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SCINTILLATION MECHANISMS IN RARE EARTH ORTHOPHOSPHATES

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ABSTRACT

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In this Communication we present results of our studies on scintillation properties of rare earth orthophosphates. Despite of the PO_4 group high frequency vibrations, which limit the conversion efficiency in orthophosphate lattices, some of them are very promising, as evidenced by the exceptionally good scintillation properties of $\text{LuPO}_4:\text{Ce}$. We have studied the following orthophosphate crystals: $\text{YbPO}_4:\text{Ce}$, YbPO_4 , and $\text{Lu}_x\text{Yb}_{1-x}\text{PO}_4:\text{Ce}$. Both Ce and Yb ions scintillate (through $d-f$ transition and charge transfer state decay, respectively) but, unfortunately, they also show strong tendency toward mutual quenching. We propose that nonradiative Yb-Ce energy transfer and the nonradiative decay of the $(\text{Yb}^{2+} + \text{Ce}^{4+})$ charge transfer state are responsible for the observed effect. Therefore ytterbium does not provide cheaper substitute for the optically inactive RE ion (lutetium) in the orthophosphate lattice, on the contrary, it has to be carefully avoided whenever a Ce-activation is used.

key words: scintillation mechanism, orthophosphate scintillators, nonradiative processes.

Running head: Scintillation mechanisms...

INTRODUCTION

Cerium-activated lutetium orthosilicates (LSO) and orthophosphates (LOP) have recently been identified as outstanding scintillators [1,2]. Although the role played by lutetium has not yet been elucidated, the search for cheaper replacement for Lu is being vigorously pursued [2,3]. Ytterbium seems to present a viable alternative since the $4f^{13}$ electronic configuration of this ion produces only low energy $f-f$ transitions ($\sim 10,000 \text{ cm}^{-1}$) while the free ion $4f^{13}-4f^{12}5d$ transition energies at $88,195 \text{ cm}^{-1}$, are almost as high as those of Lu ($100,000 \text{ cm}^{-1}$) [4]. However Yb^{3+} activated orthophosphates (LuPO_4 and YPO_4) have been found to produce luminescence assigned to transitions connecting the charge transfer state (CTS, $\text{Yb}^{2+} + h_\nu$, a bound valence hole) and two states ($^2F_{7/2}$ and $^2F_{5/2}$) of the $\text{Yb}^{3+} 4f^{13}$ configuration [5]. The corresponding absorption band peaks at about 204 nm. The absorption edge in LuPO_4 lies at about 8.6 eV [6], therefore the unrelaxed 2+ charge state energy level of Yb ion is stable (about 2.5 eV below the conduction band). The presence of the stable 2+ charge state has been related before to inefficient scintillation in Ce-activated materials [7,8].

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EXPERIMENTAL RESULTS

The samples used in this study were characterized before [9]. Also the growth method [2] and experimental details [7] have been described previously. The emission spectra under γ -excitation are shown in Fig. 1. Spectrum a (LuPO_4 , 6 ppm of Ce, 14 ppm of Yb) shows two peaks at 334 and 360 nm (2160 cm^{-1} apart), a clear mark of the Ce^{3+} ion. On the other hand spectrum d (YbPO_4 :Ce, 1.4 ppm) shows two peaks, at 300 and 430 nm ($10,070 \text{ cm}^{-1}$ apart), due to the charge transfer transition involving Yb ion [5,14]. Spectra b and c ($\text{Yb}_x\text{Lu}_{1-x}\text{PO}_4$:Ce, 0.18 wt %, $x=0.01$ and 0.1 , respectively) show a dip in Yb 300 nm emission band at about 320 nm obviously due to Ce ions. Although this indicates efficient radiative (and, possibly, nonradiative) energy transfer processes from Yb to Ce, the detectable Ce emission unexpectedly diminishes with increasing Yb content (compare spectra b and c).

In Fig. 2 we show scintillation light output vs Ce content for YbPO_4 crystals. The Yb scintillation efficiency diminishes with increasing Ce concentration although there is no increase in Ce emission contribution as evidenced by scintillation spectra. Therefore we conclude that in addition to quenching of Yb emission by Ce ions also Ce emission must be quenched by Yb ions.

In Fig. 3 we present scintillation pulse shapes under γ -excitation at room temperature for different emission wavelengths. As shown by trace a the Yb emission (LuPO_4 :Yb, no Ce) shows a rise time and a longer decay time contrary to Ce emission [2,9]. However, with intentional Ce doping the decay time of the Yb emission decreases (compare traces b, c and d) and there is a faster decaying component which is partially due to overlapping emission from the quenched Ce ions but also, very likely, to nonradiative energy transfer to Ce ions.

DISCUSSION AND CONCLUSIONS

Perhaps the most important consequence of the simultaneous presence of Yb and Ce is their mutual quenching. This observation can be explained in terms of the mechanism proposed earlier for the other rare earths combination, Ce and Eu [10], and for the Ce self-quenching in CeF_3 [11]. Whenever one of the ions (e.g. Eu, Yb or even Ce itself) has a stable $2+$ state, then the emission from the other ion (Ce) can be severely quenched by the formation of a metal-metal charge transfer state which decays nonradiatively to the ground state as shown in Fig. 4. This process can be described as follows:

The exchange of electron between two neighboring ions, a highly excited Ce^{3+} ion designated as Ce^{4+} plus loosely bound electron e_b , and unexcited Yb^{3+} , leads to formation of the oppositely charged metal-metal ion pair far from the equilibrium point in the configuration coordinate space. After relaxation there

will be a repeated electron exchange leaving two ions in unexcited 3+ charge states. In this way the Ce^{3+} ion preserves a high quantum efficiency when excited directly into its lower excited states but, after ionization, the new nonradiative recombination channel is open, where the energy of Ce^{3+} electronic excitation is carried away by lattice and/or local vibrations. Therefore, if the Yb concentration is high enough, the energy gathered by Ce ions is lost nonradiatively. Also, the preceding radiative and nonradiative energy transfer from excited Yb ions to Ce ions will, by virtue of the same process, waste the energy gathered by Yb ions. The final conclusion is that intentional or unintentional codoping of Ce and Yb ions into the lattice of scintillator material has to be carefully avoided.

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FIGURE CAPTIONS

Fig. 1. Room temperature emission spectra under γ -excitation. (sample 10 trace a, sample 7 trace b, sample 8 trace c, and sample 1 trace d).

Fig. 2. Scintillation light output under γ -excitation (compared to BGO) of YbPO_4 vs Ce concentration.

Fig. 3. Spectrally resolved pulse shapes of γ -excited scintillations taken at room temperature: a, $\text{Yb}_x\text{Lu}_{1-x}\text{PO}_4$ ($x=0.01$, 10^{-3} wt % Ce), $\lambda = 430$ nm, rise time 3.3 ns, decay time 125 ns; b, $\text{Yb}_x\text{Lu}_{1-x}\text{PO}_4\text{:Ce}$ ($x=0.01$, 0.18 wt % Ce), $\lambda = 430$ nm, no rise time, first component 21% zero-time amplitude and 15.7 ns decay time, second component 79% zero-time amplitude and 100 ns decay time; c, same sample as b, $\lambda = 360$ nm, no rise time, first component 63% zero-time amplitude, 12 ns decay time, second component 37% zero-time amplitude, 90 ns decay time; d, $\text{Yb}_x\text{Lu}_{1-x}\text{PO}_4\text{:Ce}$ ($x=0.1$, 0.18 wt % Ce), $\lambda = 360$ nm, no rise time, first component 36% zero-time amplitude, 19 ns decay time, second component 64% zero-time amplitude, 84 ns decay time.

(sample 6 trace a, sample 7 traces b and c, sample 8 trace d)

Fig. 4. The proposed model of radiative and nonradiative decay channels of the excited Ce^{3+} ion by interaction with the close neighbor Yb^{3+} ion. The stability of the Yb 2+ charge state and efficient exchange of electron between highly excited Ce^{3+} and Yb in 2+ state is a necessary condition.

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