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Journal of Alloys and Compounds 311 (2000) 33–39

Journal of ALLOYS AND COMPOUNDS

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Phosphors for plasma display panels

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Abstract

Excitation and emission characteristics were reviewed for phosphors which were reported, applied, or suggested for the plasma display panel (PDP). Correlation of luminescence characteristics to the host crystal structure and the activator of the phosphor was explained. Improvements of the PDP phosphor for practicality were considered. © 2000 Elsevier Science S.A. All rights reserved.

Keywords: Phosphors; Plasma display panels

1. Introduction [1–4]

High definition television (HDTV) sets of large screen cathode ray tubes (CRT) are too bulky and take up too much space for the wide spread acceptance. Thus flat panel displays (FPD) such as the liquid crystal display (LCD), the electroluminescence display (ELD) and the plasma display panel (PDP) have a competitive edge in the large screen display market.

The LCD is one of the most advanced technologies of FPDs. Rather restricted viewing angle of the LCD, which was one of the weaknesses of the LCD, has been relieved by employing the thin film transistor (TFT) active matrix system. However, drawbacks such as the assembly difficulty of the larger screen and the slow response speed are main obstacles for the commercialization of LCDs with screens larger than 30 inches. The ELD also is fairly advanced, but full color ELDs are not available commercially. Only monochrome and multicolor ELDs are available for portable computers and medical instruments. The PDP would be the most promising FPD for the wall-hanging HDTV because the larger sized PDP could be made relatively easily. Moreover, it offers a fast response, a wide viewing angle, a low energy consumption and other advantages.

In PDPs, three primary color phosphors are excited by the vacuum ultraviolet (vuv) radiation from an inert gas plasma, which imposes a unique requirement on the phosphors. In this paper we will discuss characteristics of phosphors and some guidelines on designing new materials for PDPs.

2. Phosphors for PDPs

The gas discharge FPD, i.e. PDP, was first suggested in 1964 by D.L. Bitzer at the University of Illinois [5]. The general structure of a PDP cell is shown in Fig. 1 [6]. Phosphors are excited by more energetic vuv radiation of wavelengths of 130 nm, 147 nm and 172 nm from Xe and Xe–He discharges as shown in Fig. 2. The vuv radiation

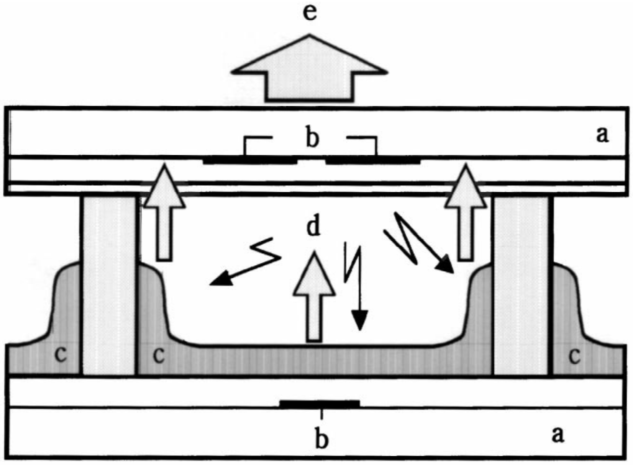

Fig. 1. A typical cell structure of a PDP (a: glass substrate, b: electrodes, c: R, G, or B phosphor, d: plasma discharge, e: visible light output).

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PII: S0925-8388(00)00856-2

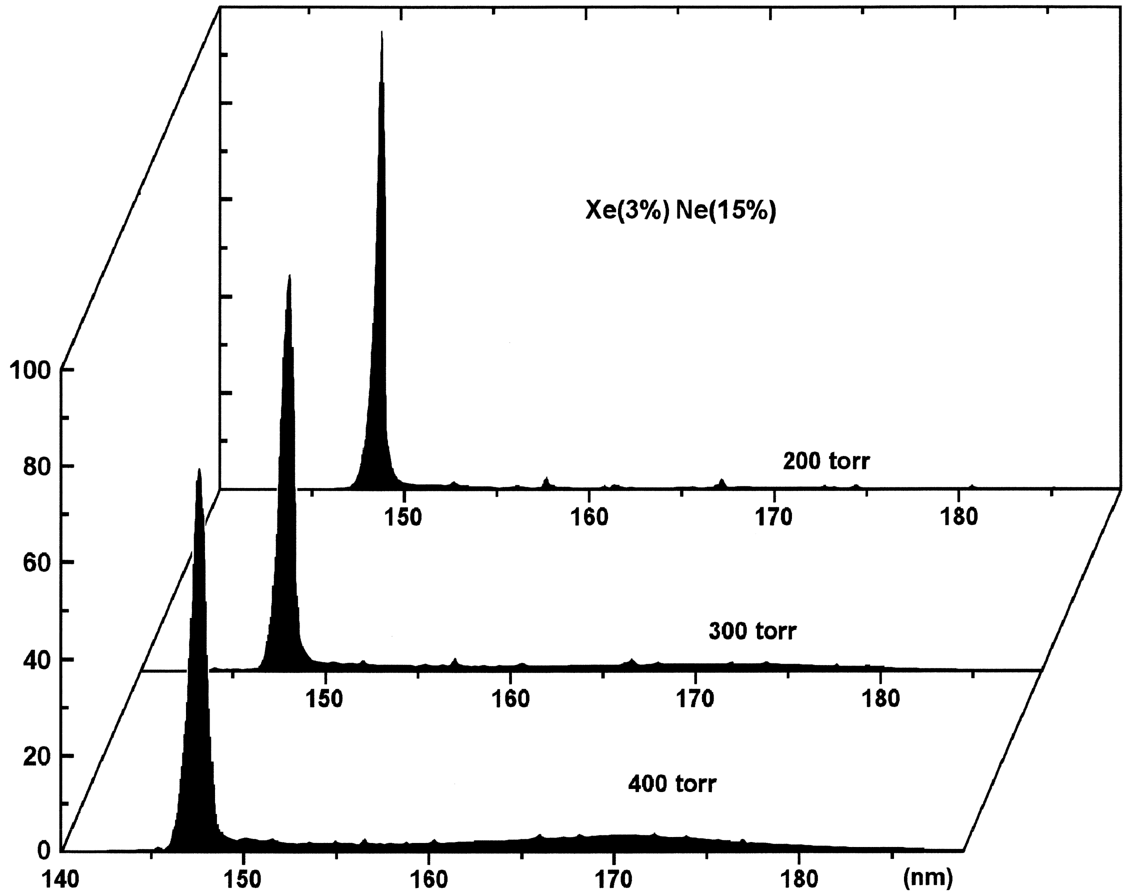


Fig. 2. Emission spectra of Penning gas.

output of the plasma source depends on the gas constituent, composition and pressure [7]. The energy conversion efficiency of the vuv in the range of 7–12 eV into the visible is generally higher at lower energies. Thus the xenon is the preferred constituent for the PDP.

PDP phosphors strongly resemble fluorescent lamp phosphors. Some of the phosphors are listed in Table 1 along with standard color coordinates of the NTSC red, green, and blue phosphors [8–17]. From Table 1, fairly low (near 1%) radiant efficiencies for these phosphors are noticeable. Various hosts and activators have been studied but phosphors with better performances should be found for a competitive PDP realization. Until recently, the main PDP phosphors have been Y_2O_3:Eu and (Y,Gd)BO_3:Eu for red, Zn_2SiO_4:Mn and $BaAl_{12}O_{19}$:Mn for green, and $BaMgAl_{14}O_{23}$:Eu and $BaMgAl_{10}O_{17}$:Eu for blue. Excitation and emission spectra of these tricolor phosphors are shown in Fig. 3a and b.

As listed in Table 1, decay times of (Y,Gd)BO_3:Eu^{3+} and $BaAl_{12}O_{19}$:Mn are somewhat longer, but those of $Zn_3(PO_4)_2$:Mn and Zn_2SiO_4:Mn are too long for practical application. Since decay times of red and green phosphors are longer to exploit the fast response of the PDP, they should be improved. The blue phosphor $BaMgAl_{14}O_{23}$:Eu^{2+} has a fast decay time which is obscured by the plasma discharge decay, thus accurate measurement is not easy.

3. Host sensitization

When phosphors are excited by vuv, the influence of the host lattice is very important. For example, the emission spectrum of (Y,Gd)BO_3:Eu^{3+} peaks at about 595 nm which is shorter than the peak emission wavelength of Y_2O_3:Eu. However, its performance on excitation in the vuv region is better than that of Y_2O_3:Eu as shown in Fig. 4. The host excitation band of (Y,Gd)BO_3:Eu^{3+} appears at near 160 nm.

Comparing the Tb^{3+}-activated Y borates with Gd borates, we could note that they all show a wide range of strong excitation spectra below 160 nm (see Figs. 5 and 6) with some differences in the peak shape and intensity. But GdB_3O_6:Tb shows a strong band with a peak at around 155 nm. The Tb^{3+}-activated Gd borates, in particular, show high quantum efficiencies. Fig. 6 suggests there are some differences in the host band gap between the borates and these gaps match well with the excitation energy of activators (here Tb^{3+}) except GdB_3O_6:Tb.

Because peaks near 160 nm are present in several

Table 1
Characteristics of some phosphors

Phosphor	CIE coordinate		Relative radiant efficiency	$\tau_{1/e}$ (ms)	Brightness (cd/m^2)
	x	y			
NTSC Red	0.67	0.33			
Y_2O_3:Eu	0.648	0.347	0.67	1.3	62
(Y,Gd)BO_3:Eu	0.641	0.356	1.2	4.3	
YBO_3:Eu	0.65	0.35	1.0		
$GdBO_3$:Eu	0.64	0.36	0.94		
$LuBO_3$:Eu	0.63	0.37	0.74		
$ScBO_3$:Eu	0.61	0.39	0.94		
Y_2SiO_5:Eu	0.66	0.34	0.67		
$Y_3Al_5O_{12}$:Eu	0.63	0.37	0.47		
$Zn_3(PO_4)_2$:Mn	0.67	0.33	0.34	15.1	
NTSC Green	0.21	0.71			
Zn_2SiO_4:Mn	0.242	0.708	1.0	11.9	365
$BaAl_{12}O_{19}$:Mn	0.182	0.732	1.1	7.1	
$SrAl_{12}O_{19}$:Mn	0.16	0.75	0.62		
$CaAl_{12}O_{19}$:Mn	0.15	0.75	0.34		
$ZnAl_{12}O_{19}$:Mn	0.17	0.74	0.54		
$BaMgAl_{14}O_{23}$:Mn	0.15	0.73	0.92		
YBO_3:Tb	0.33	0.61	1.1		
$LuBO_3$:Tb	0.33	0.61	1.1		
$GdBO_3$:Tb	0.33	0.61	0.53		
$ScBO_3$:Tb	0.35	0.60	0.36		
$Sr_4Si_8O_6C_{14}$:Eu	0.14	0.33	1.3		
NTSC Blue	0.14	0.08			
$BaMgAl_{10}O_{17}$:Eu	0.147	0.067		<1	
$BaMgAl_{14}O_{23}$:Eu	0.142	0.087	1.6	<1	
Y_2SiO_5:Ce	0.16	0.09	1.1		51
$CaWO_4$:Pb	0.17	0.17	0.74		

Tb^{3+}-activated borates, the absorption in this region is most probably due to the host lattice, i.e. in the BO_3 groups. Excitation spectra of $Eu_{0.05}La_{0.95}MgB_5O_{10}$ and $BaLa_{0.9}Tb_{0.1}B_9O_{16}$ show also the weak host sensitization band of BO_3 groups at around 150 nm along with a strong Tb excitation band as in Fig. 7.

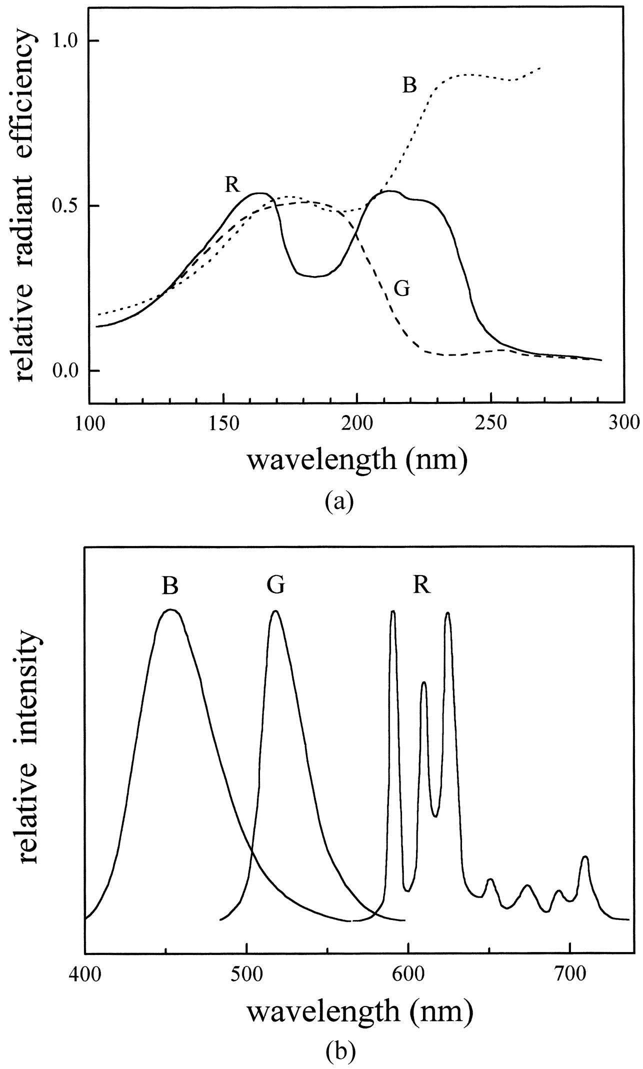
The excitation spectra of $Tb_xY_{1-x}PO_4$ are shown in Fig. 8. Hoshina [18] reported that peak A is a spin-forbidden transition and B is a spin-allowed 4f–5d transition. It is found that in $Tb_xY_{1-x}PO_4$ peaks C and A have one type of concentration dependence, while peaks B and D exhibit another type of concentration dependence. The peak C can be ascribed to a spin-forbidden transition as A, and the peak D to a spin-allowed transition as B. The band at 150~160 nm is assumed to be a host sensitization band of the PO_4^{3-} group. The fact that this excitation band is observed for YPO_4 host can be interpreted as a result of an efficient energy transfer from the PO_4^{3-} group to the activator.

Excitation spectra of $K_3Tb(PO_4)_2$ and polyphosphates are shown in Fig. 9 and a weak excitation band around 130–150 nm is observed. While 4f–5d transitions of Tb^{3+} in TbP_5O_{14} are nearly the same as in other type of phosphates as shown in Fig. 9, the host sensitization band of $P_5O_{14}^{3-}$ groups is very weak and red-shifted compared to diphosphates and tetraphosphates. This indicates the low efficiency of the energy transfer from the host to Tb.

Aluminates, $BaAl_2O_4$:Eu, $BaAl_8O_{13}$:Eu, $BaAl_{12}O_{19}$:Eu and $BaAl_{10}O_{17}$:Eu show a strong and broad excitation below near 175 nm as shown in Fig. 10. This can be attributed to the host sensitization of aluminates and indicates good match of the excitation energy of the host with that of the activators in this range.

As shown in Fig. 11, CaO:Eu^{3+} gives an absorption band at 205 nm which is presumed to be a host excitation band due to a transition from the valence band to the conduction band, i.e. the excitation energy is absorbed by the host and transferred to the activator in relaxation processes [19]. The 254-nm band is a well known charge transfer band of the Eu–O, i.e. the electron transfer from oxygen to the Eu^{3+} ion.

In the oxyfluoride system (CaF_2+CaO):Eu^{3+} a broad band merged with additional features from CaF_2:Eu^{3+} in the higher energy region appears with increased vuv absorption as shown in Fig. 12. By comparing the excitation spectrum of CaO:Eu^{3+} with that of (CaF_2+CaO):Eu^{3+} it is quite easy to notice that the introduction of F^- ions in the host lattice shifts all the features to a higher energy region. This is in full agreement with the fact that the charge transfer occurs at higher energy in the



(a)

(b)

Fig. 3. a) Excitation spectra of R, G, and B phosphors. b) Emission spectra of R, G, and B phosphors. (R: (Y,Gd)BO_3:Eu^{3+}, G: $BaAl_{12}O_{19}$:Mn and B: $BaMgAl_{14}O_{23}$:Eu^{2+}).

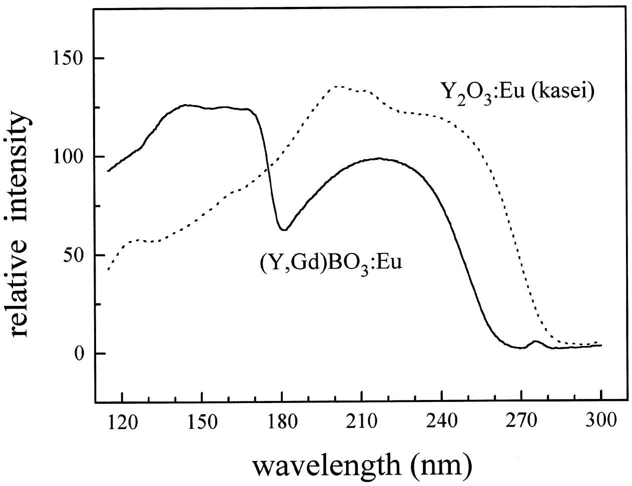


Fig. 4. Excitation spectra of Y_2O_3:Eu and (Y,Gd)BO_3:Eu.

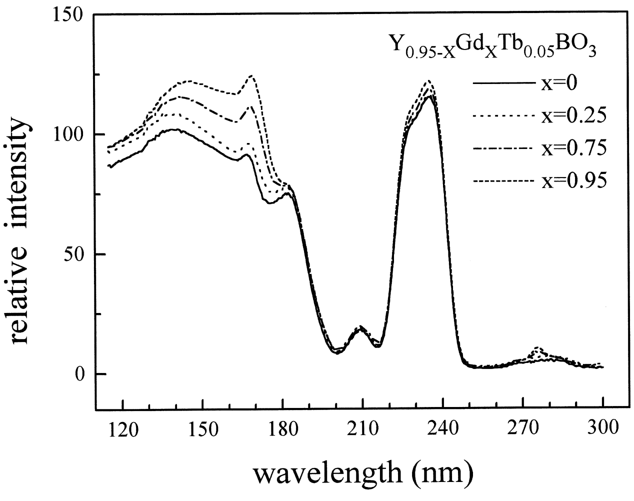


Fig. 5. Excitation spectrum of $Y_{0.95-x}Gd_xTb_{0.05}BO_3$.

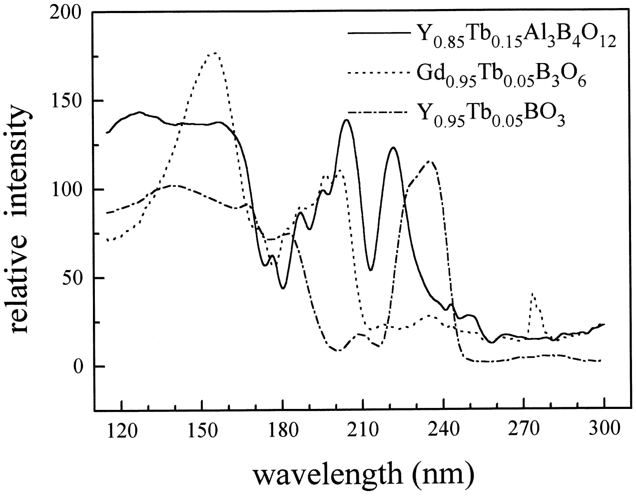


Fig. 6. Excitation spectra of $Y_{0.85}Tb_{0.15}Al_3B_4O_{12}$, $Gd_{0.95}Tb_{0.05}B_3O_6$ and $Y_{0.95}Tb_{0.05}BO_3$.

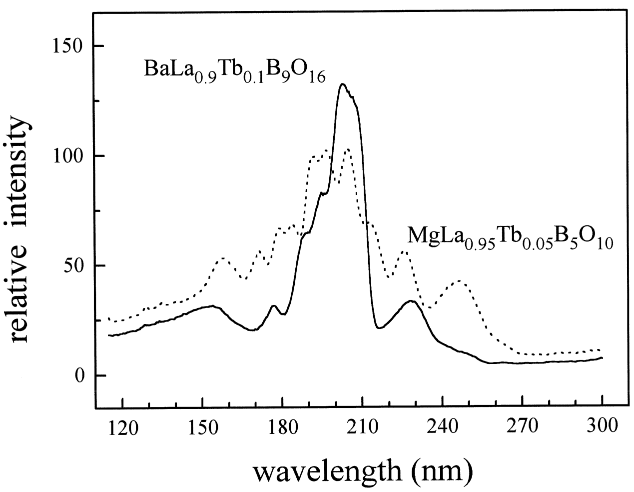


Fig. 7. Excitation spectra of $BaLa_{0.9}Tb_{0.1}B_9O_{16}$ and $MgLa_{0.95}Tb_{0.05}B_5O_{10}$.

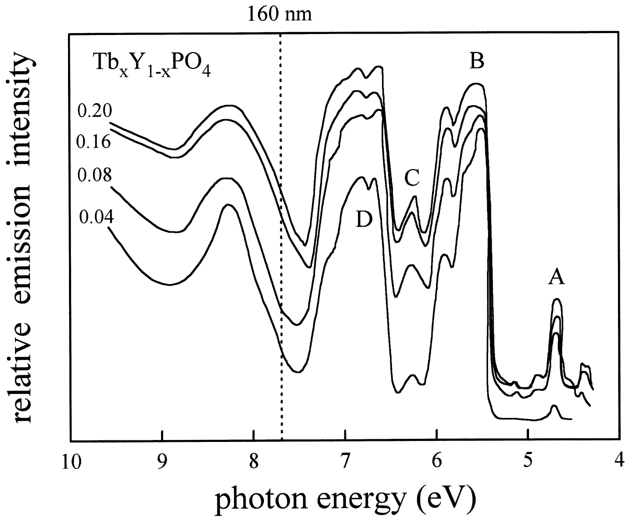


Fig. 8. Excitation spectrum of $Tb_xY_{1-x}PO_4$.

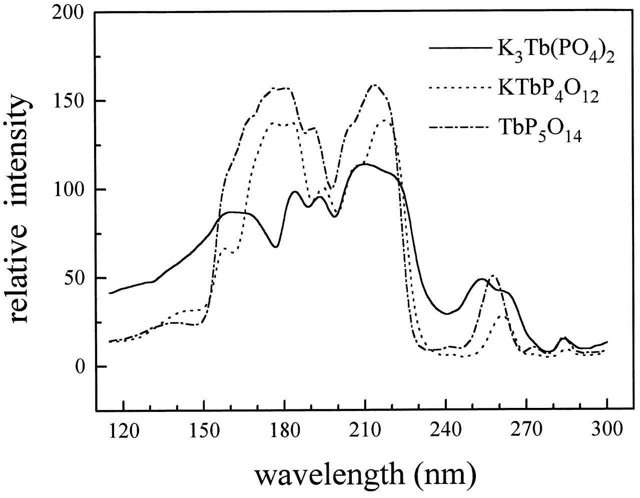


Fig. 9. Excitation spectra of $K_3Tb(PO_4)_2$, $KTbP_4O_{12}$ and TbP_5O_{14}.

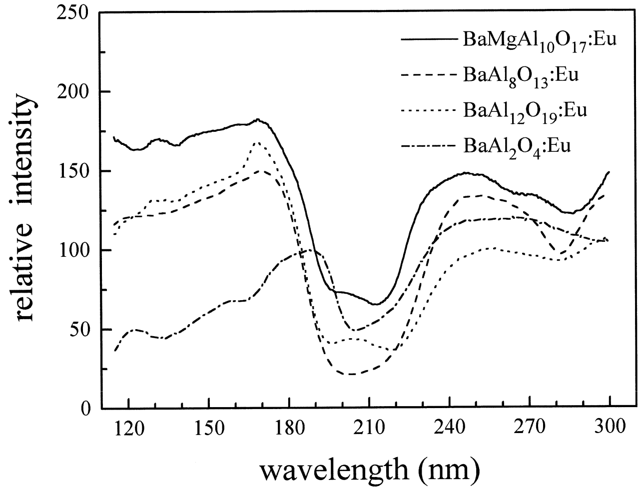


Fig. 10. Excitation spectra of $BaMgAl_{10}O_{17}$:Eu, $BaAl_8O_{13}$:Eu, $BaAl_{12}O_{19}$:Eu and $BaAl_2O_4$:Eu.

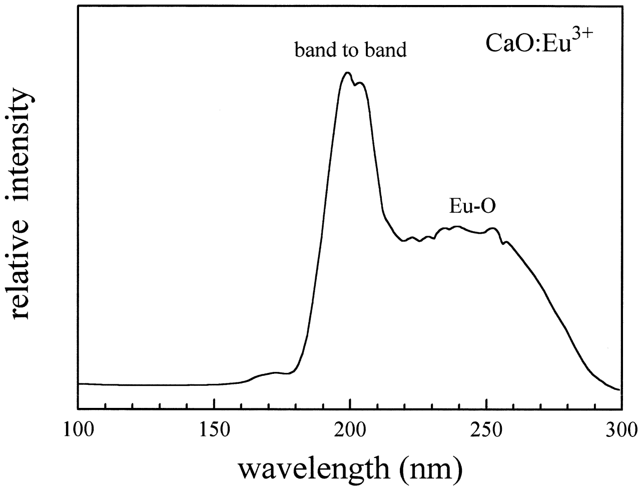


Fig. 11. Excitation spectrum of $CaO:Eu^{3+}$.

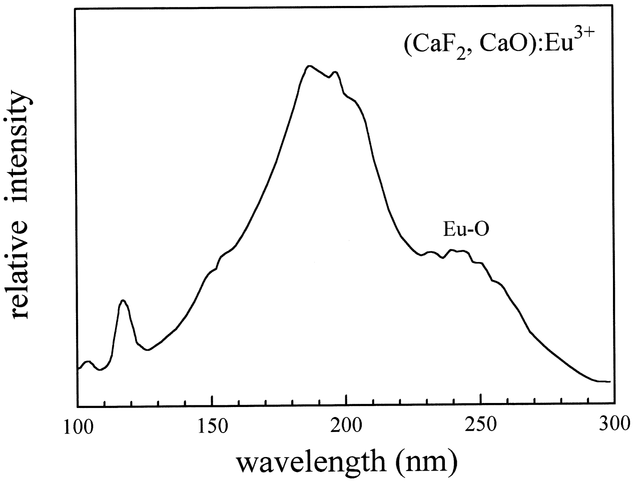


Fig. 12. Excitation spectrum of $(CaF_2, CaO):Eu^{3+}$.

Eu–F system than in the oxygen dominating lattice, according to the respective electronegativity of the ligand.

In order to check the fluoride effect, the $LaF_3:Eu^{3+}$ phosphor was investigated as shown in Fig. 13. The features in the excitation spectrum are clearly identifiable: the charge transfer (CT) band occurs at 170 nm and the band to band transition at 125 nm. The host sensitization bands in rare earth ion activated $LiYF_4$, LaF_3 and YF_3 are reported to be around 120 nm [20–25].

As explained above each host shows it own excitation band position, and the host sensitization band positions are: oxide (CaO:Eu, ~200 nm)>polyaluminate ($BaMgAl_{10}O_{17}$:Eu, ~175 nm)>silicates (Mg_2SiO_4:Tb, 160~170 nm)>Eu or Tb activated borates (150~170 nm)> phosphate (YPO_4:Eu, ~150 nm)>pentaphosphate (TbP_5O_{14}, ~135 nm)>diphosphate ($K_3Tb(PO_4)_2$, $Ba_3(PO_4)_2$:Eu, ~125 nm)>fluoride (LaF_3:Eu or $LiYF_4$:Eu, ~120 nm). These results would be the basis of designing new materials for PDP phosphors.

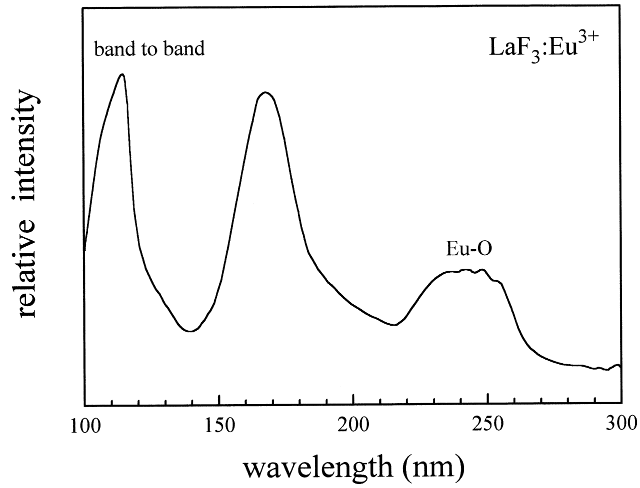


Fig. 13. Excitation spectrum of LaF$_3$:Eu^{3+}.

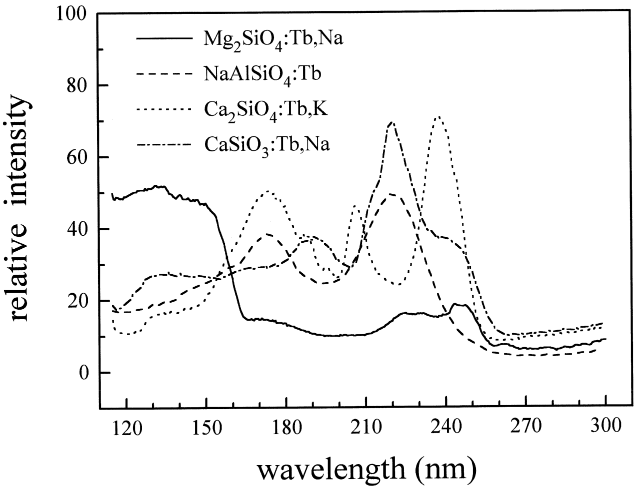


Fig. 14. Excitation spectra of Tb activated silicates.

4. The effect of cation (rare-earth ion)

The energy of the first f–d transition in trivalent lanthanide ions and the band gap energy of the three different fluorides [26] are summarized in Table 2. Table 2 shows that the energy levels of rare earth trivalent ions are spread over the range of vuv and the phosphors with these hosts are excited by the vuv.

The excitation spectra of terbium (Tb) in different silicates are shown in Fig. 14. The host excitations are around 160 nm and very strong for magnesium silicate, Mg$_2$SiO$_4$:Tb. But for calcium silicates host excitations are very weak with strong excitations by f–d transitions. The peak separation between f–d transitions of Tb^{3+} ion in the silicate crystals of NaAlSiO$_4$ and Ca$_2$SiO$_4$ are wider than that in CaSiO$_3$, which may be due to the different crystal field strength. This indicates that both the position of the energy level and the crystal field strength of the lanthanides at the lattice sites are very important parameters in addition to the band gap of the host for more efficient host excitation.

Excitation spectra of red-emitting phosphors with different rare earth ions in LnBO$_3$:Eu^{3+} are shown in Fig. 15. As the radius Ln^{3+} increases, the host sensitization band moves to longer wavelengths. The same trend could be observed as shown in Fig. 16 in the system of

Table 2
The first f–d transition energy of lanthanides in fluoride hosts

Element	No. of f-electrons	E_{f-d}[a] of tri-valent RE ions in					
		LiYF$_4$		YF$_3$		LaF$_3$	
		(eV)	(nm)	(eV)	(nm)	(eV)	(nm)
Ce	1	4.19	296	4.90	253	4.96	250
Pr	2	5.85	212	6.59	188	6.59	188
Nd	3	7.1	175	7.33	169	7.65	162
Pm	4	–	–	–	–	–	–
Sm	5	–	–	–	–	–	–
Eu	6	8.67	143	9.31	133	9.5	130.5
Gd	7	–		–	–	–	–
Tb	8	4.86	255	5.82	213	6.13	202
Dy	9	6.48	191	8	155	8	155
Ho	10	8.05	154	8.85	140	9.2	135
Er	11	8.05	154	8.38	148	8.65	143
Tm	12	7.95	156	8.33	149	8.65	143
Yb	13	–	–	–	–	–	–
E_{band}[b]		10.55	117.5	10.53	118	10.51	118
E_{charge}[c]		7.9	157	7.88	157	7	177

[a] E_{f-d}: the first f–d transition energy.
[b] E_{band}: band to band transition energy of the host.
[c] E_{charge}: charge transfer energy of the host.

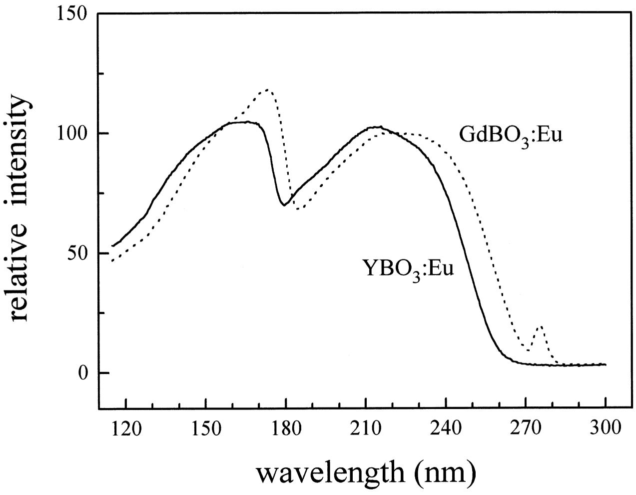


Fig. 15. Excitation spectra of YBO$_3$:Eu and GdBO$_3$:Eu.

LnBO$_3$:Tb^{3+} (Ln=Gd, Y, or La) i.e. the order of the host sensitization bands are: λ_{exc}(LaBO$_3$:Tb)> λ_{exc}(GdBO$_3$:Tb)>λ_{exc}(YBO$_3$:Tb).

5. Conclusion

In conclusion, the performance of the state-of-the-art commercial PDP phosphors is still not good enough for practical application. For the design of new phosphors some parameters must be taken into account: selection of host materials with suitable band gaps and modification of the host with cations, which can modify the crystal field at the lattice sites for better energy match and more efficient energy transfer.

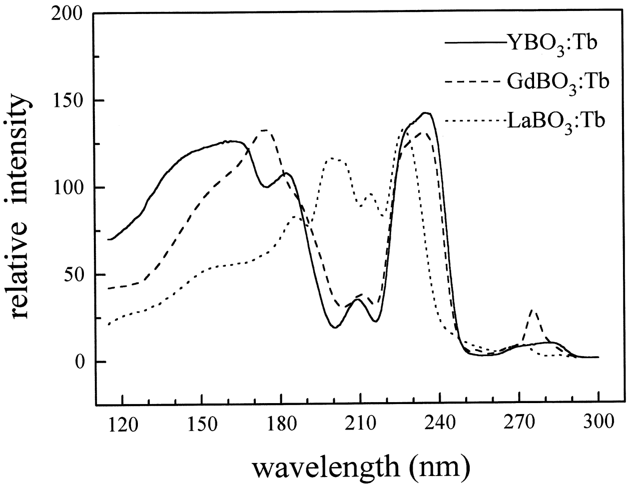


Fig. 16. Excitation spectra of YBO$_3$:Tb, GdBO$_3$:Tb and LaBO$_3$:Tb.

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