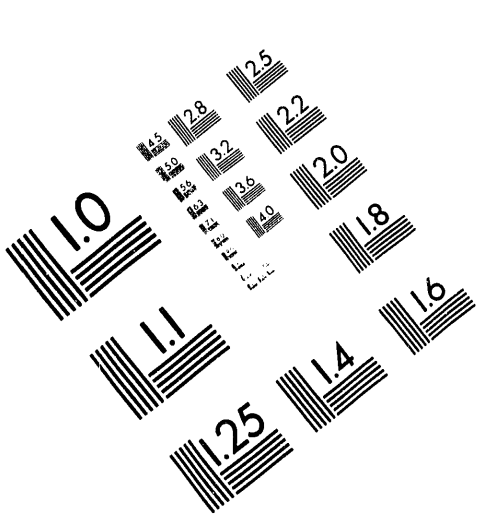

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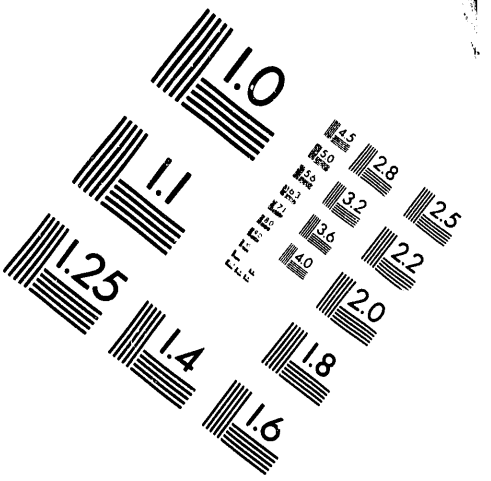

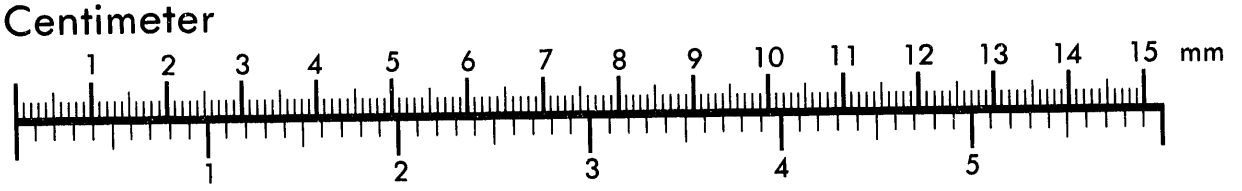

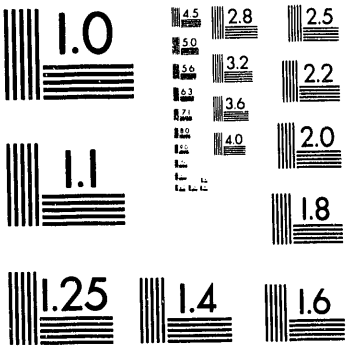

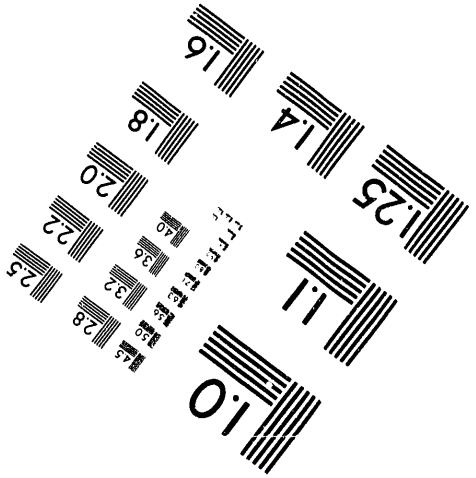

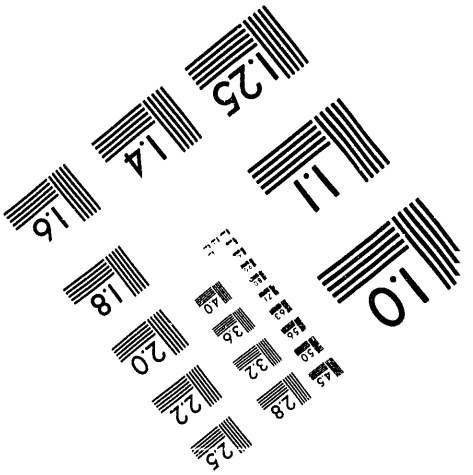

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SCINTILLATION MECHANISM IN STOICHIOMETRIC CERIUM COMPOUNDS

A.J. Wojtowicz*), A. Lempicki and E. Berman

Chem. Dept. Boston Univ., 590 Comm. Ave. Boston, MA 02215 and

ALEM Associates 303A Comm. Ave. Boston, MA 02115

*)On leave from Institute of Physics, N. Copernicus Univ. Torun, Poland

ABSTRACT

In this paper we consider fundamental limitations of scintillators based on stoichiometric Ce materials. These materials constitute a new class of scintillator media, which are characterized by a high speed and a reasonably high light output. We illustrate our considerations using two different systems, CeF_3, (cerium trifluoride), and CeP_5O_{14}, (cerium pentaphosphate). While speed, being limited by a radiative lifetime of an allowed d-f transition on the Ce^{+3} ion, cannot be improved (without loss of the light output), the light output in both cases falls significantly below the estimated theoretical limit. To explain this we propose a mechanism of scintillation process, in which transfer of excitation energy from the lattice to the d-f electronic structure of Ce^{+3} ions is absent and the light output of the scintillator is limited to the excitation energy directly intercepted by Ce ions. The efficiency depends, therefore, on the competition for holes between Ce^{+3} ions and anions, determining the share of the total energy deposited by a high energy particle, which can be transformed into scintillation photons. The mechanism requires that the Ce ion has a stable 4+ charge state. Ionization of Ce^{+3} is followed by capturing of an electron and creation of the Ce bound exciton. In the next step the energy of the bound exciton is transferred to the d-f structure of the Ce ion and, in the final step, a scintillation photon is emitted. The relatively high light output characteristic of these materials is due to the high concentration of Ce ions. The reasons for the lack of efficient energy transfer from the lattice may reside in large relaxation energies of lattice excitations. We use this model to discuss potential improvements in the light output of CeF_3.

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I. INTRODUCTION.

The last few years have witnessed an increased activity in the area of scintillator materials in response to new and demanding applications in science, medicine and industry. Potential applications of the newly discovered scintillator CeF_3,[1,2] include a new calorimeter at CERN and positron emission tomography (PET). While speed and homogeneity of the material are important for high energy physics applications[3], the key factor for PET is the light output.[4] There were some hopes to utilize a ultra-fast (2-5 ns) component of the scintillation decay,[5] until it was proved that this component is not due to a separate process but, instead, results from quenching of the Ce emission.[6] Initial optimistic estimates of the potential improvements of the light output were based on the assumption that the loss in the Ce emission was non-radiative and that, so-called, perturbed Ce ions were competing for the energy deposited in the lattice with regular Ce ions.[6] It is now accepted,[3,7] that actually the perturbed Ce ions are fed by a non-radiative energy transfer from regular Ce ions, and there is no obvious reason for significant loss in the combined light output. Therefore the prospects of substantial improvement of the light output of CeF_3 have to be reexamined more carefully again.

Cerium pentaphosphate, CeP_5O_{14}, was considered as an electron beam indexing phosphor.[8] Although not a viable scintillator material, it has attracted some attention as an interesting model case material.[9] The reasons are in large distances between Ce ions in pentaphosphate lattice which isolate them and reduce all metal-metal interactions. As a result the material is free of many complications typical of, e.g. CeF_3, and can be used to study the scintillation mechanism in concentrated Ce-materials.

II. EXPERIMENTAL.

A description of experimental set-up is given elsewhere.[6,9] Here we summarize the most important experimental results. In CeF_3 [6] two kinds of emission were identified. Short wavelength emission (288 and 300 nm) with decay times of about 2 and 20 ns (at RT), was ascribed to Ce ions in "regular" sites while longer wavelength emission (340 nm), with decay time of 33 ns, was ascribed to the, so-called, "perturbed" Ce ions. In CeP_5O_{14} [9] one

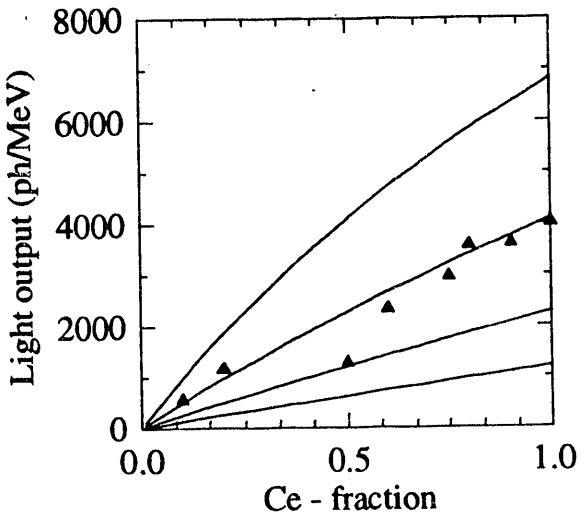

Fig 1. Light output of $Ce_xLa_{1-x}P_5O_{14}$ under ionizing excitation (^{207}Bi)

kind of emission typical of Ce^{3+} (312 and 332 nm) with single exponential decay (33.4 ns at RT) was found. While light output of CeF_3 changes strongly from sample to sample it remains reasonably constant for different samples of CeP_5O_{14}. Although emission spectra of $Ce_xLa_{1-x}P_5O_{14}$ with x changing between 0.05 and 1 are similar[9], light outputs under γ-excitation change significantly, as shown in Fig. 1. Solid lines present model calculations to be discussed in the next section.

III. DISCUSSION.

The light output of scintillator is established as a result of a three step process. In the first step (conversion) the energy of a high energy particle is converted into $n_{e\text{-}h}$ electron-hole pairs (per 1 MeV), in the second (energy transfer) the energy of e-h pairs is transferred to the active ion (with efficiency η_{tra}) and, in the final step (luminescence), the excited ion emits a photon (with quantum efficiency η_q). While the knowledge and expertise gathered in the field of luminescence and phosphors can be used effectively to determine the efficiency η_q,[10] much less is known about the first two steps which explains why they are often underestimated or even totally neglected.

Robbins[11] proposed a scheme to evaluate an efficiency of conversion process. The efficiency strongly depends on the loss ratio K:

$$\mathbf{K} = 0.244 * 10^4 * \frac{1}{\bar{\varepsilon}} * \frac{(\hbar\omega_{LO})^{3/2}}{1.5 * \mathbf{E_g}} \qquad (1)$$

where $\bar{\varepsilon}$ stands for the effective dielectric constant, $\hbar\omega_{LO}$ is the optical phonon energy and E_g is the bandgap. Having K one can calculate $n_{e\text{-}h}$, which often appears much lower than suggested by the "3*E" law. We have calculated $n_{e\text{-}h}$ and arrived at values of 20,430 and 37,500 e-h pairs for CeP_5O_{14} and CeF_3 respectively. The relatively low values are due, for fluoride, to the large bandgap energy (8.7 eV) and, for pentaphosphate, to the

high energy of characteristic PO_4 vibration (1300 cm^{-1}). Experimental values of $\eta_{e\text{-}h}$ are about 4000 for both pentaphosphate and fluoride. Since these numbers are much lower than theoretical estimates and, at the same time, η_q of the Ce ion is known to be high, we have to assume, that the transfer efficiency, η_{tra} must be low.

To rationalize this result it is important to observe that in these materials the final outcome of the conversion process is likely to be reduced to only two distinct types of lattice excitations (excitons). The first consists of the hole localized on the anion (fluorine or phosphate group) and an electron bound by the net Coulomb potential of the localized hole (lattice exciton) and the second consists of the hole and electron bound by the Ce ion (Ce-bound exciton). While the Ce-bound exciton efficiently transfers its energy to the d-f structure of Ce^{3+} ion, the large lattice relaxation may prevent such a transfer in the case of lattice excitons. We assume, therefore, that the low transfer efficiency of pentaphosphate and fluoride is due to the inability of Ce^{3+} ion to effectively use the energy of lattice excitons. The partition of the total energy between two types of lattice excitations determined by an initial distribution of holes between anions and Ce ions, will, therefore, define the transfer efficiency and the total light output of the material. For Ce-La-pentaphosphate ($Ce_xLa_{1-x}P_5O_{14}$) a modified formula expressing η_{tra} is:[9]

$$\eta_{tra} = \frac{x\,\omega_{Ce}}{x\,\omega_{Ce} + 5\,\omega_{PO_4}} \qquad (2)$$

where ω_{Ce}, ω_{PO4} are characteristic volumes expressing the relative probabilities of generating holes localized on Ce cation or PO_4 anion. Solid lines in Fig. 1 were calculated using formula (2) with ω_{PO4}/ω_{Ce} equal to 0.4, 0.8, 1.6 and 3.2 (the best fit is for ω_{PO4}/ω_{Ce}=0.8).

The interesting problem is, whether CeF_3 could be improved. It is clear, that elimination of "perturbed" Ce ions would improve the speed (single exponential decay ot 20 ns instead of three component decay, 2, 20 and 33 ns). If we assume that ω_F/ω_{Ce} = 0.8 than η_{tra} and light output would be 0.3 and 10,000 photons per 1 MeV, respectively. A possibility of the light output improvement is suggested by some correlation between the amount of the long wavelength emission (hence the concentration of "perturbed" Ce ions)

and the light output. However, the limit of 10,000 photons per 1 MeV has to be treated very cautiously.

IV. CONCLUSIONS.

The light output **per ion** in concentrated Ce-materials is unexpectedly low. The reasonably high **total** light outputs are entirely due to large concentrations of Ce ions. A significant part of the energy deposited in the lattice does not show up in the scintillation light and, consequently, the light output of these materials is limited. Most likely, the condition for the energy transfer from lattice excitons to the Ce ions is not fulfilled, despite the observed efficient transfer from the Ce-bound excitons. The reason may be the large relaxation energies of lattice excitons.

V. ACKNOWLEDGMENTS

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