Luminescence and excitation energy transfer in new fluoride crystals containing rare earth ions

W. Ryba-Romanowski*, P. Solarz, M. Gusowski, G. Dominiak-Dzik

Institute of Low Temperature and Structure Research Polish Academy of Sciences, ul. Okólna 2, PL-50422, Wrocław, Poland

Received 19 December 2006; accepted 1 February 2007

Abstract

Spectroscopic characteristics of Pr^{3+} and Eu^{3+} in $\text{K}_2\text{Na}_2\text{GdF}_7$, $\text{K}_5\text{Li}_2\text{GdF}_{10}$ and K_3GdF_6 fluoride matrices are considered. Crystal structures of these compounds have been ascertained based on X-ray measurement on single crystal samples. Energies of lattice vibrations have been derived from IR and Raman spectra. Spectroscopic features of crystals in the VUV region were studied using experimental facilities of the Superlumi station at HASYLAB in Hamburg. High-resolution spectra and decay curves of luminescence in the visible were used to determine the energy levels and excited state relaxation dynamics of luminescent ions. Relevance of energy transfer processes, which feed the $^5\text{D}_j$ levels of Eu^{3+} and the $^3\text{P}_0$ level of Pr^{3+} , is discussed.

© 2007 Elsevier Ltd. All rights reserved.

Keywords: Fluoride crystals; Luminescence; Energy transfer; Vacuum ultraviolet

1. Introduction

Fluoride crystals are wide band-gap matrices that offer the opportunity to investigate the phenomena of excitation and relaxation of high energy levels within $4f^n$ configurations and lowest energy $5d$ levels of rare earth ions. Knowledge on these phenomena was poor for long time because of experimental problems imposed by measurement in the VUV–UV spectral region combined with a lack of practical motivations. In early works, reported in the sixties and seventies of the last century, assignment of the VUV rare earth absorption bands in the wide band-gap matrices was proposed (Loh, 1966). A “catalogue” of VUV absorption spectra of rare earth ions in CaF_2 was presented and interpreted in (Szczurek and Schlesinger, 1985). Recent increase in the interest in this field is stimulated by the search for new laser materials operating in the UV, scintillators and efficient phosphors that are able to convert the VUV emission of noble gases into the visible luminescence. An impressive number of the published works related to the optical

spectra, excitation and relaxation processes and energy transfer involving transitions between high energy states within the $4f$ configuration and interconfigurational $4f$ – $5d$ transitions of rare earth ions has appeared during the last decade (Wegh and Meijerink, 1996; Krupa and Queffelec, 1997; Wegh et al., 1997; Wegh and Meijerink, 1999; Rodnyi et al., 2000; Makhov et al., 2000; Dorenbos, 2000; Karimov et al., 2001; Guyot et al., 2002; Wojtowicz et al., 2006). As a consequence, the phenomena mentioned above are rather well understood now.

2. Concept of “photon-cutting”

The photon-cutting (termed also “downconversion”) is related to the ability of a luminescent material to emit more than one photon per one photon absorbed. This ability combined with the noble gas discharge may be useful in the design of mercury free luminescent light sources, provided that the photons are emitted in the visible region. The photon-cutting phenomenon involving transitions within the $4f^2$ configuration of Pr^{3+} was demonstrated in the past (Sommerdijk et al., 1974). It is depicted schematically in Fig. 1(a). Excitation of $5d$ levels by the VUV radiation is followed by nonradiative relaxation to the $^1\text{S}_0$ level, which is located at about $50\,000\text{ cm}^{-1}$. From this

* Corresponding author. Tel.: +4871 343 50 21; fax: +4871 344 10 29.

E-mail address: W.Ryba-Romanowski@int.pan.wroc.pl

(W. Ryba-Romanowski).

Crystal structure of $\text{K}_2\text{Na}_2\text{NdF}_7$ has been determined quite recently (Solarz et al., 2004). Examination of the $\text{K}_2\text{Na}_2\text{GdF}_7 \cdot \text{Eu}^{3+}$ small single crystals revealed that substitution of Nd atoms by Gd atoms brings about smaller lattice constants but preserves the crystal structure. The $\text{K}_2\text{Na}_2\text{NdF}_7$ host contains two kinds of nonequivalent distorted NaF_6 octahedra. The Gd^{3+} ions occupy positions with the C_{4v} site symmetry in the centre of polyhedra with nine F ligands and form the

Table 1
Structural characterisation of fluoride crystals

	K ₅ Li ₂ GdF ₁₀	K ₂ Na ₂ GdF ₇	K ₃ GdF ₆
Crystal system and space group	Orthorhombic Pnma	Cubic Im-3m	Monoclinic P2 ₁ /n
Symmetry of Gd site	C _s	C _{4v}	C _i
Gd ³⁺ coordination number	8	9	6
Minimal Gd–Gd distance (nm)	0.681	0.363	0.644
Minimal Gd–F distance (nm)	0.239	0.236	0.221
Density (g/dm ³)	3170	3788	3367

Table 2
Spectroscopic features of Eu³⁺ doped crystals

	K ₅ Li ₂ GdF ₁₀ :Eu	K ₂ Na ₂ GdF ₇ :Eu	K ₃ GdF ₆ :Eu
² S+ ¹ L _j lifetime (μs)			
⁵ D ₀	12 500	6400	8400
⁵ D ₁	2845	1750	6000
⁵ D ₂	58	450	41
⁵ D ₃	240	–	–
² S+ ¹ L _j energy (cm ^{−1})			
⁵ D ₀	17 279	17 286	17 273
⁵ D ₁	19 025, 19 037, 19 059	19 034	19 034
⁷ F ₁	308, 370, 426	263, 294	290, 373, 437
Cut-off phonon energy (cm ^{−1})	680	425	465

Gd₂F₁₄ groups. Such pairs of Gd³⁺ ions are linked together by four common F[−] ions. The shortest distance of 0.36 nm between the neighbouring Gd³⁺ ions is relatively small.

Crystal structure of K₃GdF₆, determined at 300 K, is composed of the distorted GdF₆ and K(1)F₆ octahedra and K(2)F₄ tetrahedra. The GdF₆ and K(1)F₆ octahedra are linked together by the F(3) fluorine atoms and form chains which expand along the *c* direction. The site symmetry of Gd³⁺ ions is C_i and the nearest Gd³⁺ ions are separated by more than 0.6 nm. Structural data of the compounds under study are gathered in Table 1.

4.2. Luminescent properties of Eu³⁺ and Gd³⁺–Eu³⁺ energy transfer

Spectroscopic parameters characterising luminescence of Eu³⁺ ions in the three matrices are gathered in Table 2. The Eu³⁺ ion with its unsplit ⁷F₀ ground state is a convenient probe of strength and symmetry of the crystal field at cationic sites. It can be seen in the Table 2 that the crystal-field splitting of multiplets and relative energies of the crystal-field components do not depend significantly on the host. Relaxation dynamics of the Eu³⁺ excited states is influenced strongly, however. The contribution of multiphonon relaxation to the ⁵D₀ decay is negligible owing to a large energy separation between emitting level and the next lower one. As a consequence, the ⁵D₀ measured lifetimes may be considered as radiative lifetimes. Their values differ considerably (see Table 2) in the three systems studied. This indicates that degree of mixing of opposite parity functions into the 4f functions so as to relax the parity selection rules is significantly different. The ⁵D₂ decay is governed by multiphonon relaxation. Relation between multiphonon

relaxation rates and cut-off phonon energy in the three systems studied is not consistent with dependence predicted by energy gap law which states that the lowest order process is the most likely to occur. This implies different electron–phonon coupling or contribution of lower energy phonons in multiphonon relaxation process.

In the three systems studied the luminescence originating in the ⁵D_{0,1,2} multiplets of Eu³⁺ appear when excitation wavelength is scanned in the VUV–UV spectral range between ~ 100 and 330 nm, exactly.

Excitation spectra of Eu³⁺ emission obtained under such excitation have a broad band appears between about 175 nm and the host absorption edge located at about 125 nm. It is believed to be associated with the Eu³⁺–F[−] charge transfer transition. At longer wavelengths a rich excitation spectra contain lines associated with Gd³⁺ and Eu³⁺ transitions. Excitation spectra of the ⁵D₀ and ⁵D₁ emissions, acquired from the 1.5 at% Eu³⁺: K₅Li₂GdF₁₀ single crystal at room temperature, are compared in Fig. 2. The excitation spectrum of the ⁵D₁ emission is inverted in this figure for the sake of clarity. It can be seen that the intensities of Eu³⁺ lines are the same for the both spectra, whereas the intensities of Gd³⁺ lines are significantly higher in the ⁵D₀ excitation spectrum. Accordingly, the energy transfer mechanism, which feeds the ⁵D₀ level, bypasses the ⁵D₁ level of Eu³⁺. At excitation wavelengths equal to 202 nm or shorter, the photon-cutting mechanism involving cross-relaxation scheme, depicted in Fig. 1, takes place. At longer excitation wavelengths a more complex mechanism contributes. A three-ion mechanism in which Gd³⁺ excitation is transferred simultaneously to two nearby Eu³⁺ ions can account for the experimental results but this hypothesis has to be verified.

Fig. 2. Excitation spectra of the 5D_0 and 5D_1 emission (inverted) recorded at room temperature for the single crystal of $K_5Li_2GdF_{10}$ containing 1.5 at% of Eu^{3+} .

4.3. Luminescent properties of Pr^{3+} and Pr^{3+} – Gd^{3+} energy transfer

The visible emission in the crystals doped with trivalent praseodymium is associated with transitions originating in the 3P_0 and 1D_2 multiplets and terminating in the 3H_J and 3F_J multiplets, all belonging to the $4f^2$ configuration. Lifetime of luminescence originating in the 3P_0 level amounts to 41 μs in 1 at% $Pr:K_3GdF_6$ and to 51 μs in 1 at% $Pr:K_5Li_2GdF_{10}$, at room temperature. Relatively longer lifetimes, of the order of hundreds of microseconds, were found for the 1D_2 level.

However, the 1D_2 emission has to be excited directly because phonon energies of the host crystals are too low to provide the excitation by multiphonon relaxation from higher energy levels. Accordingly, all Pr^{3+} emission lines in the visible range, recorded upon excitation in the blue, are associated with transitions originating in 3P_0 . The emission spectra recorded upon excitation in the VUV spectral region (between 150 and 220 nm) do not contain additional lines characteristic for the 1S_0 emission. Such results indicate that in systems studied the 1S_0 level is located higher than the lowest energy 5d levels of Pr^{3+} . Fig. 3 shows the emission spectrum of 1 at% $Pr:K_3GdF_6$ excited at 195 nm. The spectrum consists of a huge band, centred at 32 000 cm^{-1} , related undoubtedly to the 6P_J – $^8S_{7/2}$ transition of Gd^{3+} , and of much weaker group of closely spaced lines between 15 500 and 17 000 cm^{-1} . This part of spectrum is significantly more complex than that recorded upon excitation into the 3P_J multiplets of Pr^{3+} since it contains lines related to the $^6G_{7/2}$ – $^6P_{7/2,5/2}$ transitions of Gd^{3+} . The appearance of lines associated with emission of gadolinium in the spectrum excited in the UV range implies that the Pr^{3+} – Gd^{3+} energy transfer takes place. This conclusion is confirmed by the UV excitation spectra of the Pr^{3+} emission at 607.8 nm and of the Gd^{3+} emission at 312 nm, shown in Fig. 4. The excitation spectrum of the Pr^{3+} emission consists of a broad double band stretching from about 225–160 nm, which we assign to the f–d transitions of the Pr^{3+} ions. Its spectral position is consistent with the corresponding f–d bands in the excitation spectra reported for other fluoride crystals doped with trivalent praseodymium (Kück et al., 2005).

It can be seen in Fig. 4 that the double band assigned above to the f–d transitions of Pr^{3+} contributes to the excitation spectrum of the 6P_J – $^8S_{7/2}$ transition of Gd^{3+} at 312 nm. This is evidence

Fig. 3. Emission spectrum of 1 at% $Pr:K_3GdF_6$ recorded at 9 K upon excitation at 195 nm.

Fig. 4. Excitation spectra of the Pr^{3+} emission at 607.8 nm (a) and of the Gd^{3+} emission at 312 nm (b), recorded for the 1 at% $\text{Pr}:\text{K}_3\text{GdF}_6$ crystal at 9 K.

that the energy transfer from the 5d levels of praseodymium to the high energy levels belonging to the $4f^7$ configuration of gadolinium takes place. The intensity of this band in the excitation spectrum is even higher than intensities of the Gd^{3+} lines associated with the $^8\text{S}_{7/2}-^6\text{I}_J$ and the $^8\text{S}_{7/2}-^6\text{D}_J$ transitions around 270 and 250 nm, respectively. The excitation energy is transferred from praseodymium ions to the $^6\text{G}_J$ and/or higher energy levels of Gd^{3+} , as indicated by the contribution of Gd^{3+} lines to the emission spectrum shown in Fig. 3.

5. Summary and conclusions

Crystal structures and spectroscopic features of Eu^{3+} and Pr^{3+} in fluorides of gadolinium and alkali metals differing in shape and size of Gd^{3+} surrounding and energy of lattice vibrations were determined.

In the systems studied, the Eu^{3+} ion shows an intense visible luminescence upon the VUV and UV excitation into the Gd^{3+} levels. The cross-relaxation process contributing to the photon-cutting phenomenon was evidenced in the $\text{K}_5\text{Li}_2\text{GdF}_{10}:\text{Eu}^{3+}$ system.

An efficient energy transfer from the 5d levels of Pr^{3+} to high energy levels of Gd^{3+} occurs in the systems studied. No clear trend in the relationship between the characteristics of fluorine ion coordination polyhedron around rare earth ions and their spectroscopic properties was found, however.

Acknowledgements

This work was supported by the European Community—Research Infrastructure Action under the FP6 “Structuring the European Research Area” Programme through the Integrated

Infrastructure Initiative “Integrating Activity on Synchrotron and Free Electron Laser Science”.

We are grateful to Toyo Tanso Co., Ltd., Osaka, Japan for providing high quality IG-110 purified graphite.

The Polish Committee for Scientific Research partly supported this work as research project in 2005–2007.

References

- Babin, V., Oskam, K.D., Vergeer, P., Meijerink, A., 2004. The role of Pb^{2+} as a sensitizer for $\text{Gd}^{3+}-\text{Eu}^{3+}$ downconversion couple in fluorides. *Radiat. Meas.* 38, 767–770.
- Dorenbos, P., 2000. 5d-Level energies of Ce^{3+} and crystalline environment. I. Fluoride compounds. *Phys. Rev. B* 62, 15640–15649.
- Guyot, Y., Collombet, A., Somatri, T., Tkachuk, A., Joubert, M.-F., 2002. Spectral and dynamic study of the broad band UV $4f^2-4f^3$ emission in Nd-doped double sodium yttrium fluoride crystals and comparison with Nd:LiYF₄. *J. Alloys Compd.* 341, 174–178.
- Karimov, D.N., Kirm, M., Makhov, V.N., Ouarova, T.V., Vielhauer, S., Zimmerer, G., 2001. VUV spectroscopy of a new fluoride system NaF-(Er, Y)F₃. *Opt. Mater.* 16, 437–444.
- Krupa, J.C., Queffelec, M., 1997. UV and VUV optical excitations in wide band gap materials doped with rare earth ions: 4f–5d transitions. *J. Alloys Compd.* 250, 287–292.
- Kück, S., Sokólska, I., Henke, M., Scheffler, T., Osiac, E., 2005. Emission and excitation characteristics and internal quantum efficiencies of vacuum-ultraviolet excited Pr^{3+} -doped fluoride compounds. *Phys. Rev. B* 71, 165112-1–165112-15.
- Loh, E., 1966. Lowest 4f–5d transition of trivalent rare-earth ions in CaF₂ crystals. *Phys. Rev.* 147, 332–335.
- Makhov, V.N., Khaidukov, N.M., Kirikova, N.Yu., Kirm, M., Krupa, J.C., Ouarova, T.V., Zimmerer, G., 2000. VUV emission of rare-earth ions doped into fluoride crystals. *J. Lumin.* 87–89, 1005–1007.
- Rodnyi, P.A., Mikhailik, V.B., Stryganyuk, G.B., Voloshinovskii, A.S., van Eijk, C.W.E., Zimmerer, G.F., 2000. Luminescence properties of Ce-doped Cs₂LiLaCl₆ crystals. *J. Lumin.* 86, 161–166.
- Ryba-Romanowski, W., Gołab, S., Dominiak-Dzik, G., Solarz, P., 2002. Eu^{3+} luminescence and $\text{Gd}^{3+}-\text{Eu}^{3+}$ energy transfer in $\text{K}_5\text{Li}_2\text{GdF}_{10}:\text{Eu}^{3+}$. *Appl. Phys. A* 74, 581–586.
- Solarz, P., Pietraszko, A., Dominiak-Dzik, G., Ryba-Romanowski, W., 2004. Crystal structure and spectroscopic properties of a new fluoride compound Na₂K₂NdF₇. *Chem. Phys. Lett.* 400, 286–289.
- Sommerdijk, L., Bril, A., Jager, A.W., 1974. Two photon luminescence with ultraviolet excitation of trivalent praseodymium. *J. Lumin.* 8, 341–343.
- Szczurek, T., Schlesinger, M., 1985. In: Jeżowska-Trzebiatowska, B., Legendziewicz, J., Stręk, W. (Eds.), *Rare Earth Spectroscopy*. World Scientific, Singapore, pp. 309–330.
- Wegh, R.T., Meijerink, A., 1996. First observation of visible luminescence from trivalent gadolinium. *Acta Phys. Polon.* A90, 333–337.
- Wegh, R.T., Meijerink, A., 1999. Spin-allowed and spin-forbidden $4f^n-4f^{n-1}5d$ transitions for heavy lanthanides in fluoride hosts. *Phys. Rev. B* 60, 10820–10830.
- Wegh, R.T., Donker, H., Meijerink, A., Lamminmaki, R.J., Holsa, J., 1997. Vacuum ultraviolet spectroscopy and quantum cutting for Gd^{3+} in LiYF₄. *Phys. Rev. B* 56, 13841–13848.
- Wegh, R.T., Donker, H., Oskam, K.D., Meijerink, A., 1999. Visible quantum Eu^{3+} cutting in doped gadolinium fluorides via downconversion. *J. Lumin.* 82, 93–104.
- Wojtowicz, A.J., Drozdowski, W., Wiśniewski, D., Lefaucheur, J.-L., Gałazka, Z., Zhenhui, G., Łukasiewicz, T., Kisieliński, J., 2006. Scintillation properties of selected monocrystals activated with Ce and Pr. *Opt. Mater.* 28, 85–93.