the latter only fast 5d→4f radiative transitions will be observed (ErF_3), or both fast 5d→4f and slow 4f→4f emission takes place. In the latter case (observable in most crystals) the excited 4f level is populated via energy transfer from the 5d level (resonance energy transfer to neighbouring RE^{3+} ions or multi-phonon relaxation within RE^{3+}). Due to this the excitation spectra for these two kinds of emission are very similar. If the energetic separation of both levels is small enough the multi-phonon relaxation rate will exceed the probability of radiative decay of the 5d level. Accordingly, only the slow component will have high intensity. On the contrary, if the energetic separation of the corresponding 5d and 4f levels is large enough the fast component will be dominant (compare emission spectra of Er^{3+} and Tm^{3+}-doped BaY_2F_8). The situation looks very similar to the case of Pr^{3+} in different matrices [10].

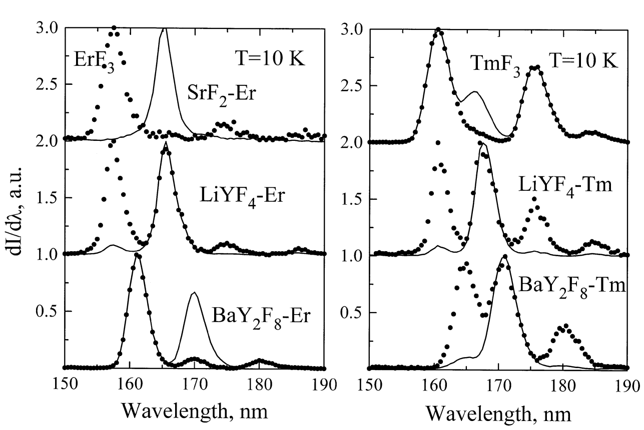

Fig. 1. Emission spectra of Er^{3+} in ErF_3, SrF_2:Er (0.5%), $LiYF_4$:Er (1%) and BaY_2F_8: Er (5%); and Tm^{3+} in TmF_3, $LiYF_4$:Tm (1%) and BaY_2F_8:Tm (2%). $T = 10$ K. (———) Total emission, (●) ''fast component''. All spectra are normalised to their maxima.

As observed for many other RE^{3+}-doped fluoride crystals the quantum yield of the 5d→4f emission is rather high in the spectral region of the direct 4f→5d absorption of RE^{3+} up to the energy of the intrinsic absorption edge of the matrix (Fig. 2) where the efficiency of the energy transfer from the matrix to the RE ion is very low (for all studied fluoride crystals). Upon excitation in the region of the direct 4f→5d absorption of RE^{3+} the decay of the 5d→4f emission is single exponential but upon high-energy excitation the decay kinetics become more complicated and both the acceleration and the delay of the decay can be observed [11].

The time-resolved studies of the emission properties of new scintillator materials YPO_4:Nd^{3+} and $LuPO_4$:Nd^{3+} were performed. Nd^{3+} in both matrices shows intense 5d→4f emission, the main short wavelength band peaking at 189 nm (Fig. 3). Upon excitation in the region of the direct $4f^3 \rightarrow 4f^2 5d$ absorption of Nd^{3+} the decay of the emission is single exponential with time constant 6.7 ns for YPO_4:Nd^{3+} and 6.1 ns for $LuPO_4$:Nd^{3+}, while upon high-energy excitation the decay is non-exponential with a much longer effective decay time (Fig. 4). For $LuPO_4$:Nd^{3+} a considerable contribution of the very long component (seen as the background) is observed upon high energy excitation.

Unlike fluoride crystals a very efficient mechanism of

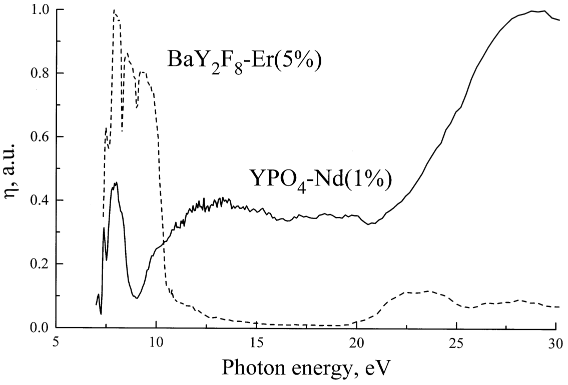

Fig. 2. Excitation spectra of the 5d→4f emission of Er^{3+} in BaY_2F_8:Er^{3+} (5%) and Nd^{3+} in YPO_4:Nd^{3+}.

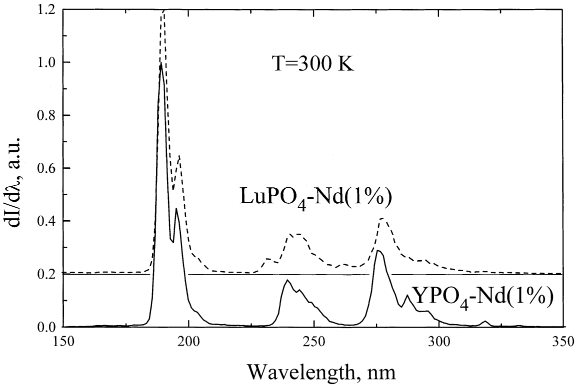

Fig. 3. 5d→4f emission spectra of Nd^{3+} in $YPO_4:Nd^{3+}$ and $LuPO_4:Nd^{3+}$.

energy transfer from the matrix to emission centres is observed in these materials. The excitation spectrum of the Nd^{3+} 5d→4f emission shows a rather high quantum yield of the emission in the region of the intrinsic absorption of the matrix (Fig. 2). The excitation spectrum looks like a classical example of a spectrum for a material with the photon multiplication mechanism (electronic excitations multiplication): a step rise of the quantum yield is observed at photon energies $h\nu > 2E_g$ (E_g is the bandgap). The value of the quantum yield at $h\nu > 3E_g$ is higher than at the intracentre excitation and is more than two times higher than at excitation before the threshold of the electronic excitations multiplication. The last property is typical for crystals with a wide width valence band when both hot photoelectrons and hot photoholes create secondary electronic excitations [12].

The effective decay time of the Nd^{3+} emission in the intrinsic absorption region of the matrix increases considerably with the excitation energy until the threshold of the electronic excitations multiplication and decreases just after the threshold. The decay kinetics at 22.5 eV excitation is similar to that observed at 11.1 eV excitation. A further increase of the excitation energy again leads to an increase of the effective decay time.

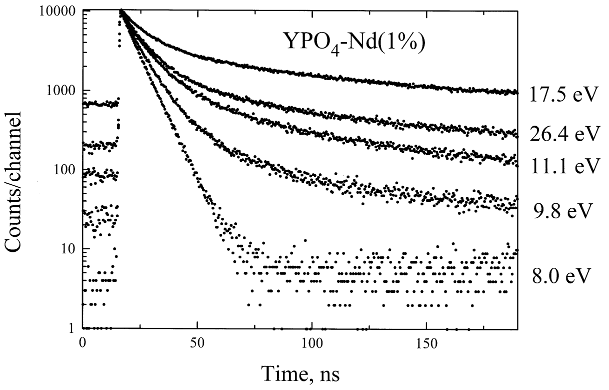

Fig. 4. Decay curves of the 5d→4f emission of Nd^{3+} in $YPO_4:Nd^{3+}$ at different excitation energies.

The mechanism of energy transfer from the matrix to Nd^{3+} in these compounds is obviously the recombinational one. This mechanism suggests that one carrier (for example, a hole) is first captured by the ion and then the partner (electron) recombines with the hole trapped on the ion resulting in the excited state of the ion. The efficiency of the recombination mechanism of energy transfer (if the hole is captured first) depends on the energy difference between the top of the valence band and the ground level of the impurity ion (see, for example, Ref. [13]). It is reasonable to assume that the high efficiency of energy transfer to Nd^{3+} in phosphate matrices is due to the fact that the above-mentioned condition is fulfilled better for $YPO_4:Nd^{3+}$ and $LuPO_4:Nd^{3+}$ than for fluoride crystals doped with Nd^{3+}, similar to many other oxygen-containing compounds (Lu_2SiO_5, $LuAlO_3$) doped with Ce^{3+} or Pr^{3+}.

Both the capture of the carrier on the ion and the recombination with the partner are fast processes and cannot lead to the delay in the energy transfer to the centre. Nevertheless, if one of the partners can be captured by some trap (intrinsic, impurity or defect centre) situated near the Nd^{3+} ion the energy (charge) transfer to the Nd^{3+} ion (thermally activated diffusion) will be delayed. The existence of such an additional channel (besides direct recombination on the emission centre) of the population of the radiative 5d level of Nd^{3+} can result in a rather complicated non-exponential shape of the summary decay kinetics of the emission with an effective decay time much longer than the radiative lifetime of the d level (if the characteristic time for the process of energy transfer exceeds the radiative lifetime of the d level).

The increase in the excitation energy means an increase in the kinetic energies of the created electrons and holes and consequently an increase in the distance between the electron and hole created in the same absorption process. This results in an increase in the number of electron–hole pairs which recombine ''non-directly'' on the centre and in an increase in the time necessary for migration and recombination of the partners of these pairs on the centre and thus in an increase in the effective decay time of the emission. The distance between electrons and holes decreases sharply at photon energies just above the threshold of the electronic excitations multiplication which leads to a shortening of the effective decay time.

The light yield of the VUV emission was measured for a series of samples with a Nd^{3+} concentration of 0.1–5%. The maximum light yield was obtained for a concentration of 1%. The light yield of the VUV emission of YPO_4:1% Nd (and $LuPO_4$:1% Nd) estimated as the quantum yield of the emission upon X-ray (1 keV) excitation is more than two orders of magnitude higher than that of LaF_3:1% Nd, i.e. comparable to that of the most efficient cerium-based scintillators. So these compounds can be considered as promising VUV scintillators (their densities are 4.31 g cm^{-3} for YPO_4 and 6.53 g cm^{-3} for $LuPO_4$), but their timing properties are not excellent to obtain a good time resolution in the nanosecond range (especially for $LuPO_4$:Nd).

4. Conclusions

The VUV emission of Er^{3+} and Tm^{3+} introduced into different fluoride matrices was detected in the spectral range 150–190 nm. The emission spectra consist of several fast emission bands (decay constant in the range from a few to tens of nanoseconds for different crystals) and (or) a slow band (decay constant in the microsecond range). In accordance with the proposed model the former bands are due to parity-allowed interconfiguration $4f^{n-1}5d \rightarrow 4f^n$ radiative transitions, while the latter band is due to the parity-forbidden intraconfiguration $4f^n \rightarrow 4f^n$ transition. Depending on the relative energy position of the lowest level of the excited $4f^{n-1}5d$ configuration and the corresponding level of the ground $4f^n$ configuration, both fast and slow emissions, or only slow, or only fast emission are observed.

Time-resolved studies of the emission properties of new VUV scintillator materials $YPO_4:Nd^{3+}$ and $LuPO_4:Nd^{3+}$ were performed. Both compounds show an intense $5d \rightarrow 4f$ emission, the main short wavelength band peaking at 189 nm. Upon excitation in the region of the direct $4f^3 \rightarrow 4f^2 5d$ absorption of Nd^{3+} the decay of the emission is single exponential, but upon high-energy excitation the decay is non-exponential with a much longer effective decay time. The complicated decay kinetics may be due to the existence of traps for free carriers which delay the charge transfer to the Nd^{3+} ion. The efficiency of the energy transfer from the matrix to the rare earth ion is very low in all the fluoride crystals studied, while in YPO_4 and $LuPO_4$ doped with Nd^{3+} the energy transfer mechanism is very efficient and leads to a high quantum yield of the VUV emission for these compounds.

Acknowledgements

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References

[1] K.H. Yang, J.A. DeLuca, Appl. Phys. Lett. 29 (1976) 499.
[2] L.I. Devyatkova, P.M. Lozovskii, V.V. Mikhailin, T.V. Uvarova, S.P. Chernov, A.V. Shepelev, P.B. Esselbakh, JETF Lett. 27 (1978) 576.
[3] P. Schotanus, C.W.E. van Eijk, R.W. Hollander, Nucl. Instr. and Meth. A 272 (1988) 913.
[4] Yu.M. Aleksandrov, V.N. Makhov, T.V. Uvarova, M.N. Yakimenko, Sov. Phys. – Lebedev Inst. Rep. 6 (1990) 46.
[5] R. Visser, P. Dorenbos, C.W.E. van Eijk, A. Meijerink, H.W. den Hartog, J. Phys.: Condensed Matter 5 (1993) 8437.
[6] N.Yu. Kirikova, V.E. Klimenko, V.N. Makhov, in: Proceedings of the International Conference on Inorganic Scintillators and Their Applications, Delft, The Netherlands, Delft University Press, 1996, p. 196.
[7] G. Zimmerer, Nucl Instr. and Meth. A 308 (1991) 178.
[8] M. Louis, E. Simoni, S. Hubert, J.Y. Gesland, Opt. Mater. 4 (1995) 657.
[9] A.A. Kaminskii, T.V. Uvarova, Izv. Akad. Nauk SSSR, Ser. Neorg. Mater. 24 (1980) 2080.
[10] P. Dorenbos, M. Marsman, C.W.E. van Eijk, M.V. Korzhik, B.I. Minkov, Radiat. Eff. Def. Solids 135 (1995) 325.
[11] A.N. Belsky, P. Chevallier, J.Y. Gesland, N.Yu. Kirikova, J.C. Krupa, V.N. Makhov, P. Martin, P.A. Orekhanov, M. Queffelec, J. Lumin. 72–74 (1997) 146.
[12] Ch.B. Lushchik, T.I. Savikhina, Bull. Acad. Sci. USSR Phys. Ser. 45 (1981) 34.
[13] C. Pedrini, A.N. Belsky, A.N. Vasil’ev, D. Bouttet, C. Dujardin, B. Moine, P. Martin, M.J. Weber, MRS Symp. Proc. 348 (1994) 225.