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Enhancement through sensitization of VUV-excited luminescence in red-emitting pentaborate phosphors

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We studied the feasibility of using sensitization for the improvement of the VUV-to-visible conversion efficiency of red-emitting pentaborate phosphor. It is shown that Tb^{3+} ions that exhibit a strong absorption throughout the 160–230 nm wavelength range facilitate enhancement of Eu^{3+} emission in $TbMgB_5O_{10}$–Eu at excitation in this spectral range. The maximum increase of the Eu^{3+} emission efficiency in a pentaborate host at excitation with 150 nm photons is ca.10%. It is also shown that substitution of Zn for Mg in $Gd(Mg,Zn)B_5O_{10}$–Mn phosphor results in strong (up to 2.4 times) enhancement of the intensity of Mn^{2+} emission. A possible reason for the observed host sensitization effect is discussed.

1 Introduction While the UV-to-visible conversion efficiency of some modern phosphors is approaching the theoretical limit there is a need for substantial improvement when VUV excitation is considered [1]. This issue has been addressed extensively over the past decade and much effort was committed to the investigation of the quantum splitting effect [1–3]. Though the effect has been studied in many systems [4–9] and research activity still continuing, no practical VUV phosphor based on this effect has been identified.

Sensitization is a traditional method used for enhancing the luminescence efficiency of a phosphor at excitation in the energy range where absorption by luminescence ions is insignificant. This phenomenon has been known for decades and a classic example of application is that of the mercury discharge fluorescence lamp [10], for which sensitization of Tb^{3+} emission by Ce^{3+} or sensitization of Eu^{3+} emission by Gd^{3+} is used. Recently we proposed to use terbium for VUV sensitization: it was suggested that Tb^{3+}, exhibiting a strong $4f^7 5d$ absorption band in the VUV [11], should provide a sensitization effect for the emission of Eu^{3+}. A study of Eu–Tb co-doped phosphates demonstrated that Tb^{3+} facilitates efficient sensitization of Eu^{3+} emission in rare-earth phosphate at excitation in the VUV region [12, 13]. The excellent performance of terbium as sensitizer in the high-energy range prompted an investigation of the sensitization effect of this ion in Eu^{3+} doped borates.

The $LnMgB_5O_{10}$ (Ln = Tb, Gd) was chosen as a host since it is a wide band-gap material that is transparent in the energy range of interest (>7 eV) and exhibits a strong absorption band around 150 nm [14]. The crystal structure of the material contains zig-zag chains of rare-earth coordinated polyedra with the shortest inter-chain distance of 0.64 nm making the energy transfer effectively one-dimensional [15]. Due to this feature of the crystal structure, the concentration quenching has a less pronounced effect, permitting a high level of doping and facilitating high emission efficiency of this phosphor [16, 17].

In addition, the $LnMgB_5O_{10}$ host offers an interesting possibility to study the effect of isovalent cation substitution of Mg^{2+} upon luminescence. It is thought that s-levels of magnesium located at higher energies are barely involved in VUV excitation of the phosphor. Therefore the substitution of Mg^{2+} for Zn^{2+} having 4s-states at much lower energies may improve the conversion efficiency of the phosphor in the energy range of interest. The effect of such 'host' sensitization in $GdEu(Mg,Zn)B_5O_{10}$–Mn was examined in this study.

2 Experimental

The samples that have been used in the experiments were synthesized from a stoichiometric mixture of high-purity raw materials, using a conventional solid-state reaction technique as described in Ref. [16]. It includes thorough mixing of the powder materials in hexane and preheating to 600 °C in air. Then the mixture was pulverized again and baked for 6 h in air at a temperature of 1000 °C.

The structure of the samples was determined using powder X-ray diffraction. The luminescence characterization of the phosphors has been carried out at the SUPERLUMI station of HASYLAB, which is designed for comprehensive investigations of luminescence materials in the VUV range [18]. The phosphor samples, prepared as pellets of the same dimensions, were glued to the sample holder of a He-flow cryostat using silver conductive paint. The excitation spectra as well as low-resolution emission spectra were recorded with a PMT (Hamamatsu, R6358P) through a SpectraPro308 (ARC) monochromator. To record the emission spectra of rare-earth ions with higher resolution a liquid nitrogen cooled CCD camera (Princeton Instruments), mounted on the second exit of the monochromator, was used. During the measurements, different samples were presented to the excitation radiation by translating the holder in a direction orthogonal to the beam. This ensured that the same geometry was kept for light collection from different samples, thereby allowing comparison of the intensities of the emitted light.

3 Results and discussion

3.1 Sensitization effect of Tb^{3+} upon emission of Eu^{3+}

Figure 1 shows the emission spectra of $Tb_{0.85}Eu_{0.15}MgB_5O_{10}$ and $Gd_{0.85}Eu_{0.15}MgB_5O_{10}$ phosphors. The figure clearly shows that the red emission of Eu^{3+} due to $^5D_0 \rightarrow {}^7F_j$ transitions dominates the spectrum of $Tb_{0.85}Eu_{0.15}MgB_5O_{10}$ while the intensity of Tb^{3+} emission (characteristic lines at 490 and 540 nm) is strongly suppressed at excitation with 150 nm photons. The Eu^{3+} emission also prevails in the emission of $Gd_{0.85}Eu_{0.15}MgB_5O_{10}$. The characteristic feature of this phosphor is an additional weak Gd^{3+} line at 312 nm due to a $^6P_{7/2} \rightarrow {}^8S_{7/2}$ transition. The total emission intensity of the $Tb_{0.85}Eu_{0.15}MgB_5O_{10}$ at $T = 300$ K is slightly (~10%) higher compared with $Gd_{0.85}Eu_{0.15}MgB_5O_{10}$ at excitation with 150 nm photons. Apparently the enhancement caused by sensitization is fairly modest when compared with the effect that has been observed in phosphates [12, 13].

It should be noted that the shape of the emission spectra of $Tb_{0.85}Eu_{0.15}MgB_5O_{10}$ exhibits no change at excitation in the region of intense $4f^8 \rightarrow 4f^7 5d$ absorption bands of Tb^{3+}. This is shown in Fig. 2, displaying the emission spectra taken at excitation with 150 and 180 nm photons. The efficiency of Eu^{3+} ion excitation is very poor at 180 nm, while Tb^{3+} ions are efficiently excited through $4f^8 \rightarrow 4f^7 5d$ transitions (see also Fig. 3). This is evidence for energy transfer from Tb^{3+} to Eu^{3+}.

Figure 3a displays the excitation spectra of pentaborate phosphors. The excitation spectrum of Eu-emission in $Gd_{0.85}Eu_{0.15}MgB_5O_{10}$ exhibits clear peaks around 275 nm associated with the $f \rightarrow f$ intraconfiguration transitions of Gd^{3+}. A broad band at 230 nm is assigned to charge transfer transitions between an oxygen ligand and Eu^{3+} [10]. An intense high-energy band at 150 nm can be attributed to host matrix excitation since this is the absorption region of oxyborate groups [19].

It was found that the excitation spectra of Tb- and Eu-emission in $Tb_{0.85}Eu_{0.15}MgB_5O_{10}$ are very similar. This provides convincing evidence that Eu^{3+} is excited through the energy transfer from terbium (see Fig. 3b). The excitation spectrum consists of a short-wavelength (150 nm) band, assigned to absorption by the host lattice, and a number of intense long-wavelength bands that can be attributed to the $4f^8 \rightarrow 4f^7 5d$ transitions of Tb^{3+} ions, superimposed upon the Eu^{3+} charge-transfer band at 230 nm. Due to crystal field

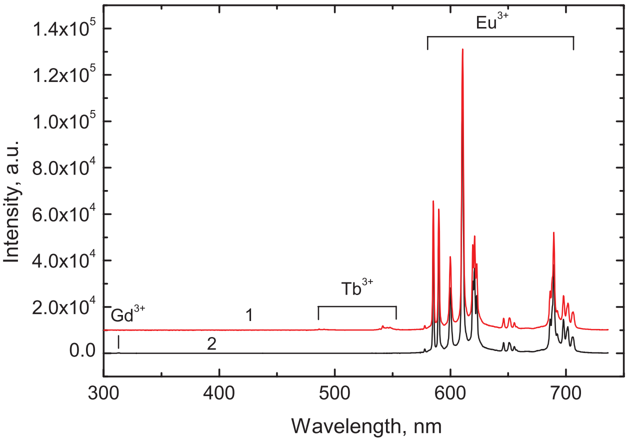

Figure 1 (online colour at: www.pss-a.com) Luminescence spectra of $Tb_{0.85}Eu_{0.15}MgB_5O_{10}$ (1) and $Gd_{0.85}Eu_{0.15}MgB_5O_{10}$ (2) measured at excitation with 150 nm photons at 300 K. Spectra are shifted vertically for clarity.

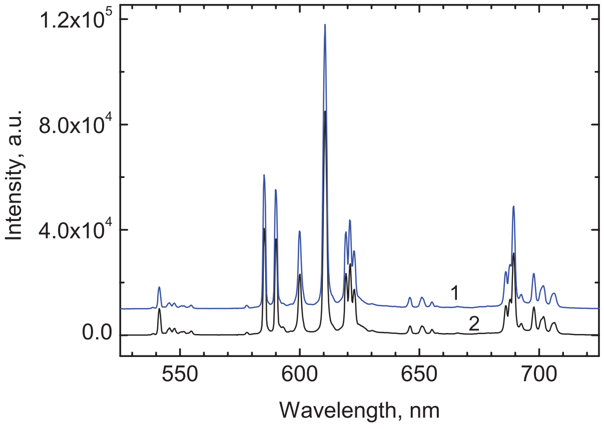

Figure 2 (online colour at: www.pss-a.com) Luminescence spectra of $Tb_{0.85}Eu_{0.15}MgB_5O_{10}$ measured at excitation with 150 nm (1) and 180 nm (2) photons at $T = 8$ K. Spectra are shifted vertically for clarity.

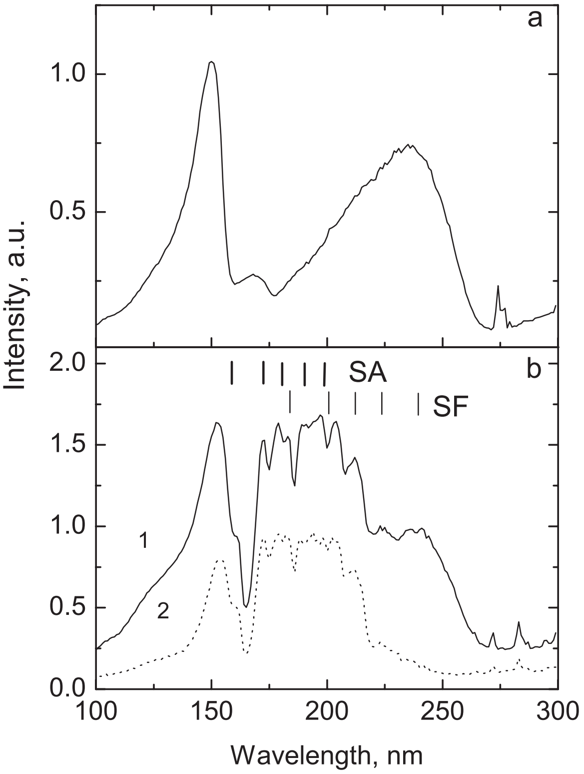

Figure 3 Excitation spectra of $Gd_{0.85}Eu_{0.15}MgB_5O_{10}$ (a) monitored at 611 nm, and $Tb_{0.85}Eu_{0.15}MgB_5O_{10}$ (b) monitored at 611 nm (1) and 543 nm (2). $T = 8$ K.

splitting of the excited energy levels of Tb^{3+}, the spectra are composed of the bands resulting from spin-allowed (SA) and spin-forbidden (SF) transitions. The occurrence of the spin-dependant transitions is the result of a change of the spin orientation and multiplicity of the excited state of the terbium ion.

The main features of the luminescence excitation spectra of $Tb_{0.85}Eu_{0.15}MgB_5O_{10}$ can be explained using a shift model developed by Dorendbos [11]. The model allows estimating the position of the $4f^{n-1}5d$ energy levels of lanthanide ions from that observed for Ce^{3+} in the same compound. This approach was applied to obtain the energy of $4f^75d$ transitions of Tb^{3+} in pentaborate, using the data on the position of the Ce^{3+} bands in this compound from Ref. [14]. As is shown in Fig. 3b, the calculated position of the $4f^75d$ transitions of Tb^{3+} reproduces the main spectrum features very well. It is worthwhile noting that the short-wavelength band of Tb^{3+} is seen as a shoulder of the band associated with the valence-to-conduction band transitions while in phosphates these bands completely overlap [12, 13]. This difference can be a cause of less efficient energy transfer between the oxyborate group and Tb^{3+} in the pentaborate phosphor, thereby reducing the magnitude of the sensitization effect of Eu^{3+} ions.

Using these results, we constructed the energy diagram and the scheme of energy transfer processes in the $Tb_{0.85}Eu_{0.15}MgB_5O_{10}$ phosphor (see Fig. 4). According to this scheme, the VUV radiation is absorbed by the terbium ions in the course of the allowed $4f^8 \rightarrow 4f^75d$ transitions. The excitations quickly relax, populating the lowest emitting levels of Tb^{3+} and then they are transferred to the Eu^{3+}. The final stage of the relaxation process, the *f–f* transition of Eu^{3+}, results in the emission of red light.

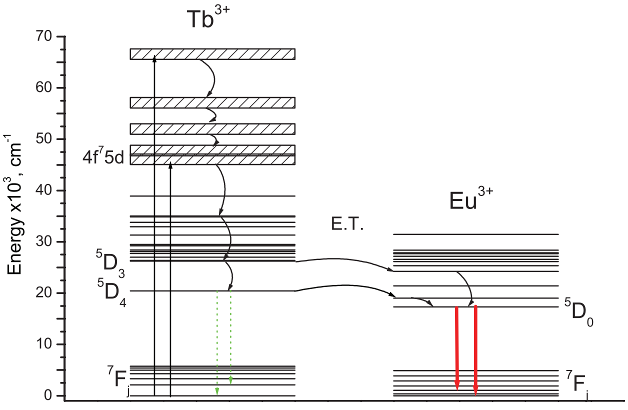

Figure 4 (online colour at: www.pss-a.com) Energy level diagram of the $Tb_{0.85}Eu_{0.15}MgB_5O_{10}$ phosphor and scheme of transitions involved in the luminescence process (E.T. stands for energy transfer).

3.2 Enhancement of Mn^{2+} emission through substitution of Mg for Zn

Doping of a pentaborate host with Mn^{2+} results in deep red luminescence (see Fig. 5) that is attributed to ${}^4T_{1g}$–${}^6A_{1g}$ transitions of the Mn^{2+} ions replacing Mg^{2+} in octahedral positions of the lattice [15, 16, 20]. At first we studied the $GdMg_{0.9}Mn_{0.1}B_5O_{10}$ sample and found that the integrated intensity of Mn^{2+} emission is ca. 65% of $Gd_{0.85}Eu_{0.15}MgB_5O_{10}$ at excitation with 150 nm photons. The excitation spectra of $GdMg_{0.9}Mn_{0.1}B_5O_{10}$ (see Fig. 6) exhibits a group of sharp lines of Gd^{3+} around 206 and 275 nm that are associated with the $f \rightarrow f$ transitions – ${}^8S \rightarrow {}^6G$ and ${}^8S \rightarrow {}^6I$, respectively – in

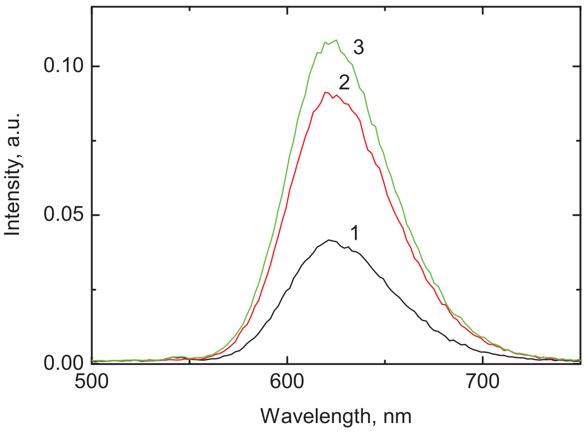

Figure 5 (online colour at: www.pss-a.com) Emission spectra of $GdMg_{0.9}Mn_{0.1}B_5O_{10}$ (1), $GdMg_{0.45}Zn_{0.45}Mn_{0.1}B_5O_{10}$ (2) and $GdZn_{0.9}Mn_{0.1}B_5O_{10}$ (3) measured at excitation with 150 nm. $T = 300$ K.

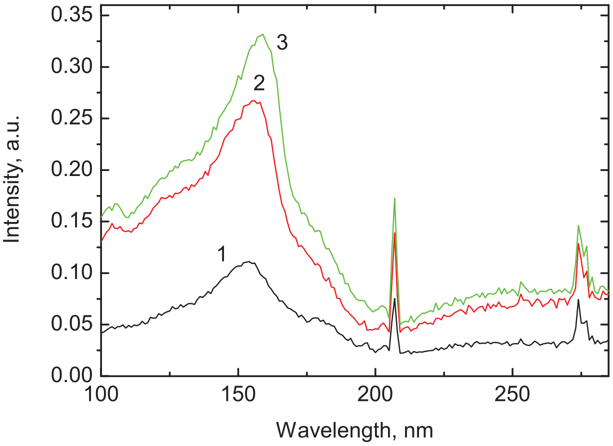

Figure 6 (online colour at: www.pss-a.com) Excitation spectra of $GdMg_{0.9}Mn_{0.1}B_5O_{10}$ (1), $GdMg_{0.45}Zn_{0.45}Mn_{0.1}B_5O_{10}$ (2) and $GdZn_{0.9}Mn_{0.1}B_5O_{10}$ (3) monitored at 620 nm. $T = 300$ K.

this ion. This shows that excitation of Gd^{3+} results in emission of Mn^{2+}, evidencing energy transfer between these ions. The strong band at 155 nm is attributed to the excitation transitions in the oxyborate group.

The Zn^{2+} ion radius in an octahedral configuration (0.088 nm) is a good match to that of Mg^{2+} (0.086 nm). This makes these elements especially suitable for experimenting with substitution. When zinc ions partially or completely substitute for Mg^{2+}, the intensity of Mn^{2+} emission increases strongly (Fig. 5). The excitation spectra demonstrate a concomitant increase of the VUV excitation band and a gradual shift of the maximum by 7 nm towards longer wavelength (see Fig. 6). The enhancement is found to be by a factor 2.1 and 2.4 for the samples of $GdMg_{0.9-x}Zn_xMn_{0.1}MgB_5O_{10}$ ($x = 0.45$ and 0.90, respectively) when compared with $GdMg_{0.9}Mn_{0.1}B_5O_{10}$. This makes the integrated emission intensity of the $GdZn_{0.9}Mn_{0.1}B_5O_{10}$ phosphor 50% higher than that of $Gd_{0.85}Eu_{0.15}MgB_5O_{10}$ at excitation with 150 nm photons.

Cation substitution is often tried, but with varied success, to enhance the efficiency of phosphor at VUV excitation [21–25]. In the cases where improvement was observed, the explanation (if present) is limited to comments on the improved absorption of VUV radiation without specifying a reason. To explain the present finding we endeavour to take a more specific approach based upon general notions on the formation of the energy band structure of the complex compounds. We recall that in borates the optical band edge is formed predominantly by the transition between O 2p valence states and delocalized B 2p conduction states [19] while s-levels of magnesium should be located at higher energies. For the emission to be efficient it is important to create favourable conditions for the localization of hot electrons at the bottom of the conduction band and an overlap with the energy levels of ions participating in the energy transfer or/and luminescence process. Thus, it might be possible to improve the localization of electrons in the conduction band and thereby reduce the losses at band excitation by introducing metal-like states close to the bottom of the conduction band. Since ZnO has a significantly lower energy gap than MgO [26], the replacement of magnesium for zinc can facilitate the necessary change. This should lead to an increase in the density of localized metal states close to the bottom of conduction band. The localized hot electrons have better chances to transfer the excitation energy to Gd^{3+} ions and luminescence Mn^{2+} ions, which in turn causes enhancement of the phosphor light yield at excitation in this range.

4 Conclusion In this study we investigated two approaches for the enhancement of red emission of pentaborate phosphors at VUV excitation. First, we investigated the effect of VUV sensitization of the Eu^{2+} emission by Tb^{3+} ions. Though the $TbMgB_5O_{10}$–Eu phosphor exhibits only moderate enhancement of the light yield in comparison with $GdMgB_5O_{10}$–Eu at excitation with 150 nm photons, the sensitization of Eu^{3+} emission by means of Tb^{3+} ions leads to a significant increase of the luminescence intensity at excitation around 172 nm, i.e. in the region where the broad band of the Xe excimer emission is observed. This allows more efficient utilization of the noble gas discharge and makes pentaborate a competitive VUV phosphor.

As a second approach we tried isovalent cation substitution, which introduces a change of the band structure of the host. It is shown that the gradual replacement of Mg for Zn in the $Gd(Mg,Zn)B_5O_{10}$–Mn phosphor results in a more than twofold increase of the luminescence intensity at VUV excitation. This host sensitization effect is discussed from the viewpoint of a possible contribution of metal states of Zn to the bottom of the conduction band and their involvement into the process of luminescence excitation.

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