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Radiation Measurements 38 (2004) 767–770
Radiation Measurements
www.elsevier.com/locate/radmeas

The role of Pb^{2+} as a sensitizer for Gd^{3+}–Eu^{3+} downconversion couple in fluorides

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Received 27 November 2003; received in revised form 27 November 2003; accepted 7 December 2003

Abstract

Spectroscopic properties of Pb^{2+} in different fluoride host lattices were studied in order to investigate if Pb^{2+} can serve as a sensitizer for the Gd^{3+}–Eu^{3+} quantum cutting system. Strong B′ emission of Pb^{2+} was found in several fluoride host lattices and for the first time B′ emission is reported at room temperature. It is shown that sensitization of the ^6G levels of Gd^{3+} is possible via B′ emission of Pb^{2+} in the host lattice $(BaF_2)_{0.6}(GdF_3)_{0.4}$ and visible quantum cutting with an efficiency of 20% is observed upon excitation in the C band of Pb^{2+}. The possibility of sensitization of Gd^{3+} by A′ emission of Pb^{2+} in $KMgF_3$ is discussed.

Keywords: Luminescence; Downconversion; Sensitizer; Fluorides

1. Introduction

The finding of multi-photon emission through downconversion has provided new excitement in the search for phosphors with quantum efficiencies exceeding unity (Wegh et al., 1999). Visible quantum cutting phosphors are required for application in mercury-free fluorescent tubes and in plasma display panels. In these devices, the VUV radiation is generated by a noble gas (Xe) discharge instead of conventional mercury. The couple Gd^{3+}–Eu^{3+} offers the possibility to obtain efficiencies close to 200%. Via a two-step energy transfer process one Gd^{3+} ion excited into the ^6G_J level will relax yielding ^5D_J emission from two Eu^{3+} ions. Due to the fact that absorption efficiency of the forbidden f–f transitions in Gd^{3+} is low, the VUV radiation is only partly absorbed by Gd^{3+}. Thus, a sensitizer is required which can absorb the VUV radiation and then transfer the energy to VUV levels of Gd^{3+}. The requirements for sensitizer are: (i) absorption in the VUV range (145–190 nm); (ii) emission between 190 and 210 nm to have a good overlap with the ^6G levels of Gd^{3+}; (iii) no quenching due to back transfer of the energy to sensitizer.

Heavy s^2 ions have absorption and emission bands in the (V)UV, therefore they may be a good candidates for sensitization. The absorption properties of s^2 ions are relatively well understood (Ranfagni et al., 1983). Upon promotion of an electron from the s orbital to a p orbital, 6s6p configurations arise. It gives rise to a triplet ($^3P_{0,1,2}$) and singlet ($^1P_1$) terms. Transitions to the lower energy triplet excited states ($^3P_{0,1,2}$) are spin forbidden, but due to spin–orbit coupling the transitions to the $^3P_1$ and $^3P_2$ are relatively intense. The transition to the $^1P_1$ state is fully allowed. In absorption spectrum the transitions to the $^3P_1$, $^3P_2$ and $^1P_1$ states are labeled in order of increasing energy by A, B and C bands. A fourth state is assigned to a charge transfer-type transition and is labelled as D (Folkerts et al., 1995). The emission usually occurs from the $^3P_{0,1}$ state (A′ emission). Often the A band is split into two bands due to dynamic Jahn–Teller effect (Ranfagni et al., 1983). In few cases the $^3P_2$ (B′ band) emission has been observed at low temperatures (Oboth et al., 1989). In the electronic transitions of Pb^{2+} non-shielded s and p orbitals are involved. This means that the positions of the absorption and emission bands, Stokes shift and quenching temperature of the emission vary strongly as a function of host lattice. The highest

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1350-4487/$ - see front matter
doi:10.1016/j.radmeas.2003.12.015

energy sp excited states are found in fluorides, and Pb^{2+} ion has the sp excited state at the highest energies in comparison to other s^2 ions. Therefore, it can be an ideal sensitizer for the Gd^{3+} ^6G level. In the past only a few studies have investigated the VUV luminescence of Pb^{2+}. A systematic VUV spectroscopic investigations of Pb^{2+} in earth alkaline fluorides has been performed by Oboth et al. (1989).

In this paper, luminescent characteristics of Pb^{2+} in various fluorides were studied in order to clarify its role as a possible sensitizer for the Gd^{3+}–Eu^{3+} downconversion couple.

2. Experimental

Measurements were performed on crystalline powder samples. MF_2 (M = Ba, Sr, Ca), LnF_3 (Ln = La, Y, Gd) and $KMgF_3$ samples doped with PbF_2 (0.2–1 mol%) were obtained by adding PbF_2 to the pure host materials, mixing and firing in an alumina crucible (typically 4–5 h at 900–1000 K) in nitrogen atmosphere. To avoid the formation of oxides and hydroxides in the samples, NH_4F was added to the mixture and in the oven a crucible with KF_2H was placed. Samples of the binary fluoride compounds $(MF_2)_{1-x}(YF_3)_x$ doped with Pb^{2+} (including BaY_2F_8) were prepared by thoroughly grinding stoichiometric amounts of the appropriate starting compounds. The firing procedure was the same (at 1100 K). In the synthesis of $LiBaF_3$ an excess amount of LiF was used. After synthesis, all samples were checked by using X-ray diffraction method.

Spectroscopic investigations were performed on two different setups in temperature range from 10 to 300 K. For low resolution luminescence investigations a VUV-adapted spectrofluorometer, equipped with double monochromators and deuterium lamp was used. Excitation and emission spectra were corrected for the lamp intensity and the transmission of the monochromators. The high-resolution measurements were carried out at HIGITI experimental station of HASYLAB at DESY, Hamburg. The excitation spectra of various emissions were normalized to equal quantum intensities of synchrotron radiation falling onto a sample. Both experimental setups are described extensively in detail in Wegh et al. (1997).

3. Results and discussion

The positions of excitation and emission bands in all MF_2 compounds doped with Pb^{2+} agree very well with the values given by Oboth et al. (1989). Peaks positions and Stokes' shift, as determined by our investigations are given in Table 1 for all compounds studied. As an example, Fig. 1 displays luminescence spectra for CaF_2:Pb^{2+}. The excitation spectrum monitoring A′ emission and emission spectrum, upon excitation in the C band are shown and the bands are assigned in the figure. In addition to the emission

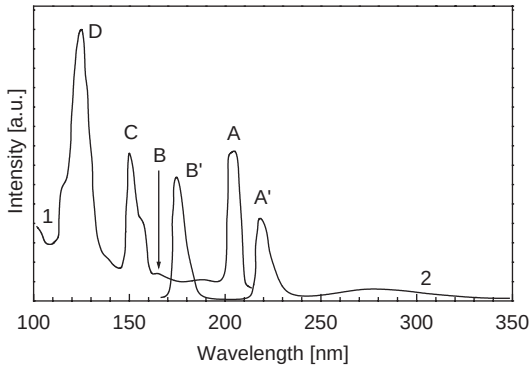

Fig. 1. Excitation spectrum (curve 1) of CaF_2:Pb^{2+} monitoring the A′ emission (219 nm) and emission spectrum (curve 2) upon excitation the C band (151 nm) at 10 K.

bands described in Oboth et al. (1989), a broad band is observed in the UV region, peaking at 275 nm. This band is ascribed to a host lattice-related emission and similar features are observed in all fluoride samples doped with Pb^{2+} described in this article which were prepared in the same manner. The spectra of SrF_2:Pb^{2+} and BaF_2:Pb^{2+} resemble those of CaF_2:Pb^{2+}. The splitting of the A′ band of Pb^{2+}, hardly visible in CaF_2, is more pronounced in SrF_2 and BaF_2 while the emission bands are shifted to longer wavelengths as the ionic radius of the alkaline earth ion increases.

Upon excitation of $(CaF_2)_{0.7}(YF_3)_{0.3}$:$Pb^{2+}$ in the A band, two emission bands are observed in the UV region. The band peaking at 246 nm is assigned to the A′ emission. The excitation spectrum of the A′ emission shows a (Jahn–Teller) split A band and a complex broad band at $\lambda < 165$ nm. This band contains the B, C and D bands. A strong B′ emission is observed upon excitation at 140 nm. From the excitation spectra of A′ and B′ bands the exact positions of B, C and D bands cannot be determined. The spectra of $(SrF_2)_{0.7}(YF_3)_{0.3}$:$Pb^{2+}$ are similar to those of $(CaF_2)_{0.7}(YF_3)_{0.3}$:$Pb^{2+}$, but the splitting of the B, C and D bands is more pronounced. The intensity of the B′ band with respect to the A′ band decreases gradually with increasing temperature, but B′ emission is still present at room temperature. $(SrF_2)_{0.7}(YF_3)_{0.3}$:$Pb^{2+}$ shows a temperature-dependent behaviour similar to CaF_2.

In the spectra of YF_3:Pb^{2+} two A excitation bands are observed. The C band in this compound is very intense. The B band is not clearly observed, but is probably positioned as a shoulder on the long-wavelength side of the C band. The D excitation band shows complicated structure with several overlapping bands. The peak at 110 nm is assigned to the host lattice absorption. No B′ emission is observed in YF_3:Pb^{2+}. In the emission spectra of GdF_3:Pb^{2+}, only emissions from Gd^{3+} levels are observed upon excitation in all levels of Pb^{2+}. The excitation

Table 1
Peak positions of excitation (A_1, A_2, B, C and D) and emission (A′ and B′) bands (in nm) of the Pb^{2+} emissions in various fluoride host lattices at 10 K. For BaY_2F_8, the data for two different Pb^{2+} sites (I and II) are shown (see text)

		A_1	A_2	B	C	D	A′	B′
CaF_2		205		165	151	128	219	176
SrF_2		204	201	165	155	134	223	177
BaF_2		203	201	165	156	136	260	189
YF_3		210	196	170	162	∼ 140	288	
GdF_3		206	195	170	163	142		
LaF_3		200	193		159	142	280	
$(CaF_2)_{0.7}(YF_3)_{0.3}$		192	186	<165	<155	<145	246	180
$(SrF_2)_{0.7}(YF_3)_{0.3}$		199	193	163	154	<150	239	181
BaY_2F_8	site I	187	184	156	148	140	228	175
	site II	200		172	167	149	289	200
$LiBaF_3$		191		158	154	141	247	185
$KMgF_3$		187		154	138	127	217	169

spectra of these Gd^{3+} emissions clearly show the absorption bands of Pb^{2+} with strong intensity. They show great similarity with the excitation spectra of the A′ emission of YF_3, although the bands are found at somewhat shorter wavelengths (see Table 1). Emission is observed from the ^6D (∼ 255 nm), ^6I (∼ 280 nm) and ^6P (∼ 310 nm) levels of Gd^{3+}, which means that energy transfer from Pb^{2+} to Gd^{3+} takes place via the A′ emission of Pb^{2+}. Excitation bands of Pb^{2+} in LaF_3 are found at even higher energies (see Table 1). The Stokes shift of the A′ emission is rather large.

Spectroscopic analysis shows that there are at least two sites for Pb^{2+} in BaY_2F_8:Pb^{2+} (see Table 1). The positions of the excitation bands are at high energy compared to those in other fluorides (site I). The A band is split with maxima at 187 and 184 nm. The corresponding A′ emission is observed at 228 nm. In the excitation spectrum of the intense B′ emission at 175 nm, the B and C bands are observed. The spectral behaviour of the bands does not depend on the Pb^{2+} concentration. The intensity of B′ emission (site I) remains strong at room temperature. The intensity of B′ (site II) decreases with increasing temperature and disappears above 200 K. The luminescence decay time for the B′ emission is 149 ns at 10 K and 93 ns at 100 K.

No splitting is observed for the A band in $LiBaF_3$. The excitation bands are at relatively high energy. The B band is seen as a shoulder on the longer wavelength side of the C band. In emission spectra upon excitation in C band, B′ and A′ emissions are observed. The decay time of the B′ emission is 165 ns at 10 K. B′ emission is not observed at temperatures higher than 210 K.

In $KMgF_3$ the Pb^{2+} ion substitutes the K^+ ion on the large site with a cubic 12-fold F^- coordination. On this large site the A, B and C absorption bands are at the highest energies in comparison with the other fluoride host lattices. The A′ emission band has a maximum at 217 nm and has a good spectral overlap on the short-wavelength side with the Gd^{3+} excitation lines around 205 nm (^6G_J levels). The A band in the excitation spectrum is situated at too high energies to allow for back transfer. Thus, among all fluorides studied, only in $KMgF_3$ the A′ emission band of Pb^{2+} fulfills the conditions for a good sensitizer for the ^6G levels of Gd^{3+}. Unfortunately, it is not possible to incorporate a large amount of Gd and Eu in the $KMgF_3$ lattice. Therefore, a host lattice with a similar large (12 coordinated) site for Pb^{2+} has to be found in which also trivalent ions like Gd^{3+} and Eu^{3+} can be incorporated.

An alternative is sensitization of the ^6G levels of Gd^{3+} via B′ band emission. This has been studied in the BaF_2–GdF_3 system. The amount of 40% GdF_3 is the maximum that can be incorporated in this lattice without getting a second phase. To ensure that the energy migration over the different levels of Gd^{3+} can occur (required for the quantum cutting process), measurements were done on samples with 40% of Gd^{3+}. When the compound is doped with only Eu^{3+} (no Pb^{2+} added), the relative emission intensity of the $^5D_0$ emissions compared to the other ^5D_J emissions increases upon excitation in the ^6G_J levels of Gd^{3+} in comparison with the spectrum for ^6I excitation (Fig. 2). This is characteristic for the presence of quantum cutting and following the method of Wegh et al. (1999), we determined from the integrated emission intensities a quantum cutting efficiency of 50%, i.e. a total quantum efficiency through downconversion can be as high as 150%. In the compound with Pb^{2+} quantum cutting is also observed upon excitation of Pb^{2+} in the VUV. By comparing the relative intensities of the $^5D_0$ and ^5D_J emissions of Eu^{3+} upon excitation in the C band of Pb^{2+} and in the ^6I level of Gd^{3+}, we estimate a quantum cutting efficiency to be 20%. The lower downconversion efficiency in this system is explained by the fact that the A band of Pb^{2+} overlaps with ^6G levels of Gd^{3+}, which causes energy back transfer from Gd^{3+} (^6G) to Pb^{2+}. This process competes with the downconversion process from the ^6G level.

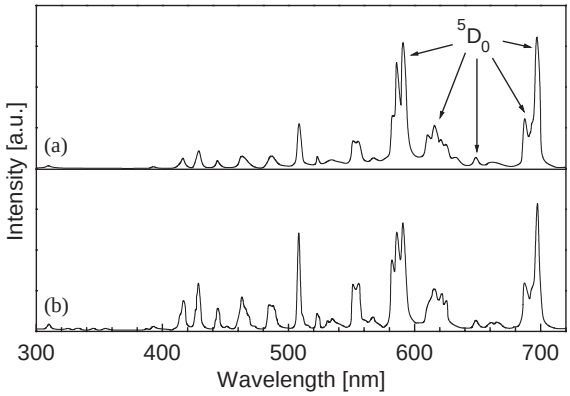

Fig. 2. Emission spectrum of $(BaF_2)_{0.6}(GdF_3)_{0.4}$: Eu^{3+} upon excitation in (a) ^6G level (184 nm) and (b) ^6I level (273 nm) of Gd^{3+}.

4. Conclusions

Research on s^2 ions can result in finding a good sensitizer for the Gd^{3+} ^6G level. Luminescence spectroscopy for Pb^{2+} in a variety of fluoride crystals shows that in some fluorides high-energy (VUV) B-band emission is observed, even at 300 K. This B-band emission is also observed to sensitize the ^6G level of Gd^{3+} but back-transfer from the ^6G level of Gd^{3+} to the A-band of Pb^{2+} competes with the quantum cutting process. In $KMgF_3$ the energy level structure of the Pb^{2+} ion resembles that of the ideal sensitizer for the ^6G level of Gd^{3+}. The A-band is at the highest energy known for Pb^{2+} and is situated above the ^6G level of Gd^{3+}. This prevents the undesired back-transfer. Further research should be focused at finding host lattices where (i) the B band emission is not quenched at room temperature and with a proper tuning of the A band (no absorption around 205 nm), or, alternatively, (ii) the A′ band is located at high energy enough to overlap with the ^6G levels of Gd^{3+}. In this case a host lattice with trivalent cation sites (for Gd^{3+} and Eu^{3+}) and large divalent cation sites, resembling the K^+ site in $KMgF_3$, is the most promising.

Acknowledgements

This project is supported by Philips Lighting, Eindhoven and Dutch STW project no. 349-5086. Authors are grateful to Prof. C. Ronda and Dr. C. Feldmann from Philips Research, Aachen; Dr. S. Poort, Dr. B. Smet and Dr. J. de Hair from Philips Lighting, Eindhoven for discussions. Dr. P. Gürtler from HASYLAB at DESY, Hamburg; Dr. L. van Pieterson and P. Peijzel from Utrecht Univesrity are acknowledged for help with experiments.

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