MANGANESE-ACTIVATED LUMINESCENCE
IN Cd₂PO₄F

by W. L. WANMAKER, J. G. VERRIET and J. W. ter VRUGT

Abstract

With ultraviolet excitation Cd₂PO₄F shows a broad emission band with a peak at 505 nm. With manganese activation energy transfer from the host lattice to the manganese occurs, resulting in an emission band at 590 nm, showing a quantum efficiency (254-nm excitation) of about 40 per cent. Partial substitution of Zn (25 at. per cent) for Cd gives a quantum efficiency (of the manganese emission) of about 55 per cent, with an emission maximum at 600 nm. Remarks are made about the luminescence of manganese-activated cadmium compounds.

1. Introduction

Several Mn-activated cadmium phosphates have been described in the literature. For instance Ropp ¹) observed a red emission band (λ_max=618 nm) in Cd₂P₂O₇–Mn. The phosphor should be of the host-sensitized type, with partly reduced Cd²⁺ ions acting as a sensitizer for the Mn²⁺ ions. A similar excitation mechanism has been proposed by the same author for manganese-activated cadmium-chlorophosphate phosphors, having the apatite crystal structure ²). In these phosphors the absorption of the exciting radiation should be due to a charge-transfer complex between a chlorine ion and a neighbouring cadmium ion. The luminescence of the manganese-activated cadmium fluorophosphate (apatite structure) sensitized by lead ³) and of the corresponding bromo compound ⁴) have also been described in the literature.

Recently Engel ⁵) prepared the new isotypic compounds Cd₂XO₄F (with X = P, As and V), showing structural relations to the minerals of the wagnerite (Mg₂PO₄F) group. We investigated whether these compounds can also sensitize the luminescence of manganese. Furthermore we tried to obtain luminescence by activation with Pb, Ti, Sb, Bi, Tb, Eu, Sm and Dy respectively.

2. Experimental

According to Engel ⁵) Cd₂PO₄F can be made by heating equimolar mixtures of Cd₃(PO₄)₂ and CdF₂ at a temperature of 850 °C. In most cases in our investigations we proceeded in a different way, viz. by heating a mixture of luminescent-grade CdCO₃, CdF₂, (NH₄)₂HPO₄ and MnCO₃ (or MnNH₄PO₄) for 2 h at 600 °C, followed (after grinding and sieving the reaction product) by a second heating, also for 2 h at 760 °C. In most cases the heating was done in air; only when using manganese and antimony as activator ions, was the heating
carried out in an atmosphere of nitrogen. From X-ray-diffraction analysis of the reaction products it followed that with our preparation technique pure Cd$_2$PO$_4$F can also be made. The performance of the optical measurements has been described previously 6).

3. Results and discussion

3.1. Excitation, emission and temperature dependence

With ultraviolet excitation the activators mentioned above did not yield a noticeable luminescence in the arsenic compound. In the vanadium compound a weak luminescence (red emission) was observed with europium activation only. In Cd$_2$PO$_4$F a weak luminescence was observed in the unactivated compound and also when activating with Eu, Tb, Sm, Dy and Sb, but a far more intense luminescence was found with manganese activation. In this paper we will mainly deal with the luminescence of manganese-activated Cd$_2$PO$_4$F.

Figure 1 shows the diffuse reflection, excitation and emission spectra of unactivated Cd$_2$PO$_4$F. In fig. 2 the corresponding spectra are given for manganese-activated Cd$_2$PO$_4$F phosphors.

It can be seen from fig. 1 that Cd$_2$PO$_4$F shows two peaks in the excitation spectrum and that it has a broad emission band ($\lambda_{\text{max}}$=505 nm) with ultraviolet excitation.

By substituting manganese for cadmium in Cd$_2$PO$_4$F the same peaks can be observed in the excitation spectrum as in that of the pure Cd$_2$PO$_4$F, the relative intensity of the short-wavelength excitation band being even higher than in the unactivated Cd$_2$PO$_4$F. By increasing the amount of Mn in Cd$_2$PO$_4$F the intensity of the 505-nm emission band gradually decreases and that of the manganese emission band (at 590 nm) increases. From this fact and from the close

![Fig. 1. Diffuse reflection spectrum (r), excitation spectrum (q) and emission spectrum (mainly 254-nm excitation) of Cd$_2$PO$_4$F.](image-url)
Fig. 2. Diffuse reflection spectra (r), excitation spectra (q) and emission spectra (mainly 254-nm excitation) of Cd$_{2-x}$Mn$_x$PO$_4$F phosphors. Curve 1: $x = 0.005$; curve 2: $x = 0.01$; curve 3: $x = 0.03$.

The following remarks can be made about the nature of the luminescent centre in Cd$_2$PO$_4$F. In Cd$_2$P$_2$O$_7$–Mn Ropp speaks of partly reduced Cd$^{2+}$ ions acting as a sensitizer for the Mn$^{2+}$ luminescence and, in another paper, dealing with Cd-chloroapatite–Mn$^{2+}$, of a charge-transfer complex between a chlorine ion and a neighbouring cadmium ion. Since chlorine shows strong electronegativity the latter hypothesis is far more unlikely than the first one.

The presence of reduced Cd ions implies the presence of oxygen vacancies. It might therefore be expected that the oxygen content of the firing atmosphere should have an effect on the efficiency of the luminescence. The refiring of unactivated Cd$_2$PO$_4$F in an atmosphere of oxygen (for 1 h at 600 °C) reduces the quantum efficiency by about 30 per cent. This confirms that the luminescent centre in this compound is probably related to the presence of oxygen vacancies in the host lattice.

The preparation of Cd$_2$PO$_4$F with small quantities of Y- or Li substituted for Cd (which should affect the amount of oxygen vacancies in the host lattice), however, did not change the quantum efficiency of the self-activated emission band, or the excitation and emission spectra.

The long afterglow of the emission of both unactivated and manganese-activated Cd$_2$PO$_4$F indicates the presence of deep traps, which might be tentatively ascribed to electrons trapped in oxygen vacancies.
Figure 3 shows that in Cd$_2$PO$_4$F–Mn phosphors the intensity of the host-lattice emission band is higher at 77 K than at room temperature, while the opposite applies to the manganese emission band. Therefore the energy transfer from the host lattice to the manganese ions is apparently temperature-dependent. This phenomenon was observed earlier in many other phosphors and recently by Verstegen 7) in manganese-activated gallates.

Fig. 3. Emission spectra (mainly 254-nm excitation) of Cd$_{2-x}$Mn$_x$PO$_4$F as measured at 77 and 293 K. Curves 1: $x = 0.005$; curves 2: $x = 0.03$.

Fig. 4. Variation of brightness with temperature of Cd$_{2-x}$Mn$_x$PO$_4$F phosphors. Mainly 254-nm excitation.

<table>
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<tr>
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<tr>
<td>4</td>
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The relative brightness of some Cd$_{2-x}$Mn$_x$PO$_4$F phosphors as a function of temperature is given in fig. 4. It can be seen that the luminescence of the manganese has a much higher quenching temperature than that of the host lattice itself. The curves of fig. 4 show a maximum, the position of which is shifted to a lower temperature when increasing the amount of manganese. The latter phenomenon is in accordance with the behaviour of most phosphors, viz. the quenching temperature generally decreases when the concentration of the activator is increased. At the temperature of maximum brightness the emission band has shifted from 590 to 582 nm (bandwidth 76 nm). This shift is only partly responsible for the increase of the brightness, as measured with a barrier-layer cell. About 50 per cent of this increase must be ascribed to a higher efficiency.

3.2. Cd$_x$PO$_4$F–Mn made with various substitutions

Various elements were substituted for Cd and F respectively. The upper limit of a number of elements which can be substituted for Cd without the appearance of new phases is:

- calcium — 10 atom per cent
- strontium — 5 atom per cent
- barium — 2.5 atom per cent
- magnesium — 10 atom per cent
- lead — 20 atom per cent
- zinc — 50 atom per cent

The substitution of 1 atom per cent of chlorine for fluorine in Cd$_2$PO$_4$F gives rise to the appearance of Cd-chloroapatite, whereas the X-ray pattern of Cd-bromoapatite appears when substituting 10 atom per cent of bromine for fluorine in Cd$_2$PO$_4$F.

In most cases the luminescence of substituted Cd$_2$PO$_4$F–Mn phosphors can be correlated with the results of X-ray-diffraction data: the efficiency of the luminescence decreases with the appearance of a new crystal phase; Cd$_2$VO$_4$F–Mn and Cd$_2$AsO$_4$F–Mn do not show any manganese luminescence with ultraviolet excitation. As both compounds absorb the exciting radiation, apparently no energy transfer to the manganese ions takes place. Vanadium actually absorbs a large part of the exciting radiation, resulting in totally quenching when 0.5 atom per cent of vanadium is substituted for phosphorus in Cd$_2$PO$_4$F–Mn.

The substitution of zinc for cadmium in Cd$_2$PO$_4$F–Mn results in a shift of the manganese emission band from 588 to 605 nm. A similar shift of the manganese emission band was observed by Brown and Hummel \(^8\) when substituting zinc for cadmium in Cd$_3$(PO$_4$)$_2$–Mn. This can be readily explained by an increase of the crystal-field strength, caused by the introduction of a smaller cation into the host lattice.
4. Efficiency and decay

In table I the efficiency of some phosphors is reported. It follows from these figures that with 254-nm excitation a quantum efficiency of about 43 per cent can be reached in Cd$_{1.95}$Mn$_{0.05}$PO$_4$F. When substituting zinc for cadmium the quantum efficiency increases to a value of about 55 per cent, due to a shift of the excitation spectrum to longer wavelengths. The quantum efficiency at the maximum of the excitation spectrum for all kinds of manganese-activated Cd$_2$PO$_4$F phosphors is about 60–65 per cent.

The manganese-activated Cd$_2$PO$_4$F phosphors show an exponential decay, with a decay time of about 25 ms. This decay time is of the same order as found in several other Mn$^{2+}$-activated phosphors. Moreover, in most cases, a long afterglow could be observed, indicating the presence of deep traps.

With cathode-ray excitation (20 kV) a radiant efficiency of about 5 per cent was measured for the manganese-activated Cd$_2$PO$_4$F phosphors (manganese content above 1 atom per cent).

5. Some general remarks concerning the luminescence of manganese in cadmium-containing host lattices

When determining the excitation of the Mn emission in various host lattices, excitation bands at about 400 nm are found, e.g. in MgGa$_2$O$_4$–Mn$^9$). This excitation corresponds to transitions between 3$d$ states of the Mn$^{2+}$ ions. When applying an Mn-activated phosphor in fluorescent lamps, however, excitation

<table>
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by the mercury resonance line (254 nm) is required. Since this radiation cannot
directly excite the Mn\(^{2+}\) ions an energy transfer to the activator ions is required.
This can be done in either of two ways, viz. (a) by means of sensitizer ions, such
as Ce, Sb and Sn, (b) by means of energy transfer from the host lattice to the
Mn\(^{2+}\) ions.

With the first method the host lattice itself must not show a competing absorp-
tion of the 254-nm radiation. Therefore this method of energy transfer can be
successfully applied in host lattices showing an absorption edge at wavelengths
below 250 nm, such as Ca\(_3\)(PO\(_4\))\(_2\) and Ca-halophosphates. The latter phosphors
sensitized with Sb\(^{3+}\) are widely used in fluorescent lamps.

In manganese-activated Cd-containing host lattices showing a manganese
luminescence-energy transfer to the Mn\(^{2+}\) ions apparently occurs, these lattices
showing a strong absorption of 254-nm radiation. The same applies to many
Zn-containing compounds. To have an efficient energy transfer from the host
lattice to the Mn\(^{2+}\) ions among others the following two requirements have to
be fulfilled, viz.:

(a) a low probability of radiationless transitions from the excited level of the
host lattice;

(b) an overlap of the excitation bands of the manganese with the emission of
the host lattice.

If these requirements are applied to Cd compounds, the following remarks can
be made.

Ad (a). This requirement leads to the conclusion that in many Cd-containing
host lattices showing an efficient manganese emission, a self-activated
luminescence can be expected, unless concentration quenching occurs. In
fact this is found for several host lattices, e.g. in CdGe\(_4\)O\(_9\), described
by Lange 10) and in Cd\(_2\)PO\(_4\)F as described in this study. We also tried
to detect a host-lattice emission in other Cd-containing host lattices, in
which manganese is found to be an efficient activator. In fact we were
able to observe the following emission bands.

A weak broad emission band (\(\lambda_{\text{max}}\) at about 450 nm) in Cd\(_{10}\)(PO\(_4\))\(_6\)Cl\(_2\)
(at 77 K only). At room temperature a broad emission band (\(\lambda_{\text{max}}\) at
about 450 nm) in Cd\(_3\)(PO\(_4\))\(_2\) with a quantum efficiency (254-nm exci-
tation) of about 3 per cent and about 6 per cent at the maximum of the
excitation band (230 nm). In Cd\(_{10}\)(PO\(_4\))\(_6\)F\(_2\) a weak emission band
(\(\lambda_{\text{max}}\) at about 500 nm) could be detected at 77 K only.

Ad (b). When determining the excitation spectrum of the Mn-activated Cd
compounds, in several cases an excitation peak at about 410 nm could
be observed. This is illustrated in fig. 5 for Cd\(_3\)PO\(_4\)F-Mn and
Cd\(_{10}\)(PO\(_4\))\(_6\)Cl\(_2\)-Mn respectively. The 410-nm excitation band probably
corresponds to the transition \(6S \rightarrow ^4G(^4A, ^4E)\) and the peak observed at
360 nm in Cd\(_{10}\)(PO\(_4\))\(_6\)Cl\(_2\)-Mn to the transition \(6S \rightarrow ^4D(^4T)\). Since both
cadmium compounds can show an emission band in the blue part of the spectrum an energy overlap of the host-lattice emission band with the Mn excitation band occurs, giving rise to luminescence. Since the quenching temperature of the self-activated luminescence of most Cd compounds is low (see e.g. that of CdGe₄O₉, ref. 10), at room temperature in most cases no luminescence is observed. Nevertheless, in many of these phosphors at room temperature an efficient Mn luminescence can be found, proving that the probability of energy transfer from the host lattice to Mn ions is greater than the probability of radiationless transitions in the host lattice itself.

Acknowledgement

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