Efficient VUV sensitization of Eu^{3+} emission by Tb^{3+} in potassium rare-earth double phosphate

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The luminescence properties of $\text{K}_3\text{Tb}(\text{PO}_4)_2$ activated by Eu^{3+} were studied at excitation over the 120–300 nm wavelength range. It is demonstrated that Tb^{3+} ions, exhibiting a strong absorption band in the vacuum-ultraviolet (VUV), can provide efficient sensitisation of Eu^{3+} emission in this wave

length range, giving rise to intense red luminescence at 150 nm excitation. A proof is given for the concept of VUV sensitisation enabling the engineering of luminescence materials with enhanced conversion efficiency of VUV radiation into visible light.

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The development of new efficient luminescence converters of vacuum-ultraviolet (VUV) radiation into visible light is a challenging topic in the area of phosphor studies. Research activities in this field are motivated by the need of having available efficient phosphors for plasma displays, converting the VUV emission of noble gas discharge into visible light. Exploration of innovative concepts, such as down-conversion and photon multiplication, is attracting major interest [1–4]. A further approach that can be used to enhance the light yield of phosphors is sensitisation. This phenomenon has been known for decades and a number of suitable ion pairs exhibiting efficient conversion of ultraviolet radiation into visible light has been explored and utilized in practical phosphors [5]. Little is known about VUV sensitization. This is because the majority of hosts absorb in this spectral region and hence ordinary sensitisation, as a process of energy transfer from the excited centre to the emitting one, has vanishingly low probability. Fortunately the quest for materials for VUV application resulted in the characterisation of many wide-gap oxides that can be used as suitable host for VUV sensitization. Conversely, investigation of spectroscopic properties of rare-earth (RE) ions in the high energy range [6, 7] provides important and instructive information needed for engineering VUV phosphors that utilise sensitisation for emission enhancement.

To investigate the principal feasibility of this approach for conversion of VUV radiation into visible light we selected two RE ions, Tb^{3+} and Eu^{3+} . The effect of energy transfer from the $^5\text{D}_4$ manifold of Tb^{3+} to the $^5\text{D}_1$ manifold of Eu^{3+} is known since long [8, 9] and it is natural to expect that Tb^{3+} , exhibiting a strong $4f^75d$ absorption band in VUV [6, 7], should provide a sensitisation effect for emission of Eu^{3+} . It has also been demonstrated that the energy transfer process between the two RE is particularly efficient in phosphates [9, 10]. Admittedly, this is a phonon assisted process that benefits from the high energy of internal vibration modes of the PO_4 groups. Therefore the potassium rare-earth double phosphate with the chemical formula $\text{K}_3\text{Ln}(\text{PO}_4)_2$ (Ln stands for RE ion) was chosen as a host. This is a wide band-gap material that satisfies the requirement of being transparent in the VUV range. The layered structure of the host, which results in less pronounced concentration quenching of the luminescence [11–13] is an additional advantage, as it permits experimenting with high levels of doping.

In this study we investigated and compared the luminescence properties of $\text{K}_3\text{Tb}_{1-x}\text{Eu}_x(\text{PO}_4)_2$ ($x = 0.05, 0.1, 0.2$) and $\text{K}_3\text{Gd}_{0.9}\text{Eu}_{0.1}(\text{PO}_4)_2$. Since gadolinium is known to be an efficient UV sensitizer of Eu^{3+} emission [5], the last sample serves as convenient reference for comparison. The

Figure 1 (online colour at: www.pss-rapid.com) Luminescence spectra of $\text{K}_3\text{Tb}_{0.9}\text{Eu}_{0.1}(\text{PO}_4)_2$ (1) and $\text{K}_3\text{Gd}_{0.9}\text{Eu}_{0.1}(\text{PO}_4)_2$ (2) measured at 150 nm excitation ($T = 8$ K). Spectra are vertically shifted for clarity.

phosphors were synthesised by a conventional solid-state reaction technique in air. The structures of the samples were verified, using X-ray powder diffraction, and prove to be single phase. The luminescence measurements were carried out at the SUPERLUMI experimental station of HASYLAB. This is a world-class facility for comprehensive characterisation of luminescence materials in the VUV range. Further information on SUPERLUMI can be found elsewhere [14].

The emission spectra of Eu-doped $\text{K}_3\text{Tb}(\text{PO}_4)_2$ and $\text{K}_3\text{Gd}(\text{PO}_4)_2$ are shown in Fig. 1. As can be seen, the characteristic red emission of Eu^{3+} due to $^5\text{D}_0 \rightarrow ^7\text{F}_j$ transitions dominates the luminescence spectrum, while the intensity of the Tb $4f^n - 4f^n$ emission in $\text{K}_3\text{Tb}(\text{PO}_4)_2\text{-Eu}$ is strongly reduced. The luminescence spectrum of $\text{K}_3\text{Gd}(\text{PO}_4)_2\text{-Eu}$ also exhibits an intense Eu^{3+} emission and a weak Gd^{3+} line at 312 nm that is assigned to the $^6\text{P}_{7/2} \rightarrow ^8\text{S}_{7/2}$ transition. These features of the emission spectra indicate efficient energy transfer from Tb^{3+} and Gd^{3+} to Eu^{3+} . It is important

Figure 2 (online colour at: www.pss-rapid.com) Excitation spectra of $\text{K}_3\text{Gd}_{0.9}\text{Eu}_{0.1}(\text{PO}_4)_2$ (1) and $\text{K}_3\text{Tb}_{0.9}\text{Eu}_{0.1}(\text{PO}_4)_2$ (2, 3) monitored at 617 (1, 2) and 542 nm (3) at $T = 8$ K. Spectrum (3) is scaled by factor of 5.

Figure 3 (online colour at: www.pss-rapid.com) Excitation spectra of $\text{K}_3\text{Tb}_{0.9}\text{Eu}_{0.1}(\text{PO}_4)_2$ monitored at 617 nm at $T = 295$ (1) and 8 K (2). The vertical bars show the calculated positions of SA (black, tall) and SF (red, short) $4f^8 \rightarrow 4f^75d$ transitions of Tb^{3+} .

to note that the total integrated intensity of the $\text{K}_3\text{Tb}(\text{PO}_4)_2\text{-Eu}$ under 150 nm excitation is significantly higher (by a factor of 8) compared with that of a Gd-based analogue. The emission intensity of $\text{K}_3\text{Tb}_{1-x}\text{Eu}_x(\text{PO}_4)_2$ monotonously decreases with increasing concentration of europium; the highest intensity at room temperature was observed for the sample with $x = 0.05$.

The excitation spectra of Eu-emission in the phosphates under investigation are shown in Fig. 2. The excitation spectrum of Eu-emission in $\text{K}_3\text{Gd}(\text{PO}_4)_2\text{-Eu}$ exhibits sharp peaks associated with the $4f^n - 4f^n$ intraconfigurational transitions in Eu^{3+} and Gd^{3+} , a broad band (200–270 nm) assigned to charge transfer transitions between the oxygen ligand and Eu^{3+} and a high-energy band at 160 nm, attributed to the host matrix excitation in the absorption region of the PO_4 groups [11]. As is seen in Fig. 2 the excitation spectra of Tb- and Eu-emissions (monitored at 542 nm and 617 nm, respectively) in $\text{K}_3\text{Tb}(\text{PO}_4)_2\text{-Eu}$ are very similar. This is additional evidence that Eu^{3+} ions are excited via Tb^{3+} . As the temperature increases the excitation bands associated with the Tb $4f^8 \rightarrow 4f^75d$ transitions exhibit a clear red shift and broadening (see Fig. 3) giving a good demonstration of the canonical effect of interaction of the emission centres with the lattice vibration [5]. Fortunately,

Figure 4 (online colour at: www.pss-rapid.com) Emission spectra of $\text{K}_3\text{Tb}_{0.9}\text{Eu}_{0.1}(\text{PO}_4)_2$ measured using 150 nm excitation at $T = 295$ and 8 K. Spectra are vertically shifted for clarity.

Table 1 Energies of spin-allowed (SA) and spin-forbidden (SF) $4f^75d$ bands of Tb^{3+} measured in $K_3Tb(PO_4)_2$ (meas.) and generated by a shift model [7] (calc.), using the positions of the $4f5d$ band of Ce^{3+} in this compound [15].

	E_1		E_2		E_3		E_5		E_6	
	λ (nm)	E (eV)	λ (nm)	E (eV)	λ (nm)	E (eV)	λ (nm)	E (eV)	λ (nm)	E (eV)
Ce^{3+} meas.	306	4.05	285	4.35	265	4.67	253	4.90	210	5.89
Tb^{3+} (SA) calc.	217	5.71	206	6.01	196	6.33	188	6.56	175	7.55
Tb^{3+} (SA) meas.	219	5.64	209	5.93	192	6.45	183	6.77	–	–
Tb^{3+} (SF) calc.	263	4.71	247	5.01	232	5.33	223	5.56	189	6.55
Tb^{3+} (SF) meas.	261	4.74	253	4.89	225	5.50	213	5.80	–	–

the peak of the host excitation band shifts to the higher energy; and this is very useful for practical purposes. The result of this is a significant increase of the total luminescence intensity of the phosphor at excitation with 150 nm photons at room temperature (Fig. 4).

The excitation spectra of Tb^{3+} are known to be due to characteristic $4f^8 \rightarrow 4f^75d$ (fd) transitions in the UV and VUV regions [6, 7]. Due to crystal field splitting of the excited energy levels, the spectra are composed of several bands. The broad bands are assigned to the spin-allowed fd transitions. In addition to the spin-allowed (SA) transitions much weaker bands associated with the spin-forbidden (SF) transitions can also be observed at the low-energy side of the excitation spectra. The occurrence of the spin-dependant transitions is the result of a change of the spin orientation and hence multiplicity in excited state.

A methodology has been developed, enabling the position of the $4f^{n-1}5d$ energy levels of lanthanide ions to be predicted, using that observed for Ce^{3+} in the same compound [7]. This can be easily done in the context of the empirical shift model when the energies of SA fd transitions of Tb^{3+} are constructed by adding a constant value $\Delta E = 1.66 \pm 0.12$ eV to the energies of $4f5d$ transitions of Ce^{3+} . The energies of SF transitions can be generated by applying a shift -1 eV to the energy of SA transitions of Tb^{3+} . This approach was used to obtain the positions of the Tb^{3+} bands in $K_3Tb(PO_4)_2$ (see Table 1). The bars in Fig. 3a show calculated positions of the transitions that correlate fairly well with the main features of the excitation spectrum in the low energy region (200–270 nm). The first two SF bands of Tb^{3+} (253 nm and 261 nm) are predicted well. The strong band between 200 nm and 240 nm comprises both SA and SF transitions that contribute to the observed structure of the band. It is known that the spin forbidden transitions can be sensibly intense in the low symmetry crystal field and Tb^{3+} ion does occupy a low-symmetric 7-fold coordinated position in $K_3Tb(PO_4)_2$ [13]. Furthermore, as is stated in [7], the intensity of Tb^{3+} SF excitation bands has a tendency of becoming stronger at higher energies. The assignment of the positions of the high energy band at 183 nm and 192 nm is less successful since the calculated positions for these peaks are located at larger than expected wavelengths. It should be noted that the data on the position of the Ce^{3+} band are given for

room temperature [15] and hence they are shifted to red, causing accordingly red shift of the predicted Tb^{3+} bands. Finally it is worthwhile highlighting that the highest allowed band of Tb^{3+} merges with the continuum of valence to conduction band transitions of PO_4 group [16]. This creates favourable conditions for the energy transfer from the PO_4 group to Tb ions, explaining hereby the enhanced efficiency of excitation in this energy range.

In conclusion this study clearly demonstrates the feasibility of VUV sensitization of the Eu^{3+} emission by Tb^{3+} ions in $K_3Tb(PO_4)_2$ –Eu. Under VUV excitation this phosphor exhibits significant improvement of the light yield when compared with $K_3Gd(PO_4)_2$ –Eu. An additional merit of VUV sensitization of this phosphor by means of Tb^{3+} ions is the manifestation of the strong excitation band at 160 nm. This allows better utilisation of the broad band emission by the noble gas discharge. This observation of the VUV sensitization effect in Tb–Eu co-doped systems paves the way for the creation of efficient VUV phosphors.

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