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ACTION OF EXCESSIVE FLUORINE IN Ce-Mn ACTIVATED CALCIUM FLUOROPHOSPHATE ON LUMINESCENCE AND SYNTHESIS MECHANISM

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Excessive fluorine plays a key role in the formation of Ce luminescence centers in Ce, Mn activated calcium fluorophosphate. The dominant and efficient Ce center(Ce1) is formed with a Ce^{3+} ion resided substitutionally on a Ca2 site chargely compensated by excessive F^-. Excessive fluorine in initial component of this material also make the mechanism of synthesis change and reduce its forming temperature.

Ce, Mn activated calcium fluorophosphate(FAP: Ce, Mn), as a new type of yellow phosphor with high effeciency, which is promising in two component blend lamp, has been prepared recently[1]. However, up to date, there is almost no information presented about its mechanism of luminescence and synthesis. This paper deals with the luminescence centers of Ce in FAP:Ce, Mn with excessive fluorine as well as the formation processes of this material which is different from ordinary Halophosphor.

1. Function of excessive F^- on the formation of Ce centers.

An anomalous phenomenon is found that amount of fluorine in both initial component and final product of optimizated FAP:Ce, Mn are higher than that of normal stoichiometry. With stoichiomtric component, very low efficiency of luminescence is observed when the phospher is excited at 254nm. So it is obvious that excessive fluorine plays a key role in photoluminescence.

Fig. 1 are the photoluminescence spectra of FAP:Ce, Mn within the region of Ce^{3+} emission. Two series of Ce emission corresponding to two excitation wavelengths are observed, both of which can be assigned to 5d - $^2F_{5/2}$ and 5d - $^2F_{7/2}$ transitions of Ce^{3+}. The photoluminescence excitation spectra of two series Ce emission are

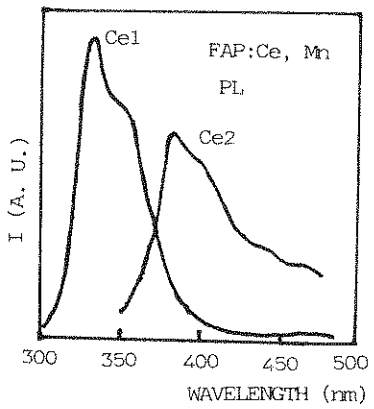

FIGURE 1
Photoluminescence Spectra of FAP:Ce, Mn in the region of Ce emission excited at 254nm (Ce 1) and 337nm (Ce 2).

shown in Fig. 2. These two spectra are very different, which indicates that two kinds of Ce centers exist (labelled Ce1 and Ce2). It can be found from the similarity between Ce1 excitation spectra and the absorption spectra measured from FAP:Ce, Mn that most of Ce^{3+} formed Ce1 centers.

A special structure of FAP with excessive fluorine was discovered by Mackie[2], in which excessive F^- insert into hexagonal axis where normal F^- is arranged. So if Ce^{3+} enters the crystal, they will chargely be compensated by F^- and so must be on one site close to hexanonal axis. Considering the situation of Ca1 and Ca2 site in this lattice[3], it is conjectured that the Ce1 center is formed with a Ce^{3+} ion resided

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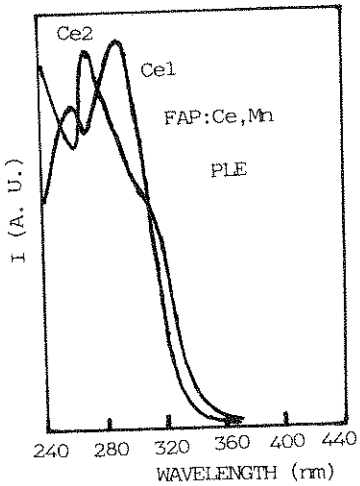

FIGURE 2
Photoluminescence excitation spectra of Ce 1 and Ce 2.

substitutionally on a Ca2 site.

So if there is no excessive F^-, Ce^{3+} could not enter host lattice and form efficient luminescence centers.

2. Effect of excessive fluorine on the formation processes of FAP:Ce, Mn.

According to Wanmarker[4], FAP is formed as

$$3Ca_3(PO_4)_2 + CaF_2 \xrightarrow{1150^oC} 3Ca_3(PO_4)_2\cdot CaF_2$$

But, in this work, the firing temperature (900° C) is lower than that way, so different process must have happened due to the excess of fluorine in initial component.

Differential thermal analysis (DT) and thermal gravimetric analysis to initial material of FAP:Ce, Mn in the range from room temperature to 1200° C. The results of DT is shown in Fig. 3, where normal FAP is used for comparison. An endothermic and weight loss process which is different from normal FAP is discovered at 650-800° C.

To study the reaction of this endothermic process, the crystal phases of the materials fired at some special temperature points are measured with x-ray diffraction. The result are:

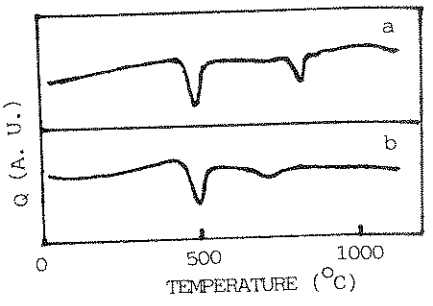

FIGURE 3
DT cuves of normal FAP(a) and FAP:Ce,Mn(b).

Firing tem.	Dominant phases				
600°C	$CaCO_3$	CaF_2	$Ca_2P_2O_7$		
700°C	$CaCO_3$	CaF_2	$Ca_2P_2O_7$	$Ca_5(PO_4)_3F$	
810°C	$Ca_5(PO_4)_3F$				

These results indicate that FAP is formed via the endothermic reaction occured in 650-800°C.

Other experiments show that some gases are involved in these process. Following reactions are put forward:

$$18Ca_2P_2O_7 + 14CaF_2 \longrightarrow 5(3Ca_3(PO_4)_2\cdot CaF_2) + 6POF_3$$

$$18CaCO_3 + 6POF_3 \longrightarrow 3Ca_3(PO_4)_2\cdot CaF_2 + 18CO_2 + 8CaF_2$$

These reaction can be completed only when flourine (CaF_2) is in super-excess. So the formation temperature of apatite based phosphor can be reduced by means of increasing amount of flourine in initial conponent.

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