# VUV and UV–vis optical study on KGd$_2$F$_7$ luminescent host doped with terbium and co-doped with europium

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### ABSTRACT

The KGd$_2$F$_7$:Tb and KGd$_2$F$_7$:Tb,Eu samples were obtained using a solid state reaction. Excitation spectra and emission spectra are reported and analyzed within the VUV–UV–vis spectral range. The intense green luminescence is observed in the KGd$_2$F$_7$:Tb while the combined emission of terbium and europium in the KGd$_2$F$_7$:Tb,Eu covers substantially the region of white light. The materials under study can be effectively excited making use of intense f–d transitions of Tb$^{3+}$ in the VUV–UV region. Experimental lifetimes of luminescent levels have been measured and discussed. It was found that the considerable energy transfer from Tb$^{3+}$ to Eu$^{3+}$ occurs.

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## 1. Introduction

At present, phosphors able to convert UV or blue light into a suitable combination of red, green and blue luminescence are highly desirable. Among numerous inorganic materials, fluoride compounds containing luminescent rare earth ions have been considered as potential visible phosphors in view of theirs physicochemical and spectroscopic properties. In fact, various fluoride materials single-doped with europium or terbium have been intensively investigated and reported in numerous papers [1–8]. Main attention has been paid to europium-doped fluoride hosts. Nevertheless, the quantum cutting phenomena in the green-emitting K$_2$GdF$_5$:Tb$^{3+}$ [9] or unusual distribution of Tb$^{3+}$ luminescence in K$_3$YF$_6$ [10] have been documented. In contrast to single-doped fluoride materials, the reports on Tb–Eu co-doped systems are rather scarce. Conversion of Eu$^{3+}$ to Eu$^{2+}$ in the Tb/Eu co-doped oxyfluoride borosilicate glass containing the Sr$_2$GdF$_7$ [11] or the emission of white light in Y$_2$O$_3$:Tb$^{3+}$, Eu$^{3+}$ phosphor have been examined [12].

KGd$_2$F$_7$ fluoride host has been also considered in the past. Detailed characterization of the KGd$_2$F$_7$ structure was performed for the specimens obtained at different temperatures from 600 to 900 °C [13]. Down conversion of UV light into visible with the contribution of quantum cutting effect has been observed in Eu$^{3+}$ doped KGd$_2$F$_7$ and KGd$_3$F$_{10}$ [14]. The efficiency of energy transfer process involved as a function of interatomic distances and Eu$^{3+}$ concentration has been discussed. Spectroscopic study has

revealed that Eu$^{3+}$ ions in KGd$_2$F$_7$ are located in numerous non equivalent sites [15,16].

The present work deals with luminescent properties of KGd$_2$F$_7$: Tb$^{3+}$ and KGd$_2$F$_7$:Tb$^{3+}$,Eu$^{3+}$systems which if known have not been studied before. Phenomena of excitation and spectral features of visible emission relevant to practical application of these systems as visible emitting phosphors are examined.

## 2. Experimental

### 2.1. Preparation of samples

The polycrystalline KGd$_2$F$_7$ samples containing Tb$^{3+}$ and Eu$^{3+}$ ions were prepared from a stoichiometric mixture of anhydrous KF, GdF$_3$, TbF$_3$ and EuF$_3$ utilizing the solid state reaction method. The substrates were thoroughly ground in a mortar, put in a graphite crucible and then, the starting materials were inserted to a growth chamber. The mixture was pre-heated at 350 °C for a period of 6 h in order to eliminate the harmful impurities as water and/or oxygen from the chamber and reagents. The preparation was carried on at 850 °C for 25 h sustaining the intensive over-pressure of Argon. Subsequent, the specimen was slowly cooled down to room temperature with the rate of 0.4 °C/min. In this way polycrystalline samples of KGd$_{2-(x+y)}$Tb$_x$Eu$_y$F$_7$ ($x=0.05, y=0$; $x=0$; $y=0.05$, and $x=0, 05, y=0.05$) were manufactured.

### 2.2. Spectroscopic measurements

Spectroscopic experiments in the VUV region were carried out using a facility available at SUPERLUMI station at HASYLAB [17] in

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the Deutsches Electron Synchrotron (DESY, Hamburg). High-resolution excitation spectra in the range of 100–300 nm were measured applying the primary 2 m McPherson monochromator and PMT (Hamamatsu R6358P) detector at secondary ARC monochromator. The excitation spectra were corrected for the incident photon flux in relation to the reference sample of NaSal (sodium salicylate), which is characterized by constant quantum efficiency assumed to be 58% for a wide spectral range up to 25 eV [18]. The emission spectra at the SUPERLUMI station were recorded with a CCD camera (Princeton Instruments, Inc.). The Dongwoo Scanning System consisting of an excitation monochromator with 150 mm focal length and emission monochromator having 750 mm focal length equipped with a photomultipler were employed to record emission and excitation spectra in the UV–vis spectral region. Luminescence decay curves were recorded upon short pulse excitation provided by a Continuum Surelite I Optical Parametric Oscillator (OPO) pumped by a third harmonic of Nd:YAG laser. Luminescence was dispersed by a grating monochromator and detected by a photomultiplier. Resulting signal was stored with a Tektronix model TDS 3052 digital oscilloscope.

## 3. Results and discussion

Schemes of energy levels for $Eu^{3+}$, $Tb^{3+}$ and $Gd^{3+}$ are depicted in Fig. 1 and may be useful in interpretation of the results. Fig. 2 presents the emission spectrum of $KGd_2F_7$:5%Tb recorded upon excitation in UV at 209 nm. Luminescent lines associated with transitions from the $^5D_4$ excited state of $Tb^{3+}$ to the $^7F_J$ multiplets

appear in the 470–700 nm spectral region. In the inset of Fig. 2 considerably less intense emission lines attributed to the $^5D_3 \rightarrow {}^7F_J$ transitions of $Tb^{3+}$ are shown. It can be seen that the green line



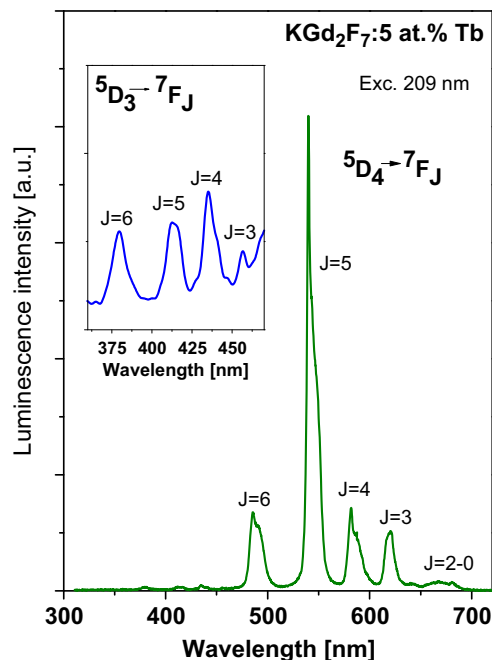Fig. 2. Room temperature emission spectrum of $KGd_2F_7$:5%Tb excited at 209 nm.



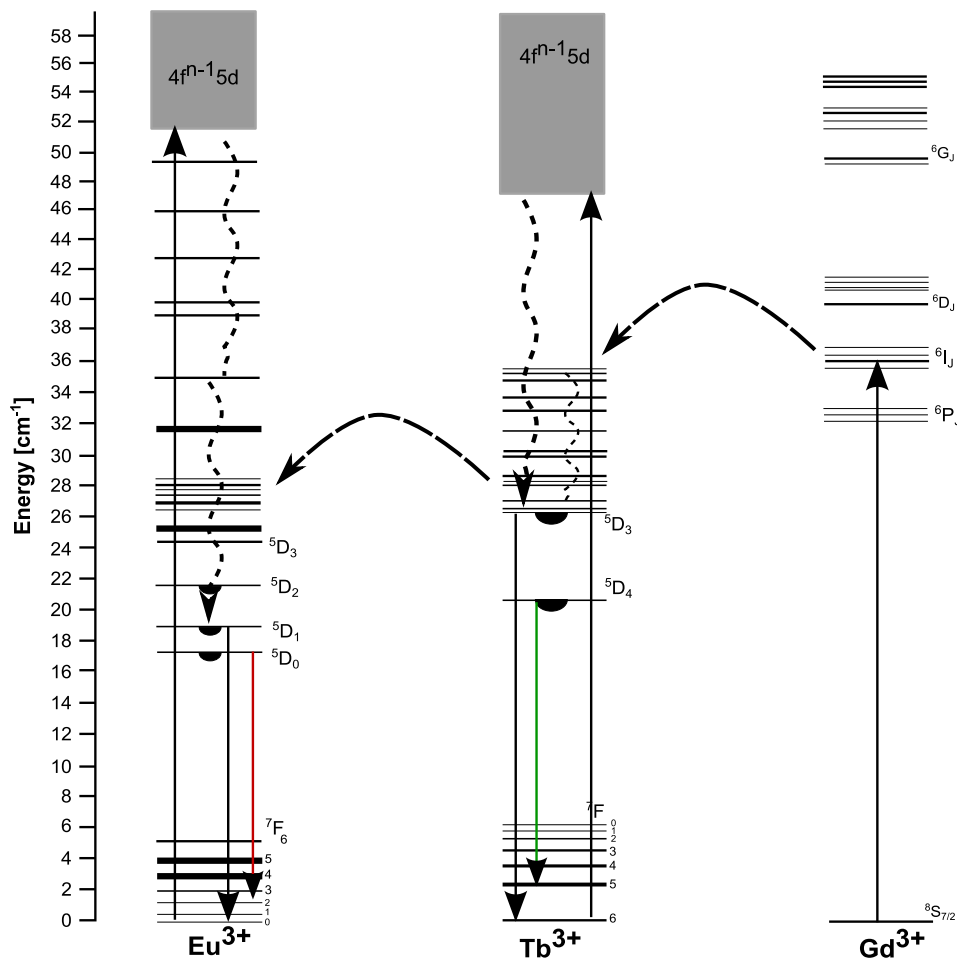Fig. 1. Energy level schemes relevant to excitation and relaxation processes in $KGd_2F_7$:$Tb^{3+}$,$Eu^{3+}$.

related to the $^5D_4 \rightarrow {}^7F_5$ transition of $Tb^{3+}$ around 540 nm dominates the spectrum. Remaining lines at 485, 582 and 620 nm related to $^5D_4 \rightarrow {}^7F_6, {}^7F_4, {}^7F_3$ transitions of $Tb^{3+}$ are considerably weaker and therefore the emission is green to eye. Experimental branching ratios for luminescence transitions from the $^5D_4$ level were calculated by numerical integration of bands presented in Fig. 2. It follows from these calculations that the $^5D_4 \rightarrow {}^7F_5$ transition at 540 nm carries about 55% of photons emitted. The contribution of emission originating in the $^5D_3$ level of $Tb^{3+}$ in the UV–blue spectral range is marginal as a consequence of the self quenching involving the cross relaxation process $^5D_3 + {}^7F_6 \rightarrow {}^5D_4 + {}^7F_0$. It is well documented in numerous papers that this process is very efficient in virtually all hosts when $Tb^{3+}$ concentration exceeds 1%, typically [10]. Fig. 3 shows excitation spectra of $Tb^{3+}$ luminescence at 540 nm recorded in the spectral region 100–333 nm utilizing the synchrotron radiation (left) and in the range 250–500 nm applying the Xenon lamp (right). The spectrum shown on the left side of Fig. 3 displays a broad and intensive band centered at 210 nm that is attributed to low-spin (LS) inter-configurational $4f^8 \rightarrow 4f^7 5d^1$ transitions of the $Tb^{3+}$ and the narrow lines associated with the f–f transitions of the gadolinium appear within 220–320 nm spectral range. The most intense line centered at 272 nm is related to transitions from the ground state $^8S_{7/2}$ to the $^6I_J$ multiplet whereas bands located at 305 nm and 312 nm are assigned to the $^8S_{7/2} \rightarrow {}^6P_J$ transitions of $Gd^{3+}$. In addition, excitation lines on the long wavelength wing of the broad band within 240–260 nm are related to the $^8S_{7/2} \rightarrow {}^6D_J$ transitions of gadolinium. This excitation spectrum indicates clearly that luminescent levels of terbium ions in the $KGd_2F_7$ are populated as a result of relaxation of $Tb^{3+}$ f–d states and efficient $Gd^{3+}$–$Tb^{3+}$ energy transfer.

High-spin (HS) f–d transitions of $Tb^{3+}$ can be observed in some fluoride hosts, as for instant in $LiYF_4$:$Tb^{3+}$ at 257 nm [19]. However, the forbidden (HS) f-d transitions are weak as compared to the allowed low-spin (LS) transitions and its contribution to the excitation spectrum in Fig. 3 cannot be discerned.

The excitation spectrum shown on the right side of Fig. 3 consists of bands corresponding to intra-configurational 4f–4f transitions of $Gd^{3+}$ and $Tb^{3+}$. The band located within 340–380 nm contains several components. They are attributed to transitions from the $^7F_6$ ground state of $Tb^{3+}$ to different closely spaced multiplets. The prominent line located at 379 nm may be related to the $^7F_6 \rightarrow {}^5D_3$ transitions whereas the single band around 487 nm is assigned to the $^7F_6 \rightarrow {}^5D_4$ transition of the $Tb^{3+}$. Two narrow lines observed at 308 and 314 nm are associated with the $^8S_{7/2} \rightarrow {}^6P_J$ transitions of $Gd^{3+}$.

For the $KGd_2F_7$ host co-doped with $Tb^{3+}$ and $Eu^{3+}$ luminescence spectra are more reach and excitation spectra are more complex as a consequence of $Tb^{3+} \leftrightarrow Eu^{3+}$ excitation energy transfer. Fig. 4 shows excitation spectra of the $^5D_4 \rightarrow {}^7F_5$ luminescence of $Tb^{3+}$ at 540 nm and the $^5D_0 \rightarrow {}^7F_2$ luminescence of $Eu^{3+}$ at 610 nm in the $KGd_2F_7$:5%Tb,5%Eu system. For a comparison, the excitation spectrum of $Eu^{3+}$ emission in singly doped $KGd_2F_7$:5%Eu is also presented in Fig. 4. It can be seen that excitation spectra of $Eu^{3+}$ luminescence in $KGd_2F_7$:5%Eu and $KGd_2F_7$:5%Tb,5%Eu systems are markedly different but there is a striking similarity between excitation spectra of $Tb^{3+}$ luminescence at 540 nm and $Eu^{3+}$ luminescence at 610 nm in the $KGd_2F_7$:Eu, Tb. These findings imply that the red emission of europium in the $KGd_2F_7$:$Tb^{3+}$,$Eu^{3+}$ is substantially activated by an efficient $Tb^{3+}$–$Eu^{3+}$ energy transfer.
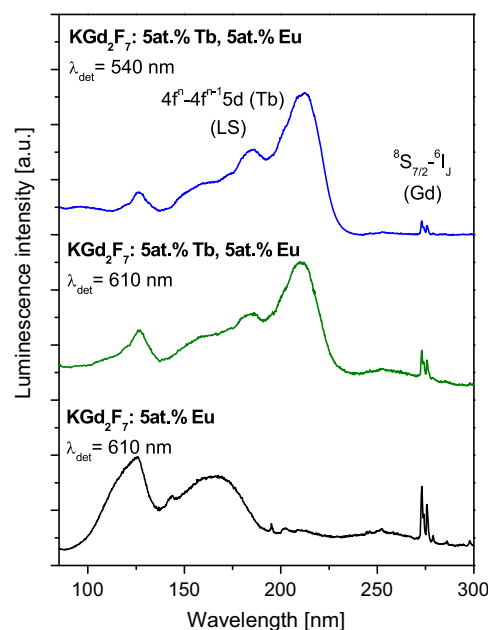
**Fig. 4.** Excitation spectra of $KGd_2F_7$:5%Tb,5%Eu emission monitored at 540 nm and 610 nm.
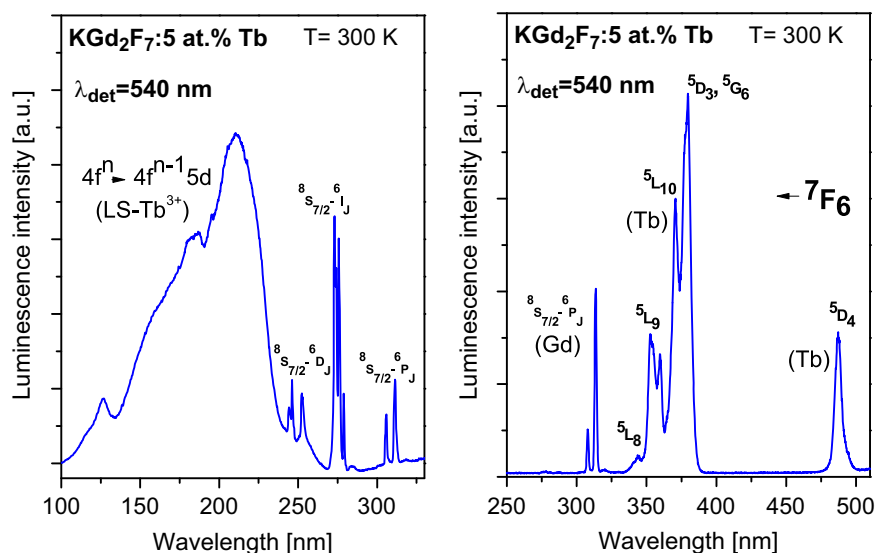
**Fig. 3.** Excitation spectra of $Tb^{3+}$:$KGd_2F_7$ luminescence monitored at 540 nm and recorded at 100–330 nm by means of synchrotron radiation (left) as well as measured at 250–500 nm with a Xenon lamp as an excitation source (right).

Contrary to that, the $Eu^{3+}$ ions do not affect the luminescence of $Tb^{3+}$ in the $KGd_2F_7:Tb^{3+},Eu^{3+}$. Furthermore, the excitation spectra of $Tb^{3+}$ and $Eu^{3+}$ luminescence comprise several broad bands in the spectral region 100–180 nm likely to be due to exciton formation. Wide band near 165 nm in the excitation spectrum of $Eu^{3+}$ emission may be due also to $F^-$-$Eu^{3+}$charge transfer process that was observed in $LiYF_4$:Eu. [20]. It follows from data presented above that the luminescence of optically active ions in the $KGd_2F_7$: $Tb^{3+},Eu^{3+}$ can be effectively excited in the VUV–UV spectral range. Emission properties of terbium and europium were further examined employing different wavelengths of excitation. It has been found that the emission spectra of the $KGd_2F_7$:5%Tb,5%Eu change little when the excitation wavelength increases from 120 to 250 nm. Some minor differences have been found in emission spectra of the $KGd_2F_7:Tb^{3+},Eu^{3+}$ excited at 210 and 273 nm as it is exemplified in Fig. 5. In order to the distribution of luminescent bands could be reasonably compared, the emission spectra were normalized in relation to the emission line at 612 nm associated with the $^5D_0 \to {}^7F_2$ transitions of $Eu^{3+}$. Intense luminescent bands at 540, 588 and 612 nm assigned to following transitions: $^5D_4 \to {}^7F_5$ ($Tb^{3+}$), $^5D_0 \to {}^7F_1$ ($Eu^{3+}$) and $^5D_0 \to {}^7F_2$ ($Eu^{3+}$) were recorded under excitation at 210 nm. The aforementioned emission of $Tb^{3+}$ and $Eu^{3+}$ are characterized by comparable intensity when the wavelength of excitation corresponds to f–d transitions of terbium. In contrast to that, the contribution of green emission of terbium at 540 nm in $KGd_2F_7:Tb^{3+},Eu^{3+}$ becomes smaller with respect to still efficient red emission of europium at 588 and 612 nm when excitation wavelength ($\lambda = 273$ nm) coincide with the f–f transition of $Gd^{3+}$. It means that the energy transfer process $Gd^{3+} - Eu^{3+}$ in $KGd_2F_7:Tb^{3+},Eu^3$ takes place. Eventually, the overall emission of terbium and europium substantially covers the spectral range of white light. The excitation spectrum of terbium luminescence in $KGd_2F_7$ displayed in Fig. 3 and absorption spectra of $Eu^{3+}$ indicate a possibility to obtain efficient luminescence in the $KGd_2F_7:Tb^{3+}, Eu^{3+}$ when employing the excitation wavelengths within 380–395 nm. Fig. 6 compares emission spectra of the $KGd_2F_7$:5%Tb,5% Eu excited at 380 nm and 395 nm. These wavelengths coincide with the absorption bands of $Tb^{3+}$ and $Eu^{3+}$ respectively. It was found that luminescence bands centered at 586, 592 and 612 nm related to the $^5D_0 \to {}^7F_J$ transitions of $Eu^{3+}$ are highly intense in the



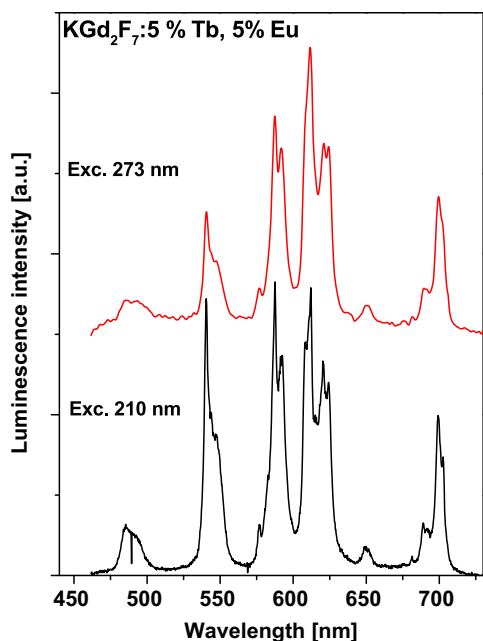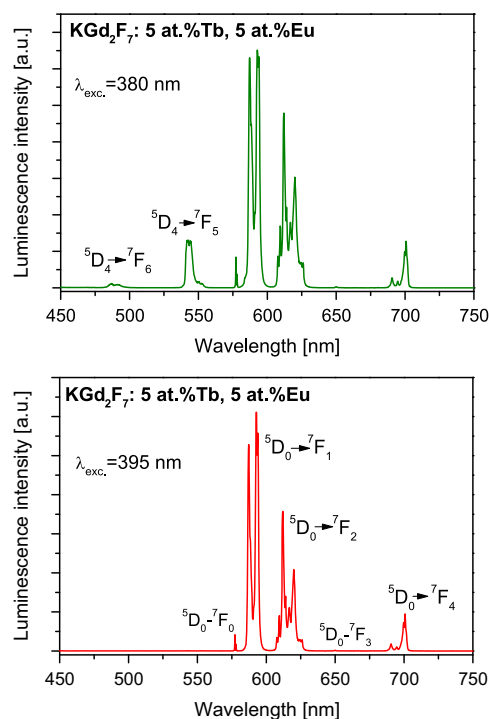Fig. 6. Emission spectra of $KGd_2F_7$:5%Tb,5%Eu excited at 380 nm and 395 nm.

two spectra whereas the $^5D_4 \to {}^7F_J$ emission of $Tb^{3+}$ contributes to the spectrum excited at 380 nm. This implies that the luminescence of $Eu^{3+}$ may be enhanced by Tb–Eu energy transfer. In contrast to that, the europium ions in $KGd_2F_7$:5%Tb,5%Eu do not affect the $^5D_4 \to {}^7F_J$ luminescence of $Tb^{3+}$.

Luminescence decay curves were measured to obtain a more detailed insight into the relaxation of excited states of $Eu^{3+}$ and $Tb^{3+}$ in the $KGd_2F_7$ host. For these systems the contribution of multiphonon relaxation is expected to be marginal because of relatively large energy gaps between emitting level and next lower energy level combined with a small cut-off phonon frequency inherent to fluoride host. Decay of the $^5D_3$ excited state of $Tb^{3+}$ is governed by competing radiative transitions and nonradiative decay involving the cross relaxation process mentioned earlier. The value of 0.12 ms was estimated for the $^5D_3$ lifetime in the $KGd_2F_7$:5%Tb. In this case, the decay curve was non-exponential. It is worth nothing that the value of $^5D_3$ lifetime in the co-doped $KGd_2F_7$:5%Tb,5%Eu has not been changed. Unlike the $^5D_3$ level the self-quenching of the $^5D_4$ and $^5D_0$ luminescence is not relevant since respective energy level schemes do not make possible to fulfill conditions of resonance required. Accordingly, quite long lifetime of $^5D_4$ luminescence of 5.2 ms measured for $KGd_2F_7$:5%Tb system is assumed to be close to radiative lifetime. Moreover, the decay curve of $^5D_4$ luminescence was found to be single-exponential indicating that $Tb^{3+}$ ions accommodated in different available sites decay with comparable rates. The $^5D_4$ decay curve is still single-exponential in the co-doped sample $KGd_2F_7$:5%Tb,5%Eu but the lifetime is reduced to a value of 3.2 ms. This gives an evidence that the nonradiative energy transfer from $Tb^{3+}$ to $Eu^{3+}$ ions occurs in the $KGd_2F_7$:5%Tb,5%Eu.

Lifetime of 6.2 ms was determined for the $^5D_0$ level of $Eu^{3+}$ in the $KGd_2F_7$:5%Tb,5%Eu, a value consistent with 4 ms and 6.8 ms reported for two different sites of $Eu^{3+}$ in $KGd_2F_7$:$Eu^{3+}$ system [16]. This means that $Tb^{3+}$ ions do not influence the decay kinetics of the $^5D_0$ excited state of $Eu^{3+}$ in the $KGd_2F_7$:5%Tb,5%Eu.



Fig. 5. Emission spectra of $KGd_2F_7$:5%Tb,5%Eu excited at 210 nm and 273 nm.

## 4. Conclusions

The $KGd_2F_7$:Tb and $KGd_2F_7$:Tb,Eu fluoride samples have been examined in order to evaluate their potential as a green-emitting and a white-emitting phosphor, respectively. The $KGd_2F_7$:Tb shows a strong visible emission distributed into several bands with the most intense one in the green region. This emission can be excited efficiently in the VUV–UV region, especially in the spectral range of the intense $4f^n$-$4f^{n-1}5d$ transitions of terbium. The $KGd_2F_7$:Tb,Eu luminescence consists of bands related to transitions of both luminescent ions and when excited at VUV region or at 380 nm a white light is observed. Red emission of $Eu^{3+}$ can be enhanced as result of Tb–Eu energy transfer. In particular it was demonstrated that substantial $Eu^{3+}$ luminescence occurs upon excitation in the spectral region of the f–d (202 nm) and the f–f (380 nm) transitions of $Tb^{3+}$. Analysis of luminescence decay curves corroborates the occurrence of nonradiative energy transfer from terbium to europium. Contrary to that, the luminescent levels of terbium are mainly populated as result of relaxation of higher energy $Tb^{3+}$ excited states.

## Acknowledgments

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