Abstract

Europium-activated yttrium, lanthanum and gadolinium orthophosphate, vanadate, arsenate and niobate phosphors were prepared, including also phosphors with mixed anionic groups. The ratio of the intensities of the red and the orange europium emission lines depends strongly on small variations of the surroundings of the Eu-ion. In some unactivated phosphors a strong blue emission is found and with Eu activation transfer of energy to Eu is observed. The efficiency of this transfer is found to be much higher than in the case of terbium activation of these phosphors. For the vanadates and mixed vanadate-phosphates the excitation spectra extend towards much longer wavelengths than for the phosphates. Quantum efficiencies of about 70% were found for the $\text{YV}_{1-x}\text{P}_x\text{O}_4$-Eu phosphors. Most phosphors have a high brightness at elevated temperatures with respect to the brightness at room temperature. The quenching temperatures of the mixed Y-phosphate-vanadate phosphors are higher than those of the unsubstituted $\text{YVO}_4$-Eu.

1. Introduction

Recently several new europium-activated phosphors of the type $\text{A}^{III}\text{B}^{V,IV}\text{O}_4$ were described, in which $\text{A}=$ La, Gd or Y and $\text{B}=$ P, V or Nb. For example Van Uitert, Soden and Linares 1) described the preparation and some properties of $\text{YVO}_4$-Eu, and we reported on $\text{GdPO}_4$-Eu 2). Brixner 3) studied the properties of $(\text{LnM})_4(\text{CaM})_{1-x}\text{O}_4$ where $\text{Ln}=$ trivalent rare earth, $\text{Sc}^{3+}$ or $\text{Y}^{3+}$; $\text{M}^1=$ $\text{Nb}^{5+}$, $\text{Ta}^{5+}$ and $\text{M}^{II}=$ $\text{Mo}^{6+}$, $\text{W}^{6+}$. Moreover, Ca may be replaced by $\text{Sr}^{2+}$ and $\text{Ba}^{2+}$. Borchardt 4) made both $\text{GdPO}_4$-Eu and $\text{LaPO}_4$-Eu. The application of $\text{YVO}_4$-Eu for colour-television tubes was reported by Levine and Palilla 5). Brixner and Abramson 6) prepared all the rare-earth vanadates and found that compounds of the type $\text{AVO}_4$ are the only ones formed by the rare-earth sesquioxides and vanadium pentoxide; $\text{Gd}_{1-x}\text{Eu}_x\text{VO}_4$ appeared to be an efficient phosphor, with a maximum intensity at $x=0.08$. This value accords well with our own figures 7) and is nearly the same as given for $\text{YVO}_4$-Eu in a patent by Ballman, Linares and Van Uitert 8).

In this paper we describe the preparation and some luminescent properties of Eu-activated Y, La and Gd phosphates, vanadates, arsenates and niobates, respectively. In addition phosphors were made with mixed anionic groups, as e.g. $\text{A}^{III}\text{V}_{1-x}\text{P}_x\text{O}_4$-Eu.
2. Experimental

2.1. Method of phosphor preparation

The ingredients used in the firing mixtures were reagent-grade \((\text{NH}_4)_2\text{HPO}_4\), \(\text{NH}_4\text{VO}_3\) from Riedel de Haën (code nr. 31.153), \(\text{Nb}_2\text{O}_5\) (99.9%) from Th. Schuchardt or the firm Hopkins and Williams, \(\text{As}_2\text{O}_3\) from Baker. The rare-earth oxides were obtained from the Lindsay Chemical Division of American Potash and Chemical Corporation in purities of 99 - 99.9% or from Michigan Chemical Corporation. In some cases the rare-earth oxides were first transformed into the oxalates by dissolving the oxides in hydrochloric acid and precipitating the oxalates by the addition of oxalic acid.

The required amounts of the dry materials were thoroughly mixed and subsequently fired in air. Samples of 3-10 g were fired twice for 2 hrs in small quartz crucibles at a temperature of 1000 - 1300 °C.

2.2. Optical properties

The excitation, diffuse-reflexion and emission spectra, as well as the efficiencies and decay times were measured by a procedure described earlier \(^9\). The radiant efficiency of the phosphors, with cathode-ray excitation, was determined by a method also reported before \(^10\).

2.3. Crystal structure and X-ray analysis of the \(\text{A}^{\text{III}}\text{B}^\text{V}\text{O}_4\) compounds

X-ray powder-diffraction patterns were taken at room temperature, using the CuKα radiation from a Philips Norelco unit. The crystal structure of the \(\text{A}^{\text{III}}\text{B}^\text{V}\text{O}_4\) compounds belong to at least four types \(^11\). In table I the crystal structures for the \(\text{A}^{\text{III}}\text{B}^\text{V}\text{O}_4\) compounds with which we are dealing in this paper are given. Except for \(\text{LaAsO}_4\) and \(\text{LaVO}_4\) the cell dimensions were already given in the literature. The powder diagram of these \(\text{A}^{\text{III}}\text{B}^\text{V}\text{O}_4\) compounds could be indexed using these known cell dimensions. The powder diagram of

<table>
<thead>
<tr>
<th>(\text{A}^{\text{III}})</th>
<th>(\text{B}^\text{V}\text{O}_4)</th>
<th>(\text{PO}_4)</th>
<th>(\text{VO}_4)</th>
<th>(\text{AsO}_4)</th>
<th>(\text{NbO}_4)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Y</td>
<td>X</td>
<td>X</td>
<td>X</td>
<td>F</td>
<td></td>
</tr>
<tr>
<td>La</td>
<td>M</td>
<td>M</td>
<td>M</td>
<td>F</td>
<td></td>
</tr>
<tr>
<td>Gd</td>
<td>M</td>
<td>X</td>
<td>X</td>
<td>F</td>
<td></td>
</tr>
</tbody>
</table>
No1 LaPO₄ - Eu

No2 LaVO₄ - Eu

No3 YAsO₄ - Eu
LUMINESCENT PROPERTIES OF Eu-ACTIVATED PHOSPHORS OF TYPE AIII\text{B}VI\text{O}_4

Fig. 1. Spectral distribution of the emission of some $\text{A}^{\text{I}}\text{II}\text{B}^{\text{IV}}\text{O}_4$ - 0.06 Eu phosphors. Short-wavelength ultraviolet excitation. The dashed curve gives the factor by which the ordinate has to be multiplied to get radiant power.

Curve 1: $\text{LaPO}_4$ - Eu, curve 2: $\text{LaVO}_4$ - Eu, curve 3: $\text{YAsO}_4$ - Eu, curve 4: $\text{GdVO}_4$ - Eu, curve 5: $\text{GdAsO}_4$ - Eu, curve 6: $\text{LaNbO}_4$ - Eu.
the lanthanum vanadate could also be indexed and so the hitherto unknown cell dimensions of this compound were found, viz. \( a = 6.935 \, \text{Å} \), \( b = 7.09 \, \text{Å} \), \( c = 6.69 \, \text{Å} \), \( \beta = 104^\circ 38' \). A determination of the also unknown lattice dimensions of GdPO\(_4\) and LaAsO\(_4\) was not successful up to now.

The powder diagrams of the niobates were not in exact agreement with the published lattice dimensions of the monoclinic compounds. It is possible that under the preparation conditions a gradual transition into the tetragonal form occurs.

For the mixed yttrium phosphate-vanadates it follows from the X-ray data that a gradual transition from the cell dimensions of the phosphate to those of the vanadate occurs. Although this transition is not quite regular it cannot account for the clear difference between the fluorescence spectra of the europium-activated YPO\(_4\) and of mixed Y phosphate-vanadates, as will be discussed in the next section; GdV\(_{1-x}\)P\(_x\)O\(_4\)-Eu phosphors crystallize in the xenotime form.

3. Results and discussion

3.1. Emission spectra

3.1.1. Compounds with unsubstituted anions

Figure 1 gives the spectral-energy distribution of the emission of some unsubstituted Eu-activated phosphors and fig. 2 those of YV\(_{1-x}\)P\(_x\)O\(_4\)-Eu phosphors. All phosphors show emission lines characteristic of europium. For most of the phosphors the strongest lines are located near 593 nm and between 610 and 620 nm. The orange lines near 593 nm, mainly corresponding to transitions of the \( ^5D_0 \)-level to the \( ^7F_1 \)-level (split by the crystal field) are interpreted as magnetic-dipole transitions. The red lines near 610-620 nm correspond to \( ^5D_0 \rightarrow ^7F_2 \) transitions. When these lines are interpreted as electric-dipole transitions, they are strictly parity-forbidden in free ions, because these transitions occur between states of the same configuration. In crystals this selection rule may be violated when the Eu\(^{3+}\) site symmetry has no centre of inversion, so that states of opposite parity can be mixed in. The red lines \( ^5D_0 \rightarrow ^7F_2 \) therefore will often be present and in many cases they are even predominant. Only in the case of the presence of a centre of symmetry does the mixing of states not occur and then the red lines should be absent. From the ratio of the intensities of the red and orange lines in the spectral-energy-distribution curves of YPO\(_4\)-Eu and YVO\(_4\)-Eu (fig. 2), which are quite different, we might conclude that the surroundings in the former are more symmetric than in the latter, although both compounds possess the tetragonal xenotime crystal structure (see also table 1). The rule mentioned above, concerning the increase of the intensity of the red lines \( ^5D_0 \rightarrow ^7F_2 \) with respect to the orange lines \( ^5D_0 \rightarrow ^7F_1 \) with decreasing symmetry of the Eu surrounding has been studied extensively by Blasse, Bril and Nieuwoort.

LUMINESCENT PROPERTIES OF Eu-ACTIVATED PHOSPHORS OF TYPE \( \text{Al}_{11}\text{BVO}_4 \)

Fig. 2. Spectral distribution of the emission of \( \text{YV}_1-x\text{P}_x\text{O}_4 \cdot 0.05 \text{Eu} \) phosphors. Curve 1: \( x = 0 \), curve 2: \( x = 0.8 \), curve 3: \( x = 1.0 \). For the dashed curve, see fig. 1.

In \( \text{YVO}_4 \cdot \text{Eu} \) the widths of the orange emission lines are smaller than those of the red lines. At liquid-nitrogen temperature the widths of the orange and red lines are about 0.15 and 0.35 nm, respectively, at room temperature 0.30 and 0.65 nm. Because all the lines originate from the \( 5D_0 \) level, it may be concluded that the \( 7F_1 \) levels are narrower than the \( 7F_2 \) levels. In \( \text{GdVO}_4 \cdot \text{Eu} \) we found that the 619-nm and 615-nm lines (both \( 5D_0 \leftrightarrow 7F_2 \)) had equal widths at room temperature, namely 0.65 nm. At liquid-nitrogen temperature the widths were 0.35 and 0.65 nm, respectively. This is in accordance with the observation of Bril, Wannemaker and Broos \(^7\) that at liquid-nitrogen temperature the ratio of the peak intensities of the 619 and 615 lines is higher than at room temperature (i.e. the integrated intensity ratio remains unchanged).

In addition to the Eu-emission lines in a large number of the phosphors inves-
tigated also a broad deep-blue emission band is found. Apparently this emission band is due to self-activation, as it is also present in the unactivated phosphors. The reflexion of the activated vanadate phosphors does not differ much from that of the unactivated sample. Strong absorption of the exciting radiation occurs up to long wavelengths, i.e. about 330 nm. When increasing amounts of europium are added, the intensity of the self-activated emission band decreases while the intensity of the Eu emission increases. This is shown in table II.

TABLE II
Quantum efficiencies of YNbO₄₋ₓEu and YNbO₄₋ₚTb; excitation 250-270 nm; \( r = \) reflexion

<table>
<thead>
<tr>
<th>YNbO₄₋ₓEu</th>
<th>( r ) (%)</th>
<th>( \text{quantum eff.} )</th>
<th>YNbO₄₋ₚTb</th>
<th>( r ) (%)</th>
<th>( \text{quantum eff.} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( x = 0 )</td>
<td>11</td>
<td>46 (%) blue</td>
<td>0</td>
<td>14</td>
<td>46 (%) blue</td>
</tr>
<tr>
<td>( x = 0.005 )</td>
<td>12</td>
<td>34 (%) red</td>
<td>0.015</td>
<td>14</td>
<td>21 (%) green</td>
</tr>
<tr>
<td>( x = 0.015 )</td>
<td>12</td>
<td>24 (%) red</td>
<td>0.09</td>
<td>13</td>
<td>7 (%) green</td>
</tr>
<tr>
<td>( x = 0.06 )</td>
<td>7</td>
<td>10 (%) blue</td>
<td>0.15</td>
<td>7</td>
<td>3.5 (%) green</td>
</tr>
<tr>
<td>( x = 0.15 )</td>
<td>7</td>
<td>3 (%) red</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

where the efficiencies of the blue emission and of the red Eu emission in YNbO₄₋ₓEu are given. We conclude that transfer of energy takes place from the host lattice to Eu. It can be seen that in the phosphor with the highest Eu content about 90\% of the total emission is due to Eu. The quantum efficiency of the unactivated phosphor is 46\%, while for YNbO₄₋₀.15 Eu it is 31\%. The efficiency of transfer in the case of Eu is rather high when comparing it with the results found with YNbO₄₋ₚTb \( ^{15} \), also shown in table II.

3.1.2. Compounds with substituted anions

When phosphor is incorporated into the lattice of YVO₄₋Eu, the wavelength location of the emission lines and also the relative intensities of the red and orange emission lines do not change very much up to a composition of 80 mole per cent of PO₄. The line width of the red emission increases with increasing amounts of phosphate added, from about 0.65 nm to about 2.5 nm with 80 mole per cent of PO₄ as may be seen in fig. 2. The emission spectrum of the pure YPO₄₋Eu is quite different from that of the mixed Y vanadate-phosphates. The lines in YPO₄₋Eu are again narrow, but there is a large number of lines present (see fig. 2). Moreover, the ratio of the intensities of the red and orange lines has decreased as discussed in the previous section. Results, similar to those,
as reported above, were found for the Gd vanadate-phosphates. Again the emission spectrum of the pure phosphate is quite different from that of the mixed phosphate-vanadate phosphors. In this case, however, it is less surprising because the crystal structure of GdPO₄ (monazite crystal structure) is quite different from that of GdVO₄ and the GdV₁₋ₓPₓO₄ compounds (xenotime crystal structure).

The emission spectra of Y and Gd arsenate are not very different from those of Y and Gd vanadate. The mixed vanadate-arsenates again show line broadening.

3.2. Excitation spectra

The excitation spectra of YV₁₋ₓPₓO₄-Eu phosphors are given in fig. 3. They are quite similar to those of the corresponding Gd-containing phosphors.

![Fig. 3. Excitation and reflexion spectra of YV₁₋ₓPₓO₄ - 0·05 Eu phosphors.](image)

Curve 1: x = 0, curve 2: x = 0·8, curve 3: x = 1·0.

In the vanadates the absorption (also for the unactivated sample) and the efficiency remain high up to 330 nm. The energy is absorbed in the host lattice and is efficiently transferred to Eu. Both for ultra-violet and cathode-ray excitation high efficiencies are found.

The fluorescence mechanism in phosphors as Gd₂O₃-Eu, Y₂O₃-Eu and GdBO₃-Eu is different. In the unactivated Gd₂O₃, for instance, there is only a small absorption of 254-nm radiation. When Eu is incorporated, a broad excitation band is found in this region. This corresponds probably to a charge-transfer transition from oxygen to europium in the europium-oxide complex. The quantum efficiency in this excitation band is high. Hence at first sight one does not expect a high efficiency under cathode-ray excitation. However, it is known that e.g. Gd₂O₃-Eu is a very efficient phosphor with cathode-ray excitation ¹⁶). This shows that apparently excitation in the fundamental absorption band of the lattice will also lead to an efficient transfer to the activator. This is in accordance with the increase in quantum efficiency for wavelengths below about 200 nm in e.g. Y₂O₃-Eu.
In addition to the broad excitation band mentioned above, some excitation peaks are also found, viz. at wavelengths of 360, 375, 380, 395, 418, 440, 465 and 535 nm, respectively. These lines correspond to excitation in the unperturbed Eu³⁺ ions.

When phosphate is incorporated the cut-off wavelength of the excitation spectra gradually shifts somewhat (∼10 nm) to shorter wavelengths. The pure YPO₄-Eu, however, shows excitation and reflexion spectra quite different from the corresponding vanadate and vanadate-phosphate phosphors. The maximum in the excitation spectra is located at much shorter wavelengths, viz. below 225 nm for YPO₄ (fig.3) and at about 240 nm for GdPO₄. The absorption edge in the pure phosphates is also shifted to shorter wavelengths as compared with those of the mixed vanadate-phosphate phosphors.

In GdPO₄-Eu the excitation spectrum of the Eu emission shows sharp peaks at λ = 275-280 nm, corresponding to Gd-absorption lines. This is an example of energy transfer from Gd to Eu, which we have already reported for other phosphors ²). In fig. 4 the excitation and reflexion spectra of Eu-activated LaPO₄,

![Graphs showing excitation and reflexion spectra of various AIIIByVO₄ - 0.06 Eu phosphors.](image-url)

Curve 1: LaPO₄ - Eu, curve 2: LaVO₄ - Eu, curve 3: YAsO₄ - Eu, curve 4: GdAsO₄ - Eu, curve 5: LaNbO₄ - Eu.
Luminescent properties of Eu-activated phosphors of type AlIIbVO4

LaVO₄, YAsO₄, GdAsO₄, and LaNbO₄ phosphors are given. Similar to the excitation spectra of YVO₄-Eu and YV₁₋ₓPₓO₄-Eu phosphors, discussed already above, in all cases a broad excitation band is present and also excitation peaks, due to excitation in unperturbed 4f-levels in the Eu³⁺-ions. From the excitation spectrum it may be concluded that in GdAsO₄-Eu also energy transfer from Gd to Eu takes place.

3.3. Efficiencies

Absolute efficiencies of some phosphors were determined at room temperature for excitation in the 250-270-nm region. The method of measurement has been described by Bril and Hoekstra ⁹). The results are given in table III. The efficiencies are corrected for the reflexion, thus giving the amount of radiance (or quanta) in proportion to the amount of absorbed exciting power (or quanta, respectively).

We see from the table that the quantum efficiency of the Y vanadate-phosphates-Eu is high, viz. up to 69%. This is comparable with the efficiencies of commercially available lamp phosphors. The efficiency remains about constant up to the incorporation of 80% PO₄; the variation of 10% in the figures may be due to small differences in preparative conditions and to the errors of measurement.

The europium-activated mixed phosphate-vanadate phosphors are very well suited for application in high-pressure mercury-vapour lamps, due to the
high brightness at elevated temperatures (see sec. 3.4). the high amount of red
radiation and their white body colour.

Concerning the other types of phosphors with mixed anionic groups, it was
found that substituting AsO₄ for VO₄ also gives efficient phosphors, whereas
substitution by NbO₄ groups results in a pronounced drop in quantum effi-
ciency. A low quantum efficiency was also found for the substituted lanthanum
compounds and the unsubstituted orthoarsenates.

Due to the relatively high efficiencies of the phosphate-vanadate compounds,
these phosphors are very suitable for use as a red component in colour television
16). The efficiencies of YV₁₋ₓPₓO₄-Eu phosphors with cathode-ray excitation
are nearly constant with x increasing from 0 to 1.

In GdV₁₋ₓPₓO₄-Eu phosphors also high efficiencies can be obtained.

3.4. Temperature dependence

The brightness of YV₁₋ₓPₓO₄-Eu phosphors as a function of the tempera-
ture is given in fig. 5. It can be seen that with increasing amounts of PO₄ sub-
stituted for VO₄ the quenching temperature of the emission gradually increases.

Among the compounds reported in fig. 5, those possessing the crystal struc-
ture of xenotime show the highest brightness at elevated temperatures. The
phosphors YPO₄-Eu, YVO₄-Eu and GdVO₄-Eu also obey the general rule
that compounds with the crystal structure of xenotime have a high brightness
at elevated temperatures. The phosphors having the crystal structure of mon-
azite, e.g. LaPO₄-Eu and LaVO₄-Eu, in general have a lower quenching temperature than those with xenotime crystal structure; GdPO₄-Eu also having the monazite crystal structure, however, has a high quenching temperature.

It follows from fig. 6 that in LaNbO₄ - 0·01 Eu, the quenching temperature of the blue niobate emission is much lower than that of the Eu emission. A higher quenching temperature of the rare-earth emission than that of the self-activated emission was already described before in CaWO₄-Sm ¹⁷).

Acknowledgement

The authors are indebted to Dr G. Blasse and Dr W. C. Nieuwpoort for valuable discussions; to Mr J. G. Verlijsdonk, Mr J. A. van Bommel and Mr N. A. F. van Soerland for the preparation of the phosphors and the measurements of the temperature dependence and to Mr J. A. A. Bertens, Mr C. D. J. C. de Laat, Mr C. J. Loyen and Mr J. de Poorter for carrying out the measurements of various optical properties.

Eindhoven, March 1966

REFERENCES

A. Bril in Kallmann-Spruch (ed.), Luminescence of organic and inorganic materials,