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CERIUM COMPOUNDS AS SCINTILLATORS

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ABSTRACT

Stoichiometric Ce—materials with negligible Ce—Ce interactions should have superior scintillator properties. We present two materials: CeF_3 and $Ce_xLa_{1-x}P_5O_{14}$. While cerium trifluoride is a known scintillator, pentaphoshate is of a limited usefulness, except as a remarkable model material. We show that quenching in fluoride is responsible for loss of 50% of the light output and is the cause of the, so—called, ultra fast component (2 ns). Light output of fluoride (about 50% of BGO) could be significantly improved. Deeper understanding of Ce—systems is needed to fully exploit their potentials.

I. INTRODUCTION

The Ce^{3+} ion and its stoichiometric compounds are important for scintillators. Luminescence of Ce is fast, efficient and relatively free of self—absorption. The 4f level inside the bandgap creates a hole capturing mechanism necessary for energy transfer, [1]. The lack of extended f—f structure ensures non—existance of competing and slow transitions. In comparison to Tl, Ce is characterized by much smaller concentration quenching. In stoichiometric Ce compounds one expects a significant increase of the "prompt" or "thermally independent" hole trapping, [2], without reduced luminescence efficiency. Therefore a scintillator, combining the speed of cerium (20—30 ns) and efficiency of thallium is a possibility. The proper choice of the host, taking into account density and radiation hardness, would make this hypothetical scintillator an ideal choice for applications like PET camera or γ—spectroscopy.

The pentaphosphate, with its low density, is not a viable scintillator. However its lattice allows for maximum isolation of Ce ions which reduces strongly all metal—metal interactions. We will demonstrate that phosphate is free of all the complications typical for fluoride.

II. MATERIALS

The more detailed account of work on the series of $Ce_xLa_{1-x}F_3$ samples obtained from the Optovac Inc. North Brookfield, MA, will be published later. These samples are characterized by emission spectra similar to those published before, [3]. In this paper we shall present results on recent ("new") samples (Optovac SA91054) which clearly show an improvement in the level of uncontrolled impurities. Samples of cerium—lanthanum ultraphosphate were grown in our lab using the method described in [4].

II. RESULTS

Fig. 1 presents emission spectra of CeF_3. It is well known that ionic Ce emission consists of a doublet in the range between 280 and 310 nm. The spectra of Fig. 1 show a much more complicated structure, extending to the red, especially at low

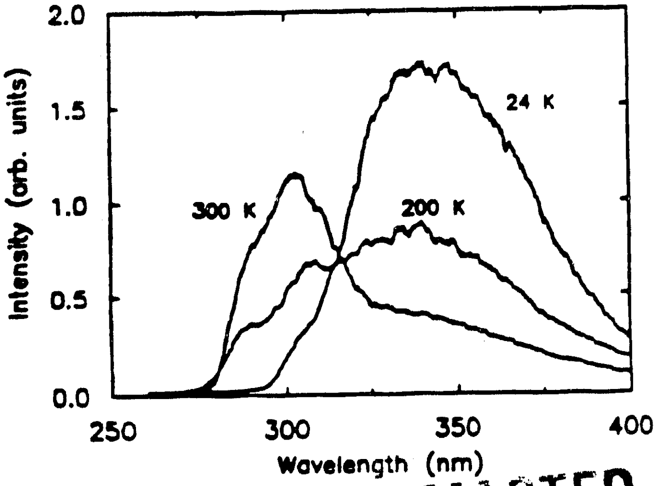

Fig. 1. Time integrated luminescence spectra of "new" CeF_3 for different temperatures. Excitation was by frequency doubled dye laser (270 nm). The boxcar gate width was 100 ns.

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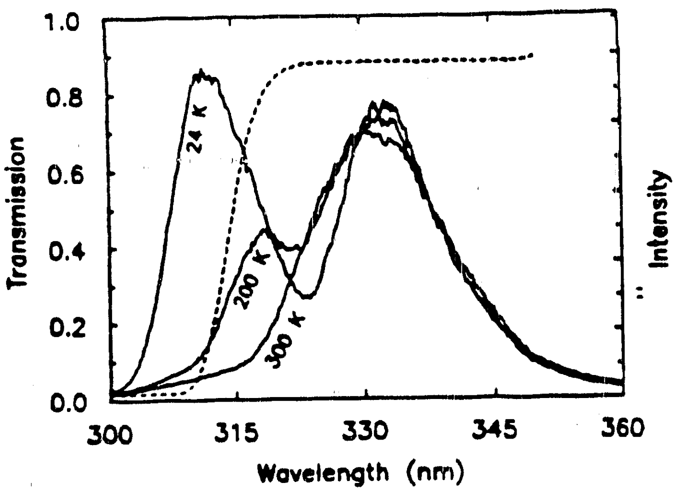

Fig. 2. Luminescence spectra of $Ce_{.75}La_{.25}P_5O_{14}$ for different temperatures. Dashed line shows transmission spectrum at RT. The RT luminescence is partially self-absorbed.

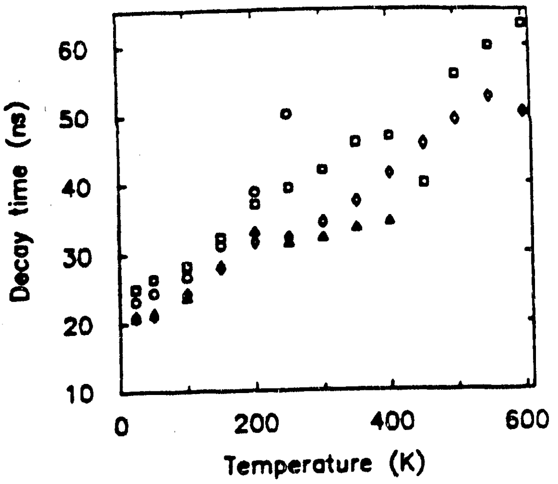

Fig. 4. Temperature dependence of decay times for two pentaphosphate crystals, (.75 and .20 percent of Ce) and two wavelengths, (313 and 333 nm). The samples were excited using 288nm laser pulses.

temperatures. In contrast emission spectra of the pentaphosphate shown in Figs. 2 and 3 are, as reported previously, [5], much more characteristic of simple Ce emission which should consist of a doublet separated by some 2000 cm^{-1}, the ground state splitting of the 4f levels. There are no additional features in the pentaphosphate spectra. In both CeF$_3$ and the pentaphosphate the short wavelength component of doublet is likely to be partially self absorbed in view of the limited Stokes shift. It is always much more clearly visible at low temperature because of the blue shift of the absorption edge. In pentaphosphates there are no surprises in decay times as shown in Fig. 4. The two compo-

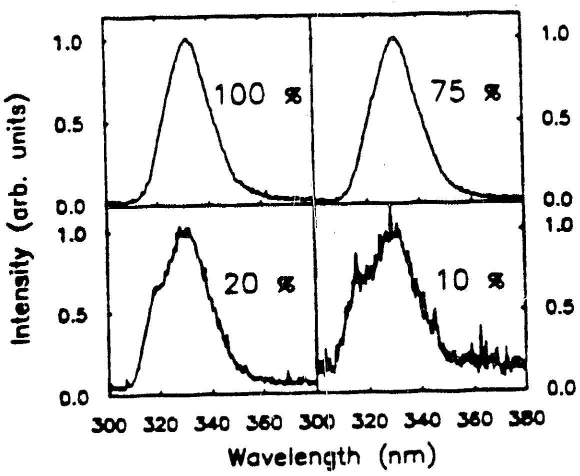

Fig.3 Luminescence spectra of $Ce_xLa_{1-x}P_5O_{14}$ for x=1, .75, .20, and .10 respectively. The samples were excited with ionising radiation from a Ru/Rh source. Temperature, 300 K.

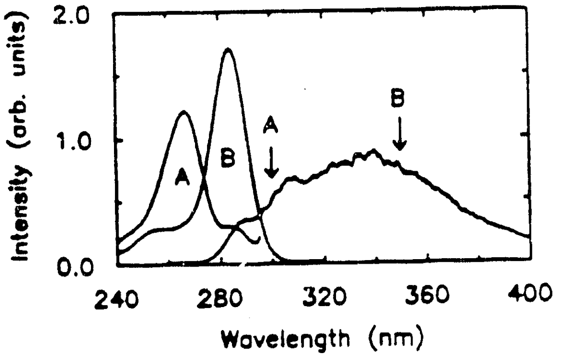

Fig. 5. Luminescence excitation spectra of two emission bands (300 and 340 nm) of "new" CeF_3 at 200 K. Luminescence spectrum at 200 K is also shown and relevant positions of luminescence are indicated, (300 and 350 nm).

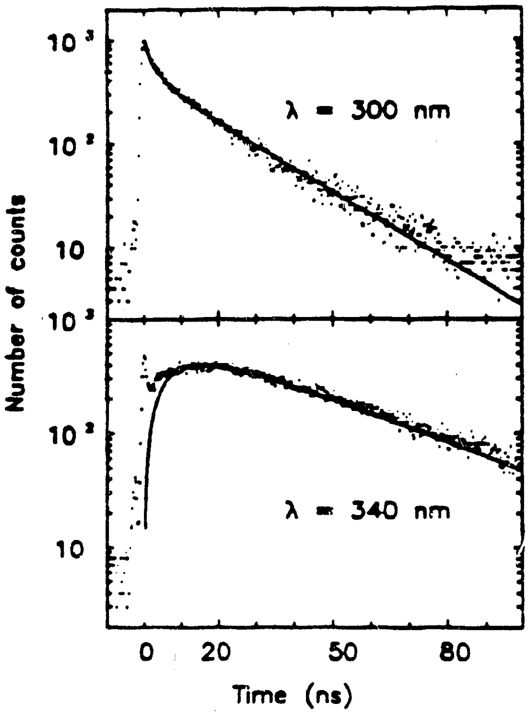

Fig. 6. Scintillation decays of CeF$_3$ for two emission wavelengths, 300 nm and 340 nm, under Ru/Rh excitation. Sharp peak at zero time is due to the Cerenkov radiation. Note the fast component at the shorter wavelength and the slow rise for the longer wavelength component. Solid lines show results of model calculations.

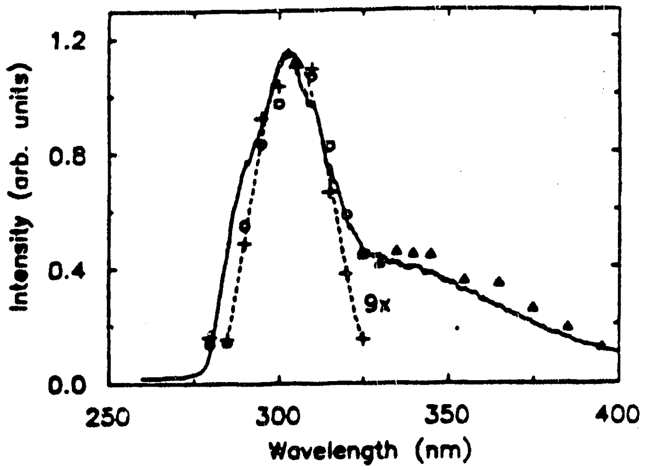

Fig. 7. Solid line shows a laser excited, (270 nm), time integrated spectrum of "new" CeF$_3$. Points correspond to different components in scintillation decays (× – 2.1 ns, ○ – 17.3 ns and Δ – 32.6 ns) for different wavelengths under Ru/Rh excitation. Broken line is a polynomial fit to points corresponding to the 2.1 ns component.

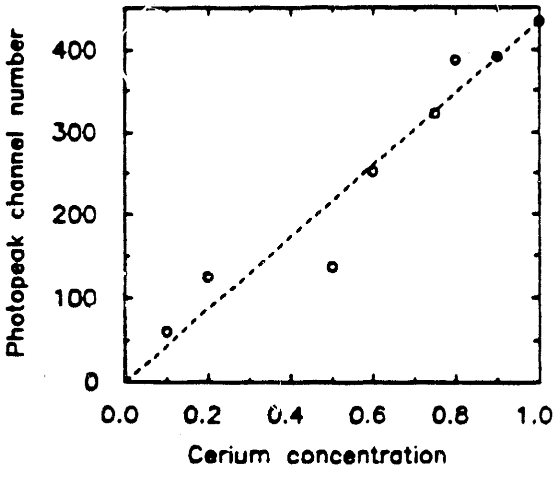

Fig. 8. Concentration dependence of light output for ultraphosphates.

nents of the doublet show the same decay and the same temperature dependence. The very curious increase of decay time with temperature is an anomaly worthy of further study. The complexity of CeF$_3$ spectra shown in Fig. 1 is confirmed by the excitation spectra of the short and long wavelength sides of the luminescence, as shown in Fig. 5. The spectra are similar but there is a 2200 cm^{-1} difference between their peaks. This clearly demonstrates the presence of two emitting entities. Since there is only one Ce site in the fluoride structure, we suggest that a fraction of the Ce ions is perturbed by some impurity. Fig. 6 presents the scintillation decays of CeF$_3$ for two regions of its spectrum. Clearly the short wavelength components represents a prompt excitation, while the long wavelengths' slow risetime is indicative of a transfer process. The kinetics of this transfer is described elsewhere, [6]. Fig. 7 shows a comparison of laser excited luminescence and scintillator time resolved spectra. This figure confirms the origin of the fast component as due to the ionic Ce emission. Fig. 8 shows that in pentaphosphates the scintillation light output is a linear function of the Ce concentration. This demonstrates the validity of going to

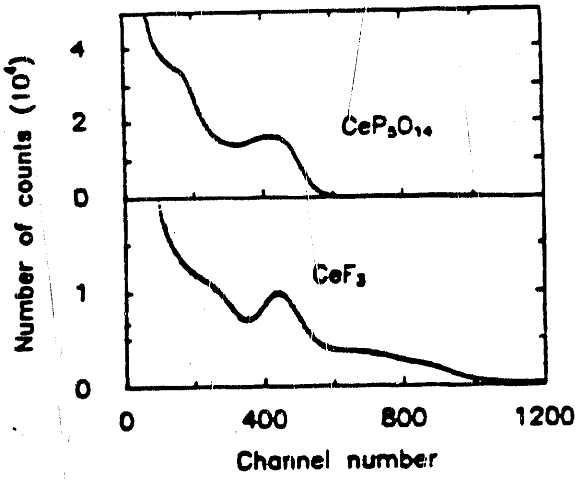

Fig. 9. Energy spectra of CeF_3 and $Ce_{.75}La_{.25}P_5O_{14}$. The was source Bi^{207}.

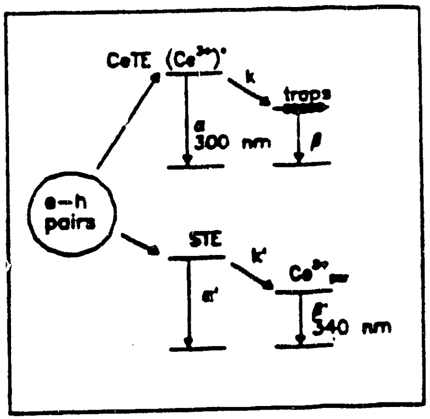

Fig. 10. Excitation processes caused by an electron – hole pair. Possibility (a): the electron – hole pair decays to exciton trapped on Ce^{3+} (CeTE) with subsequent radiative decay or transfer to trap; Possibility (b): Self trapped exciton (STE) transfers its energy to a perturbed Ce ion.

the stoichiometric limit in non quenchable materials. Fig. 9 presents the energy spectra of the "new" CeF_3 and $Ce_{.75}La_{.25}P_5O_{14}$. The positions of photopeaks are close indicating similar light output. The phosphate samples are much smaller than fluoride, which for the same light output generates inferior resolution.

III. DISCUSSION

Results of our investigations of CeF_3 indicate that this material is generally affected by a relatively high level of impurities preventing any significant presence of the true emission of Ce ion. However we do not believe that emission being able to effectively compete with stoichiometric lattice constituent can be entirely due to impurities. It is likely that even relatively insignificant amounts of impurities can perturb quite a large number of Ce ions. We estimate that as much as 50% of the total energy deposited in the crystal may go to perturbed Ce ions, [6]. This estimate is quite close to experimental data which, at RT, suggest that about 40% of total emission comes from perturbed ions. More arguments to support the idea of perturbed Ce ions comes from experiment: somewhat longer decay times, excitation spectra showing energy shifts toward lower energies. Assuming that f levels are not perturbed the shift in electronic energy can be estimated from luminescence excitation spectra to be about 2200 cm^{-1}.

It is remarkable that decays of Ce emission and perturbed Ce emission are so different, one showing a very sharp rise (and ultra fast component) and the second a relatively slow rise (see Fig. 6). The difference in excitation mechanisms, as introduced in Fig. 10, seems to provide an adequate explanation. In the case of Ce emission there is an "instantaneous" process of, most likely, direct capturing of hole and, consecutively, of electron. In this way a CeTE (Ce trapped exciton) is formed which then transfers its energy into a d–f transition. This process is fast but not extremely efficient. Large contribution of Ce emission is due to a large concentration of Ce ions. This emission consists of both ultrafast (2 ns) and fast (20 ns) components. This is because the spectrum of the ultra fast component follows very closely the spectrum of fast component (which was clearly identified as coming from Ce). Unless there are centers which are not Ce but have exactly the same spectrum (which is not very likely) then both components have to be due to Ce ions. Then the only way to get this kind of two exponential decay is by assuming a rapid but saturable transfer to some species (acceptors) leading to quenching of Ce emission and generation of the ultra fast component. After acceptors are saturated the normal decay, characterized by the radiative lifetime, prevails. At this point the nature of those saturable acceptors is not clear. One could speculate about self–quenching by Ce ions (or perturbed Ce ions) provided that Ce^{2+} state is stable in CeF_3 and one of its f^2 levels is resonant with d level of Ce^{3+} but these speculations are not substantiated by any experimental evidence. Further studies would be required to clarify this problem.

The longer wavelength emission ($\lambda > 320$ nm) having a decay of about 35 ns must be produced by a limited number of centers which very effectively (but relatively slowly) collect energy from all STE in their neighborhood. This kind of transfer explains the observed kinetics, namely the slow rise time of scintillation pulse. For the time being, in absence of better knowledge we designate this emission as due to "perturbed" Ce ions as discussed before. This conceptual scheme fits well the observed facts but clearly the exact nature of the postulated traps and "perturbed" centers is far from known. It is, however, remarkable that the simple kinetic model based on transfer (see Fig. 6 and [..]) reproduces experimental decays.

V. CONCLUSIONS

In this paper we have presented results of our studies on two Ce–systems, CeF_3, cerium trifluoride, and $Ce_xLa_{1-x}P_5O_{14}$, cerium–lanthanum ultraphosphate. CeF_3 has focused attention of many researchers because of the discovery of its ultra fast component of decay. We conclude that this ultra fast component provides an evidence of non–radiative quenching, therefore limits the efficiency and is to be avoided rather than become an object of hope. We believe that it should be possible to improve CeF_3 light output by a factor of 2 thus achieving BGO light output with decay time more then ten times smaller (20 ns). To achieve this goal further improvement in technology is needed in order to reduce any unwanted impurities generating (directly or undirectly) a competing and slower emission. This alone can enhance a light output (by reduction of self–absorption). Even larger increase in light output (almost 100%) will be achieved if the effect of quenching of Ce emission is eliminated. This may require further studies in order to understand in more details the mechanism of this quenching.

We have demonstrated that the second material, ultraphosphate, does not show any complications characteristic of fluoride. We believe that this is due to strongly reduced metal–metal interaction because of larger metal–metal distances. Since interaction is scaled down by distances, much higher concentration of intentionally introduced dopants would be required to reproduce effects produced e.g. in fluoride by very low level of uncontrolled impurities. In this sense, phosphate is an ideal model material to be used in studies of all effects reported here for fluorides, like the nature of quenching traps or impurity luminescence.

We conclude that Ce–systems are very promising materials in pursuit of best scintillators. However there still are some problems left which should be adressed.

VI. ACKNOWLEDGEMENTS

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