Luminescence and energy transfer in $\text{K}_3\text{GdF}_6:\text{Pr}^{3+}$

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Received 8 May 2006; received in revised form 3 August 2006; accepted 6 August 2006
Available online 29 September 2006

Abstract

Single phase, polycrystalline K_3GdF_6 compound containing 1 at.% of Pr^{3+} was prepared and its luminescent properties were investigated in the 10–300 K temperature region. The temperature weakly influences the $^3\text{P}_0$ emission, whereas the $^1\text{D}_2$ emission decreases from 520 μs at 10 K to 219 μs at 290 K due to temperature dependent self-quenching effect. Excitation spectra provide evidence that the energy is transferred from the 5d levels of Pr^{3+} to the energy levels belonging to the $4f^7$ configuration of Gd^{3+} .

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Keywords: Ceramics; Solid state reactions; Optical properties; Luminescence

1. Introduction

Fluoride crystals are wide band-gap matrices that offer the opportunity to study phenomena of excitation and relaxation of high energy levels within the $4f^n$ configuration and the lowest energy 5d levels of rare earth ions. Recent increase of interest in this field is stimulated by the search for new laser materials operating in UV, scintillators and phosphors that are able to convert VUV emission of noble gases into visible emission. The latter application may offer the possibility to eliminate mercury from luminescent light sources. Based on results of investigation of numerous fluoride crystals doped with rare earth ions, it has been concluded that singly doped matrices are not able to fulfil the requirements of high conversion efficiency needed in practice [1,2]. Particular attention was directed to praseodymium-doped crystals, in which the $^1\text{S}_0$ level is located at lower energy than the 5d levels [3–10]. As a result, VUV excitation brings about the cascade emission with a theoretical efficiency exceeding 100%. A disadvantage of this system is related to the fact that the large part of emission intensity is in UV region of the spectrum. Co-doped systems seemed to be more promising. It has been demonstrated that two-step energy transfer from Gd^{3+} to Eu^{3+} in LiYF_4 is very efficient at room temperature.

Associated conversion process, denoted by down conversion or photon cutting is nearly 200% efficient when counting the number of visible photons emitted and number of VUV photons absorbed [11,12]. However, estimated overall efficiency of a broad band VUV excitation conversion into visible is only 30% since narrow absorption lines of Gd^{3+} provide poor absorption. Therefore, the search for more efficient systems seems to be justified.

In this work we deal with a new fluoride system $\text{K}_3\text{GdF}_6:\text{Pr}^{3+}$. The host crystal is uncommon in that the nearest rare earth ions in the crystal structure are well separated and do not share ligands. As a consequence the self-quenching of rare earth luminescence is reduced even at relatively high doping levels. Particular attention was directed to energy transfer processes that would make it possible to take an advantage of a broad band absorption in VUV region, related to the f–d transitions of Pr^{3+} .

2. Experimental

The polycrystalline $\text{K}_3\text{GdF}_6:(1\% \text{Pr})$ sample was prepared by heating a mixture (4N anhydrous) of KF, GdF_3 and PrF_3 , in stoichiometric ratios. The mixture was put into a platinum crucible and covered with platinum cap. Then it was placed in a quartz tube, and after filling the tube with dry argon, was heated up to 1050 °C for about 24 h under the insignificant argon overpressure. Next, the sample was cooled to room temperature in 15 h. The sample was checked for phase purity by recording a powder diffractogram using a STOE X-ray diffractometer with image plate counter, program STOE Win XPOW v. 2.11.

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Excitation spectra and luminescence spectra excited in the UV–VUV region were recorded using synchrotron radiation and the set-up of the SUPERLUMI experimental station of the Synchrotronstrahlungslabor HASYLAB at DESY in Hamburg. Excitation spectra were corrected for the beam intensity and so was the transmission of the excitation monochromator by using sodium salicylate as a standard (the absorption and quantum efficiencies are assumed to be constant in the energy range investigated).

Lifetime measurement excited in visible region was performed using an optical parametric oscillator (OPO Continuum Surelite I) pumped by third harmonics of Nd:YAG laser as an exciting source and Tectronix (TDS 3052) digital oscilloscope. The measurements were performed at liquid-helium temperatures using a (CF-1204 Oxford Instruments) cryostat on a continuous flow. The luminescence was excited with a 457.9 nm of an Argon laser line. The luminescence spectra were recorded with a double monochromator GDM 1000 equipped with a Hamamatsu photomultiplier.

The excitation spectrum in UV–VIS region was recorded using Dong Woo Optron spectrophotometer, the spectral resolution of this apparatus was approximately 0.5 nm. Xenon lamp was used as the excitation source.

3. Structural considerations

According to X-ray measurement performed on single crystal sample the K_3GdF_6 compound forms monoclinic crystals within a space group $P2_1/n$. Further details of the crystal structure investigations can be obtained from the Fachinformationszentrum Karlsruhe, 76344 Eggenstein-Leopoldshafen, Germany (fax: +49 7247 808 666, e-mail: crysdata@fiz.karlsruhe.de) on quoting the depository numbers CSD 416295 and 416296. The crystal structure shown in Fig. 1 is composed of distorted GdF_6 and $K(1)F_6$ octahedra and $K(2)F_4$ tetrahedra. The GdF_6 and $K(1)F_6$ octahedra are linked together by apical F(3) fluorine atoms and form chains along c direction. Equatorial F(1) and F(2) fluorine atoms are shared by GdF_6 and $K(1)F_6$ octahedra in the (a, b) plane. The strongly distorted $K(2)F_4$ tetrahedra join together octahedral chains. In the centre of octahedra the Gd and $K(1)$ atoms occupy positions with C_i local symmetry. The crys-

Fig. 1. The structure of K_3GdF_6 .

Fig. 2. X-ray powder diffraction pattern of $K_3GdF_6:(1\% Pr^{3+})$ (a). The comparison with K_3GdF_6 (b) pattern generated based on crystal structure.

tal structure of K_3GdF_6 is uncommon in that the neighbouring Gd atoms are located in the average distance of 6.47 Å and they do not share ligands. As a consequence the exchange interaction between gadolinium ions or other rare earth and mixtures may be neglected and multipole interactions are expected to be weak. Phase purity of the sample was determined by X-ray powder diffraction (XRD) pattern of $K_3GdF_6:(1\% Pr^{3+})$ which is shown in Fig. 2.

4. Results and discussion

4.1. Relaxation dynamics of the 3P_0 and 1D_2

Visible emission in 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. Corresponding energy levels are depicted schematically in Fig. 3. The 3P_0 emission can be excited conveniently in the blue region of the spectrum making

Fig. 3. Energy-level scheme for $Pr^{3+}-Gd^{3+}$ energy transfer in K_3GdF_6 lattice.

Fig. 4. The excitation spectrum of 3P_0 - 3H_6 emission recorded at 300 K for $K_3GdF_6:(1\% Pr)$.

use of the 3H_4 - $^3P_{0,1,2}$ transitions, which are quite intense and provide advantageous absorption efficiency. Energy separation between the 3P_J levels is comparable to phonon energy available in majority of crystal hosts, therefore, the decay of excited 3P_2 and 3P_1 levels is governed by fast nonradiative relaxation, which feeds the 3P_0 level. It follows from vibrational analysis that the highest energy phonons in K_3GdF_6 are related to the A_{1g} vibration at 456 cm^{-1} and to the T_{1u} vibration at 370 cm^{-1} of the GdF_6^{3-} moiety [13]. Mean energies of the 3P_J multiplets can be inferred from the excitation spectrum of the 3P_0 emission, shown in Fig. 4. This spectrum was recorded at room temperature, monitoring the 3P_0 - 3H_6 transition at 601 nm. Three distinct bands having maxima at $20,812\text{ cm}^{-1}$, $21,317\text{ cm}^{-1}$ and $22,487\text{ cm}^{-1}$ can be assigned unambiguously to transitions from the ground 3H_4 level to the 3P_0 , $^3P_1 + ^1I_6$ and 3P_2 levels, respectively. Their widths are rather small implying weak crystal field splitting of multiplets involved. Indeed, the 3H_4 - 3P_2 bandwidth (FWHM), representing a sum of the crystal field splitting of initial and terminal manifolds, is as low as 211 cm^{-1} . Location of the individual crystal levels from optical spectra of Pr^{3+} in K_3GdF_6 is not straightforward, however. Low temperature spectra disclose few band components, which can be assigned unambiguously. As an example, Fig. 5 shows the emission spectrum related to the 3P_0 - 3H_4 transition, recorded at 10 K. It consists of three well-resolved lines with maxima at $20,833\text{ cm}^{-1}$, $20,788\text{ cm}^{-1}$ and $20,754\text{ cm}^{-1}$. At longer wavelength side of the $20,754\text{ cm}^{-1}$ line there is a low intensity feature stretching to $20,232\text{ cm}^{-1}$. In the interpretation of the low intensity maxima appearing in the spectrum one should bear in mind that the level degeneracy is completely lifted when the Pr^{3+} ions are situated in the sites of C_i symmetry. The 3P_0 level is unsplit whereas nine crystal field components of the 3H_4 ground level are predicted. Accordingly, nine components of the 3P_0 - 3H_4 emission band are expected, whereas three of them only are clearly seen. It is likely that almost all transition intensity is contained in these three lines and the weaker maxima correspond to transitions to remaining crystal field levels of the ground multiplet. Alternatively, small features appearing on the long wavelength side of the

Fig. 5. The emission spectrum related to the 3P_0 - 3H_4 transition after excitation with Ar-laser line 457.9 nm recorded at 10 K.

$20,754\text{ cm}^{-1}$ line may be associated with a phonon side-band. Clearly the information provided by the spectrum is not sufficient to unambiguous assignment of its components.

Decay curves of luminescence originating in the 3P_0 level were recorded while changing the sample temperature from 7 K to 300 K. They followed single exponential decay with lifetime gently decreasing from $41\text{ }\mu\text{s}$ at 7 K to $57\text{ }\mu\text{s}$ at room temperature. Observed temperature dependence of the 3P_0 lifetime is similar to that reported for other praseodymium-doped fluoride crystals [14–16]. Unlike the 3P_0 luminescence, the 1D_2 emission depends significantly on the sample temperature. In Fig. 6, the 1D_2 lifetime is plotted versus temperature in the 7–300 K region. To collect these data the 1D_2 level had to be excited directly because the excitation through the 3P_J levels proved to be inefficient. Decrease of the lifetime with increasing temperature, particularly pronounced between 7 K and 100 K, can not be attributed to the growing rate of multiphonon relaxation since the energy separation between the emitting level and the 1G_4 level is too large. Accordingly, we suppose that the dependence observed is due to contribution of nonresonant cross-relaxation process. The self-quenching

Fig. 6. The 1D_2 lifetime plotted vs. temperature in the 7–300 K region.

Fig. 7. Linear fit to the temperature-dependent nonradiative relaxation from 1D_2 level for $K_3GdF_6:(1\% \text{ Pr})$. The activation energy obtained in emission-quenching process is equal to 30 cm^{-1} .

of the 1D_2 luminescence of Pr^{3+} ions in crystals and glasses is well documented. Among all luminescent states of rare earth ions the 1D_2 level of praseodymium is the most susceptible to self-quenching phenomenon and in majority of crystalline hosts it does not show any luminescence when the Pr^{3+} concentration approaches 10 at.%. The cross-relaxation process involved in the phenomenon of self-quenching proceeds probably via intermediate 1G_4 and 3F_3 , 3F_4 levels. When the requirement of resonance is fulfilled it appears to be independent of temperature, as observed in $K_3Li_2LaF_{10}:\text{Pr}^{3+}$ [14]. Temperature dependent process is predicted when the condition of resonance is fulfilled for transitions originating in thermally populated crystal field components of the ground state of acceptor ions. Otherwise, the energy mismatch has to be assisted by phonons and the temperature influences the rate of the cross-relaxation, too. In Fig. 7, the rate of nonradiative relaxation of the 1D_2 level is plotted versus inverse temperature in the 20–100 K region, where the decrease of lifetime is fast. Rates of nonradiative relaxation at different temperatures were determined by subtraction of inverse value of experimental lifetime extrapolated to 0 K from inverse values of lifetime at a given temperature. Experimental dependence is well approximated by a straight line with a slope corresponding to the activation energy of 30 cm^{-1} . This value is small and implies the effect of thermally dependent population of crystal field levels rather than activation of a phonon mode.

At this stage structural implications should be commented on. It follows from X-ray data that Gd^{3+} ions in K_3GdF_6 occupy centrosymmetric sites in distorted octahedral GdF_6^{3-} units. Accordingly, the electric dipole transitions within the $4f^2$ configuration of Pr^{3+} ions, replacing Gd^{3+} ions in the doped crystal, should be forbidden and vibronic transitions can occur solely. Although spectra recorded may not be contradictory to this conclusion, the relaxation dynamics of both the 3P_0 and 1D_2 multiplets implies that the inversion symmetry is destroyed, probably by influence of the second coordination sphere. Relaxation of excited states of rare earth ions involving vibronic transitions was studied thoroughly in the model system $\text{Cs}_2\text{NaRECl}_6$ (rare earth (RE) ions) in the past [17–19]. Characteristic features

Fig. 8. The emission spectra of $K_3GdF_6:(1\% \text{ Pr})$ after excitation with 202 nm, recorded at 10 K.

of vibronic decay, namely very small radiative transition rates and their strong temperature dependencies were then evidenced. Rather short 3P_0 lifetime of Pr in K_3GdF_6 , together with its weak temperature dependence, is not consistent with vibronic decay characteristics mentioned above.

4.2. Conversion of VUV radiation into visible emission

Excitation of the $K_3GdF_6:\text{Pr}^{3+}$ by UV radiation with wavelengths comprised between about 220 nm and 160 nm brings about an intense emission, whose spectrum is shown in Fig. 8. The spectrum consists of a huge band, centred at $32,000 \text{ cm}^{-1}$, related undoubtedly with the $^6P_7-^8S_{7/2}$ transition of Gd^{3+} , and much weaker lines in the visible ascribed to transitions originating in the 3P_0 level of Pr^{3+} . Details of the spectrum in the visible are shown in inset of Fig. 8. Emission spectrum in Fig. 8 provides important information on $K_3GdF_6:\text{Pr}^{3+}$ luminescent system. First, the emission spectrum excited at 202 nm does not contain lines related to the $^1S_0-^1D_2$ and $^1S_0-^1I_6$ transitions of Pr^{3+} around 330 nm and 400 nm, which were observed in $\text{Rb}_3\text{YF}_6:\text{Pr}^{3+}$ [9]. Accordingly, in contrast to the $\text{Rb}_3\text{YF}_6:\text{Pr}^{3+}$ the 1S_0 level of Pr^{3+} in K_3GdF_6 is energetically higher than the 5d level. Secondly, appearance of a line associated with emission of gadolinium in the spectrum excited in UV range may imply that the $\text{Pr}^{3+}-\text{Gd}^{3+}$ energy transfer takes place. The spectrum itself cannot be considered as an evidence of energy transfer because the excitation wavelength $\sim 202 \text{ nm}$ coincides with the 6G_J absorption of Gd^{3+} . However, the supposition on the $\text{Pr}^{3+}-\text{Gd}^{3+}$ energy transfer is corroborated by UV excitation spectra of the Pr^{3+} emission at 607.8 nm and of the Gd^{3+} emission at 312 nm, shown in Fig. 9. The excitation spectrum of the Pr^{3+} emission consists of a broad double band stretching from about 225 nm to 160 nm, which we assign to f–d transitions of Pr^{3+} . Its spectral position is consistent with corresponding f–d bands in excitation spectra reported for other fluoride crystals doped with trivalent praseodymium. Out of five 5d crystal field components three have been located for the $\text{LiYF}_4:\text{Pr}^{3+}$ system, based on relatively well-resolved excitation spectra recorded at

Fig. 9. The excitation spectra for $\text{K}_3\text{GdF}_6:(1\% \text{ Pr})$ at 10 K monitoring the $^3\text{P}_0\text{--}^3\text{H}_4$ Pr^{3+} transition at 607.8 nm (a) and $^6\text{P}_{7/2}\text{--}^8\text{S}_{7/2}$ transition of Gd^{3+} at 312 nm (b).

6 K [20]. Two distinct bands appear in the excitation spectra of $\text{CaF}_2:\text{Pr}^{3+}$ recorded at 77 K [21]. The onset of the lowest energy band in the excitation spectrum depends on the crystal field. In the $\text{K}_3\text{GdF}_6:\text{Pr}^{3+}$ it is at about 230 nm ($\approx 43,300 \text{ cm}^{-1}$). Precise location of this onset is not possible because the non-phonon line does not appear in the spectrum due to re-absorption effect. Nevertheless, it is clearly at lower energy than that of the $^1\text{S}_0$ level, which was located at about $46,700 \text{ cm}^{-1}$ in numerous fluoride hosts [22].

It can be seen in Fig. 9 that the double band assigned above to the f–d transitions of Pr^{3+} contributes to the excitation spectrum of the $^6\text{P}_J\text{--}^8\text{S}_{7/2}$ transition of Gd^{3+} at 312 nm. This is an evidence that the energy transfer from the 5d levels of praseodymium to the energy levels belonging to the $4f^7$ configuration of gadolinium takes place. Intensity of this band in the excitation spectrum is even higher than intensities of the Gd^{3+} lines associated with the $^8\text{S}_{7/2}\text{--}^6\text{I}_J$ and the $^8\text{S}_{7/2}\text{--}^6\text{D}_J$ transitions around 270 nm and 250 nm, respectively. Accordingly, the incorporation of Eu^{3+} ions into the $\text{K}_3\text{GdF}_6:\text{Pr}^{3+}$ system would make it possible to take an advantage of photon cutting within Gd^{3+} and Eu^{3+} pairs with efficient additional sensitisation provided by Pr^{3+} ions. In the planned work this hypothesis will be examined.

5. Conclusions

Single phase, polycrystalline $\text{K}_3\text{GdF}_6:\text{Pr}^{3+}$ material was prepared and its luminescent characteristics were determined. Efficient energy transfer from the 5d levels of Pr^{3+} to the energy levels belonging to $4f^7$ configuration of Gd^{3+} is evidenced based on excitation spectra. Presented results imply that Pr^{3+} ions may

be considered as sensitisers improving the conversion efficiency in VUV excited phosphors.

Acknowledgements

This work was supported by the European Community—Research Infrastructure Action under the FP6 “Structuring the European Research Area” Program (through the Integrated Infrastructure Initiative “Integrating Activity on Synchrotron and Free Electron Laser Science”). Contract RII3-CT-2004-506008. We are grateful to Toyo Tanso Co., Ltd., Osaka, Japan, for providing high quality IG-110 purified graphite. This work was partially sponsored by European Union—European Social Fund. The Polish Committee for Scientific Research supported this work as research project in 2005–2007.

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