THIN SINGLE CRYSTALLINE PHOSPHOR LAYERS GROWN BY LIQUID PHASE EPITAXY


Abstract
Thin single crystal garnet phosphor layers have been grown by liquid phase epitaxy. First the choice of host lattice is explained, after which film growth is discussed. Parameters that might influence the cathodoluminescent efficiency, such as the activator concentration, incorporation of unwanted ions, crystal orientation, lattice parameter, mismatch strain and segregation coefficients, were tested and the results are given. It is shown that after optimization of the melt parameters the liquid phase epitaxy process produces thin single crystal layers which are as efficient and sometimes even more efficient than the equivalent compositions in powder form.

1. Introduction
The use of powder phosphors on a glass substrate as luminescent screens in cathode-ray devices is widespread and well-known. However, in some special applications powder screens have some disadvantages. Owing to the relatively poor thermal conductivity of the powder and the far from ideal heat contact of the powder with the screen, the power handling capacity of these screens is limited. In high-resolution devices, the finite dimension of the powder particles imposes a clear limit on the resolution that can ultimately be obtained. Further it appears that in demountable devices, as for example scanning electron microscopes, the phosphor screens are subjected to mechanical stress by repeated pumping cycles, which can lead to detachment of the phosphor from the substrate. Finally, the conversion efficiency of a powder phosphor is a complicated function of the preparation technique: it depends on the particle size, homogeneity of activator ions, perfection of the host lattice, etc.

The present work is a report on the growth and the properties of monocrystalline phosphor screens with a good heat conductivity. An epitaxial process was chosen to grow the luminescent film so that a perfect thermal contact is obtained between the active layer and the substrate. In this manner it proved possible to use the screens with electron beams whose power density was two orders of magnitude greater than with powder screens). Moreover,
Thin single crystalline phosphor layers grown by liquid phase epitaxy

the monocrystalline phosphor screens were optically clear and did not limit the resolution; they were also resistant against repeated pumping cycles.

For the epitaxial process the technique of liquid phase epitaxy (LPE) was chosen because it is an isothermal growth process which results in a very homogeneous distribution of the activator ions within the film. Furthermore, the reproducibility from sample to sample is very high. This should be compared with single crystal wafers cut from Czochralski grown boules. In this case the activator ion concentration will not always be the same because of the variation along the length of the boule, due to the fact that the segregation coefficients are not equal to unity. Moreover, the epitaxial growth of these layers ensures that there is no second phase present in the films.

2. Materials

The class of cathodo-luminescent materials is very large, but decreases rapidly when the required thermal properties are discussed. The best materials that can withstand the high temperatures produced by the incident electron beams are the high melting point materials, which are usually oxidic. A number of these materials are listed in table I.

<table>
<thead>
<tr>
<th>Material</th>
<th>Chemical formula</th>
<th>Melting point (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>garnets</td>
<td>RE₃M₆O₁₂</td>
<td>1900</td>
</tr>
<tr>
<td>hexa-aluminates</td>
<td>Ba₁₋ₓAl₁₂₊₄ₓO₁₉</td>
<td>1910</td>
</tr>
<tr>
<td>borates</td>
<td>REM₉(BO₄)₄</td>
<td>Incongruently melting</td>
</tr>
<tr>
<td>silicates</td>
<td>Y₂SiO₅</td>
<td>1950</td>
</tr>
<tr>
<td>oxides</td>
<td>Y₂O₃</td>
<td>2410</td>
</tr>
<tr>
<td>vanadates</td>
<td>YVO₄</td>
<td>1750–1900</td>
</tr>
</tbody>
</table>

The technological problems of providing screens of 25 mm or larger diameters with a thin layer (3–10 µm depending on the penetration depth of the incident electrons) of active material on a monocrystalline substrate (≈ 700 µm thick to withstand the atmospheric pressure) restricts the list in table I even further. Only the garnets and the hexa-aluminates are left at the present time since those are the only materials available as good quality
crystals with diameters of 25 mm or larger and on which epitaxy has been demonstrated. One could think of hetero-epitaxy of oxidic host materials on sapphire substrates for example, but this technique is not yet developed far enough to lead to reproducible results.\(^2,^3\)

In the present paper we will restrict ourselves to the garnets because the results on hexa-aluminates have been published elsewhere.\(^4,^5\)

Among the garnets there is a choice of two host lattices for the phosphor; the rare-earth-gallium garnets and the rare-earth-aluminium garnets. From earlier work on powders\(^6,^7\) it was shown that the aluminium garnets were more efficient under cathode-ray excitation than the gallium garnets. An initial study was made to check this point for the case of epitaxially grown materials. We made rare-earth doped \(\text{Gd}_3\text{Ga}_5\text{O}_{12}\), \(\text{Y}_3\text{Ga}_5\text{O}_{12}\), \(\text{Y}_3\text{Al}_5\text{O}_{12}\) and \(\text{Lu}_{1.86}\text{Gd}_{1.64}\text{Al}_5\text{O}_{12}\) layers and measured the efficiencies. Again it resulted in the aluminium garnets being the best and the host lattice \(\text{Y}_3\text{Al}_5\text{O}_{12}\) (YAG) was chosen for further work since it was readily available as good quality boules or wafers in various diameters. In table II some properties of the \(\text{Y}_3\text{Al}_5\text{O}_{12}\) materials are listed.

### TABLE II

**Typical material properties of \(\text{Y}_3\text{Al}_5\text{O}_{12}\) (YAG)**

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Formula</td>
<td>(\text{Y}_3\text{Al}<em>5\text{O}</em>{12})</td>
</tr>
<tr>
<td>Crystal structure</td>
<td>cubic (a_0 = 12.005 \text{ Å})</td>
</tr>
<tr>
<td>Hardness</td>
<td>8–8.5 (Moh)</td>
</tr>
<tr>
<td>Molecular weight</td>
<td>(M = 594 \text{ g/mol})</td>
</tr>
<tr>
<td>Melting point</td>
<td>(T_m = 2220 \text{ K})</td>
</tr>
<tr>
<td>Density</td>
<td>(\rho = 4.55 \text{ g/cm}^3)</td>
</tr>
<tr>
<td>Thermal conductivity</td>
<td>(K = 0.13 \text{ W cm}^{-1} \text{ K}^{-1}) at (T = 300 \text{ K})</td>
</tr>
<tr>
<td>Specific heat</td>
<td>(c = 0.62 \text{ J g}^{-1} \text{ K}^{-1}) at (T = 300 \text{ K})</td>
</tr>
<tr>
<td>Thermal expansion</td>
<td>(\alpha = 7.5 \times 10^{-6}) at (T = 300 \text{ K})</td>
</tr>
<tr>
<td>Refractive index</td>
<td>(n = 1.840) at (\lambda = 550 \text{ nm})</td>
</tr>
</tbody>
</table>

3. Experimental techniques

3.1. *Film growth*

The LPE growth of iron garnets for magnetic bubble memories\(^8,^9\) has been developed to a factory scale. In fact the technique is so good that nearly defect-free films of 75 mm diameter can be grown. In the present work it was
attempted to apply the methods used for the iron-garnet layers to the non-magnetic garnets.

The procedure of melt homogenization and the dipping program was identical with that developed for the magnetic bubble garnets and will not be discussed further since refs 9, 10 and 11 give good reviews on this subject. The furnace design is shown in fig. 1.

Fig. 1. Typical design for the furnace used for the liquid phase epitaxy of phosphor garnets.

In the present work commercially available 25 mm diameter [111], 700 μm thick polished wafers of Y₃Al₅O₁₂, were used. The presence of a small core, due to facet growth in the centre of these wafers, did not affect the mechanical properties of the substrate or the film growth and luminescent properties of the films.

3.2. Thickness measurement

Since the refractive index difference between the film and the substrate is small (nearly homo-epitaxy) the normal interferometric technique of determining the film thickness cannot be used. The film thickness was calculated from the density (see table II) and the increase in weight during film growth.
3.3. Cathodo-luminescence efficiency

The cathodo-luminescence efficiency was measured in two ways. At low excitation densities we used a demountable cathode-ray tube system and at high excitation densities a modified scanning electron microscope.

The demountable assembly had a current of 10 μA of 10 kV electrons. The beam diameter at the target position was always larger than 4 mm in order to exclude the possible saturation effects. The light output was determined as the radiant intensity measured normal to the layer at the standard 10 μA, 10 kV excitation. This figure must be multiplied by $2\pi n^2$, where $n$ is the refractive index of the phosphor layer ($n = 1.84$), and corrected for the back scattered electrons and the energy loss in the aluminium metal backing (3 kV) in order to obtain the internal energy efficiency $\eta$. This is only true for films of good quality, i.e. in the absence of surface scattering. In our case this was ensured because the lattice parameter mismatch between film and substrate was always less than 0.015 Å and no cracking or facetting occurred.

The saturation of the luminescence was studied in the scanning electron microscope (SEM) where the excitation density could be varied between $10^3$ W/m$^2$ and $10^8$ W/m$^2$ by changing the diameter of a stationary beam of 20 kV electrons. Although the SEM yielded only relative figures for the light output, absolute figures for the radiance of the epitaxial screens could be obtained from a comparison of the relative values measured in the SEM at low excitation density with the absolute values measured in the demountable apparatus.

3.4. Cathodo-luminescence spectra

The spectra were measured using an optical multichannel analyser. The light from the phosphor passes through a 0.3 meter monochromator provided with a 147.5 grooves/mm grating blazed at 5000 Å and is then dispersed to the target of a silicon vidicon. The target of the vidicon is read out in 500 scans by a scanning electron beam. The luminescence spectra are plotted on an x-y plotter and calibrated against the emission lines of a mercury discharge.

3.5. Chemical analysis

The chemical composition was determined using three techniques. We used electron probe micro-analysis, spectrochemical analysis and Rutherford back scattering. Special standard samples were prepared and used for comparison. There was excellent agreement between the three techniques.
4. Results

4.1. Lead incorporation and orientation effects

During the present work the best melt composition for growing efficient YAG films on [111] substrates was found to be PbO:B$_2$O$_3$:Al$_2$O$_3$:Y$_2$O$_3$ = 450.0:11.65:6.52:3.85 (g) where the activator oxides were added in quantities of zero to 4.0 g. This melt composition had a saturation temperature around 1090 °C, depending upon the activator concentration.

The optimal growth temperature was determined by the incorporation of lead from the flux and the activator ion. In figure 2 we show, by way of example, the weight percentage of Pb and Ce in YAG LPE layers as a function of the growth temperature as determined by electron probe micro-analysis. For comparison the lead concentration in [111] Y$_3$Fe$_5$O$_{12}$ films is also shown. It is well-known in the case of iron garnets that the Pb incorporation increases as the growth temperature decreases\textsuperscript{13,14). This holds to a lesser extent for the non-iron garnets\textsuperscript{15) and in the present case the same effect is observed. In the case of YAG the Pb$^{2+}$ ions cannot easily be charge-com-

![Diagram](image-url)

**Fig. 2.** The weight percentage of Pb and Ce in Y$_3$Al$_5$O$_{12}$ layers as a function of growth temperature. Also shown are the results for Pb in [111] Y$_3$Fe$_5$O$_{12}$ layers.
pensated as they can in the case of YIG. With YAG they can only be charge-
compensated with small quantities of Pt$^{4+}$ from the crucible$^{16}$, with an
oxygen vacancy or they enter as Pb$^{3+}$ (ref. 15). The shape of the Ce curve is
similar to that of Pb in YAG, but is shifted to higher concentrations at the
same growth temperature.

The net result of the incorporation of Pb$^{2+}$ and Ce$^{3+}$ is that the light output
has a maximum as a function of the growth temperature as seen in fig. 3 or in

Fig. 3. Light output as a function of growth temperature for [111] and [110] Ce:YAG films.

fig. 3 of ref. 1. The decrease in light is due to the increase in Pb ions, which
quench the luminescence on the one hand and due to a decrease in activator
ion concentration on the other hand. This has been found for all the rare
earths that we have tried to substitute into LPE YAG films. The shape of the
curve for [110] films (fig. 3) is somewhat different and was explained by the
chemical analysis of the layers by Rutherford back scattering. A [111] layer
grown at 1038 °C has a Ce/Y ratio of 0.92–1.09 and a [110] layer from the
same melt and grown at the same temperature has a Ce/Y ratio of 2.03–2.04,
whilst the Pb/Y ratio remains constant for both samples. Thus the lower
values of light output in the case of [110] films are due to the fact that too
much Ce is present and concentration quenching occurs$^{17}$. It is not until high
growth temperatures are used and less Ce substitutes into the films that con-
centration quenching ceases and efficient light outputs are obtained.

It may thus be stated that a melt composition and growth temperature which
are optimal for the [111] films are not necessarily optimal for [110] films.
Growth of LPE films on [211] and [100] substrates confirm this point as well.
Thin single crystalline phosphor layers grown by liquid phase epitaxy

4.2. Purity of starting oxides

A parameter that can also affect the luminescent efficiency of the grown films is the purity of the starting oxides. This is also important with respect to reproducibility. Since the largest proportion of the melt (and maybe the cost) is the PbO, we compared the 6N purity PbO from "in house" sources, with Merck Optipur and Merck p.a. PbO. The rare earths, the aluminium oxide and the boron oxide were all 5N purity or better. We also made some deliberate additions of Fe₂O₃ to the melt. The melts were homogenized for 1½ hours at ≈ 1150 °C and small portions were removed from the crucible at this temperature for the chemical analysis. In table III the results of the spectrochemical analysis are shown. Only Bi, Mn and Fe are present in higher concentrations in the Merck p.a. PbO than in the 6N material. In table IV we show the light output of samples grown under the same conditions at 1060 °C from these melts and containing Tb₄O₇. It is clear that there is no difference

### TABLE III

Spectrochemical analysis (wt %) of samples of homogenized melts made from 5N oxides with PbO as 6N, Merck p.a. and with Fe₂O₃ purposely added to the p.a. melt

<table>
<thead>
<tr>
<th>element</th>
<th>6N PbO</th>
<th>p.a. PbO</th>
<th>p.a. PbO plus 0.025 g Fe₂O₃</th>
<th>p.a. PbO plus 0.050 g Fe₂O₃</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al</td>
<td>0.6</td>
<td>0.3</td>
<td>0.3</td>
<td>0.3</td>
</tr>
<tr>
<td>Au</td>
<td>0.5</td>
<td>0.8</td>
<td>0.8</td>
<td>0.8</td>
</tr>
<tr>
<td>Bi</td>
<td>&lt;0.0007</td>
<td>0.002</td>
<td>0.001</td>
<td>0.002</td>
</tr>
<tr>
<td>Cu</td>
<td>0.00003</td>
<td>0.0002</td>
<td>0.0002</td>
<td>0.0002</td>
</tr>
<tr>
<td>Fe</td>
<td>&lt;0.0002</td>
<td>0.005</td>
<td>0.01</td>
<td>0.02</td>
</tr>
<tr>
<td>Ga</td>
<td>0.0002</td>
<td>0.0002</td>
<td>0.0002</td>
<td>0.0004</td>
</tr>
<tr>
<td>Ge</td>
<td>&lt;0.001</td>
<td>&lt;0.001</td>
<td>&lt;0.001</td>
<td>&lt;0.001</td>
</tr>
<tr>
<td>Mg</td>
<td>0.0005</td>
<td>0.0005</td>
<td>0.0006</td>
<td>0.0007</td>
</tr>
<tr>
<td>Mn</td>
<td>&lt;0.0001</td>
<td>0.0003</td>
<td>0.0003</td>
<td>0.0003</td>
</tr>
<tr>
<td>Mo</td>
<td>0.0003</td>
<td>0.0006</td>
<td>0.0007</td>
<td>0.0008</td>
</tr>
<tr>
<td>Pt</td>
<td>0.1</td>
<td>0.1</td>
<td>0.1</td>
<td>0.1</td>
</tr>
<tr>
<td>Si</td>
<td>0.001</td>
<td>0.001</td>
<td>0.002</td>
<td>0.002</td>
</tr>
<tr>
<td>Tb</td>
<td>0.4</td>
<td>0.3</td>
<td>0.4</td>
<td>0.4</td>
</tr>
<tr>
<td>Y</td>
<td>1</td>
<td>1</td>
<td>0.9</td>
<td>0.9</td>
</tr>
</tbody>
</table>
**Table IV**

Light output of Tb:YAG samples grown at 1060 °C from melts containing 1.0 g Tb4O7 in a 450 g PbO melt

<table>
<thead>
<tr>
<th>Melt</th>
<th>Light Output (μW/sr)</th>
</tr>
</thead>
<tbody>
<tr>
<td>6 N PbO</td>
<td>216</td>
</tr>
<tr>
<td>P.a. PbO</td>
<td>220</td>
</tr>
<tr>
<td>P.a. + 0.025 g Fe2O3</td>
<td>190</td>
</tr>
<tr>
<td>P.a. + 0.050 g Fe2O3</td>
<td>139</td>
</tr>
</tbody>
</table>

between the results when using the two sources of PbO. Only when small quantities of Fe2O3 are deliberately added can a clear effect be seen. A similar effect with Fe2O3 has recently been reported by Kvapil et al.18). Throughout the rest of this study Merck p.a. PbO was used. An analysis was made of each incoming batch of material to check that the levels of Bi, Mn and Fe were sufficiently low.

4.3. Lattice match

A parameter that possibly could affect the efficiency of the phosphor layers is the strain induced by the lattice parameter mismatch. Brice et al.19) have shown that this parameter can have an effect on the film growth rate and on the mixing entropies in iron-garnet films. With powders and single crystals of phosphors this is a parameter that has not yet been tested.

Films of Eu:Gd3Ga5O12 were grown on [111] Gd3Ga5O12 substrates substituted with Al and In 20). All films were grown under identical conditions, only the substrate lattice parameter was changed. The results are shown in fig. 4. At first sight it might be said that the lattice mismatch increases the light output efficiency. On closer examination it appears that the increase in light output is due to multiple internal reflections and surface scattering that occur when the film is cracked or faceted by too high a lattice mismatch 12). If these two specimens are ignored, it appears that over the entire stress range in which good quality films can be produced there is no effect on the efficiency of Eu:GGG films. Also the changes in film growth rate19) do not change the segregation coefficients significantly enough to have an effect on the efficiency.

Films of Ce:Gd3Al5O12 were grown onto Y3Al5O12 (12.001 Å), Y3(AlGa)5O12 (12.119 Å) and Y3Ga5O12 (12.280 Å). These films were cracked and facetted due to the large lattice mismatch thus nothing can be said about changes in light output efficiency. However, even with this system in which changes in the
Thin single crystalline phosphor layers grown by liquid phase epitaxy

Fig. 4. Light output as a function of the lattice parameter mismatch for Eu:Gd₃Ga₄O₁₂ films.

Fig. 5. The concentration of RE/formula unit in YAG films as a function of the weight of the oxide in a 450 g PbO melt. Growth temperature was \( \approx \) 1065 °C.
Ce$^{3+}$ emission can be affected by substitution of other ions in the lattice$^{21}$ no change was found due to mismatch strain alone.

4.4. Incorporation of RE's in $Y_5Al_3O_{12}$

Using the above melt composition and growth temperature of $\approx 1065$ °C, approximately 5 µm thick films were grown, with different RE concentrations in the melt. In figure 5 the quantity per formula unit in the film is shown as a function of the weight of oxide in the melt for Tb, Eu and Ce. The analysis was made using both the electron probe micro-analysis and the Rutherford back scattering techniques. In all specimens the lead concentration was less than 0.001 (0.01 wt %). It is clear that on this log-log scale there is a linear relation between the quantities in the film and in the melt. In the case of Ce the values are more than an order of magnitude less than Tb and Eu, which may be explained by the fact that it is not possible to form a $Ce_3Al_5O_{12}$ garnet. Also it is not possible to raise the CeO$_2$ concentration above 2 g in the 450 g PbO melt without the formation of second phase on the melt surface. On removal from the melt the specimens are dirty and examination under the electron microscope shows the surface of the film to be covered with crystals of CeO$_2$ of about 1 µm in size. If CeF$_3$ is used instead of CeO$_2$ similar results are obtained both for the second phase and the concentrations of Ce incorporated into the layers.

4.5. Segregation coefficients

The data in fig. 5 may be reworked to segregation coefficients as defined by Blank and Nielsen$^{12}$:

$$K_{RE} = \frac{\text{moles in film}}{\text{moles in melt}} = \frac{\frac{\text{RE}}{\text{RE} + Y}}{\frac{\text{RE}}{\text{RE} + Y}}$$

The data are shown in fig. 6. It is clear that the segregation coefficients are a function of the concentration in the melt and are less than unity. They approach unity as the concentration increases. The value of Ce is much less than the other two due to the non-existence of $Ce_3Al_5O_{12}$. It is interesting to note that the value of 0.18 is near to the value of 0.124 published by Kvapil et al.$^{18}$) for a Czochralski melt. In general it is not possible to substitute more than 2% of the Y ion by Ce in the LPE-grown films and still obtain good quality layers. This is similar to the effect observed by Gibbons et al.$^{21}$) who found that the maximum amount of Ce accepted in a garnet powder was 2 mol % when the powder was prepared under oxidizing conditions.
Thin single crystalline phosphor layers grown by liquid phase epitaxy

Fig. 6. Segregation coefficients of Tb, Eu and Ce in YAG as a function of concentration.

4.6. Light output as a function of RE in the melt

In figure 7 the light output and the internal radiant efficiency $\eta$ of the films (see section 3.3) are plotted as a function of the weight of oxide in the standard 450 g PbO melt. The growth temperature was $\approx 1060^\circ$C. The rare earths may be divided into three characteristic groups.

In the group consisting of Sm, Pr, Dy and Tm concentration quenching occurs at small concentrations in the melt and a light output of 100 $\mu$W/sr is just reached. For Tm and Dy this is a similar result to that seen in other host lattices $^{22,23}$.

The group Tb and Eu quench at much higher values of concentration in the melt and can reach over 200 $\mu$W/sr, depending upon the growth temperature.

The last is Ce, which at first sight does not seem to have any concentration quenching. Chemical analysis of the layers shows that this effect is an artefact due to the solubility limit of Ce in YAG and that a concentration where quenching occurs has not yet been reached (see fig. 2 in ref. 1). The fact that Ce already shows a high cathode-ray efficiency at low concentrations points to a better interaction of the Ce ion with the host lattice.

From the efficiency point of view it is clear that the films prepared by LPE are as good as powders and in some cases better. For example, the efficiency of epitaxially grown Ce:YAG is significantly better than the 3.5% reported by Blasse and Bril $^{24}$ for powder material.

Philips Journal of Research Vol. 35 No. 6 1980
Fig. 7. Light output as a function of the weight of RE$_2$O$_3$ in a 450 g PbO melt for films grown at 1060 °C.

Fig. 8. Cathodo-luminescence spectrum of a Ce:YAG layer.
4.7. Luminescence spectra

Cerium-doped YAG is the only phosphor we have studied which has a band emission, the rest show predominantly line spectra. The cathodo-luminescence spectrum of YAG:Ce is shown in fig. 8. The shape of this spectrum corresponds to that of YAG:Ce powder as reported by other authors except for the emission in the violet and near ultraviolet which is completely absent in epitaxial phosphor layers. Since the violet/ultraviolet emission is reported to depend on the method of preparation and is probably related to defect states in YAG, our results indicate that the method of liquid phase epitaxy results in relatively defect-free luminescent layers.

In figures 9 and 10 the spectra for Nd and Eu-doped YAG are presented, respectively. The Nd produces an almost white emission, while the Eu gives an orange colour impression owing to the strong line at 592 nm. This line, a $^5\text{D}_0-^7\text{F}_1$ magnetic dipole transition, is relatively strong because the Eu$^{3+}$ ion occupies a centre of inversion symmetry in the YAG lattice.

The spectra of Sm, Pr, Dy and Tm-doped YAG phosphors are shown in fig. 11. These spectra show the line emissions typical of the respective rare-earth ions.

To conclude the section on cathodo-luminescence we show a series of YAG:Tb spectra in fig. 12a–d. The spectra are taken from layers grown from a melt with increasing Tb concentration (the amount of Tb$_2$O$_7$ was 0.05, 0.1,
0.2 and 0.4 g in a 450 g melt). It is clear that in epitaxial layers, too, the low concentrations of Tb$^{3+}$ ions produce a blue emission, while with increasing concentration the colour changes to the usual green owing to the increasing cross relaxation between Tb pairs\(^{28}\).

5. Conclusions

In this paper we have shown that it is possible to produce thin single crystal phosphor films of garnets by liquid phase epitaxy. For maximum cathodo-luminescent efficiency certain parameters such as growth temperature and concentration quenching must be taken into account. Melts which have been optimized for [111] substrates are not optimal for the other crystallographic orientations. Care should be taken to choose good purity starting oxides otherwise “quench-ions” will be present in the layers. Within the strain range for good quality layers no effect of strain is seen in the luminescence.

The LPE-grown films are as efficient as and in some cases more efficient than powder phosphors of the same composition. Furthermore, the disadvantages of low resolution due to powder particle size and low power handling capabilities have been solved by making these single crystal layers on substrates with good thermal properties. We believe that, owing to the unique combination of properties, the epitaxial phosphor screens will find their way to many special purpose applications for cathode-ray tube displays.
Thin single crystalline phosphor layers grown by liquid phase epitaxy

Fig. 11. Cathodo-luminescence spectra of Sm, Pr, Dy and Tm-doped YAG layers.
Fig. 12. Cathodo-luminescence spectra of Tb-doped YAG layers. (a) 0.05 g Tb₂O₃ in 450 g PbO melt; (b) 0.10 g Tb₂O₃ in 450 g PbO melt; (c) 0.20 g Tb₂O₃ in 450 g PbO melt; (d) 0.40 g Tb₂O₃ in 450 g PbO melt.

Acknowledgements

The authors would like to thank M. Klerk and P. Paans for their work with the electron microprobe, Y. Tamminga for the Rutherford back scattering and A. W. Witmer for the spectrochemical analysis. A. T. Vink, W. F. van der Weg, T. J. A. Popma and A. L. N. Stevels are thanked for their useful discussions.

Philips Research Laboratories

Eindhoven, September 1980
Thin single crystalline phosphor layers grown by liquid phase epitaxy

REFERENCES


5) J. M. Robertson and M. W. van Tol, Luminescent single crystal thin films of manganese doped barium hexaaluminate, to be published.

6) A. L. N. Stevels, private communication.


20) Crystal grown in the laboratory by J. Pistorius.


23) G. Blasse, Some considerations on rare earth activated phosphors, J. Luminescence 1,2, 766, 1970.


