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Energy transfer processes in (Lu,Gd)AlO$_3$:Ce

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ABSTRACT

In this paper we present initial results of studies on energy transfer processes in Ce-activated Lu, Y and Gd aluminum perovskite crystals that contribute to production of scintillation light in these new scintillator materials. In particular we report and analyze emission spectra, excitation spectra, and emission time profiles under pulsed synchrotron excitation in the wavelength range of 50-300 nm.

The emission spectra of $Lu_{0.65}Gd_{0.35}AlO_3$:Ce and $Lu_{0.2}Y_{0.8}AlO_3$:Ce display a characteristic double band that is due to the spin-orbit split *d-f* transition of Ce^{3+} with no indication of Gd^{3+} *f-f* emissions in the Gd-containing crystal. Nevertheless the "time-gated" and "integrated" excitation spectra of Ce-emission of this crystal in addition to the *f-d* Ce^{3+} bands reveal some additional fine features, absent in the Y-containing crystal, that are evidently related to the *f-f* transitions at Gd^{3+} ions. We also observe that the Ce-emission time profile measured under direct Ce-excitation displays fast decaying component while the Gd-tuned excitation produces slow profiles that resemble those observed under gamma or X-ray excitation.

These results directly prove that slow scintillation components characteristic of the $Lu_xGd_{1-x}AlO_3$:Ce scintillator are due to transfer of energy that was originally deposited by the ionizing radiation in the Gd-sublattice of the crystal.

Keywords: YAlO$_3$, LuAlO$_3$, GdAlO$_3$, cerium, scintillators, VUV spectroscopy, luminescence, time profiles, energy transfer

1. INTRODUCTION

The yttrium aluminum perovskite activated by Ce (YAlO$_3$:Ce, abbr. YAP:Ce) is a well established commercial scintillator material that has found a number of important applications.[1,2] Its heavier lutetium isostructural analog, LuAlO$_3$:Ce (abbr. LuAP:Ce), is a promising new addition to scintillator materials considered for modern applications involving detection of ionizing radiation such as high energy and nuclear physics and nuclear medicine (positron-emission-tomography, PET).[3] The Czochralski-grown monocrystals of LuAP:Ce were first evaluated in a garnet-free perovskite phase by Lempicki et al. in 1994.[4] More detailed studies revealed that the dominant mechanism of energy transfer from the host to the Ce^{3+} ions in both Y and Lu-perovskites involves consecutive capture of electrons and holes at Ce^{3+} sites followed by recombination and Ce-emission (scintillation).[5,6] It has also been established that traps strongly influence the basic scintillation characteristics of these materials such as scintillation light yield and scintillation time profiles (rise and decay times).[7]

Although LuAP:Ce is a reasonably efficient and fast scintillator (scintillation light yield ~11,300 photons/MeV, scintillation decay time ~17 ns)[8] it is very expensive and notoriously difficult to grow. Initial studies seem to suggest that some addition of Y or Gd helps to stabilize the perovskite phase with only a moderate loss in scintillation light yield and speed [9] but scintillation mechanisms (in particular host-to-ion energy transfer processes) in such materials have not been investigated. Therefore, as a part of a larger effort in Europe in the framework of the Crystal Clear Collaboration sponsored by CERN and aimed at perovskite scintillator materials,[3,9,10,11] we have conducted vacuum ultraviolet (VUV) studies of mixed Lu, Y and Gd aluminum perovskite crystals at Superlumi station of Hasylab, Hamburg, Germany. In this paper we report our recent results in this area.

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2. CRYSTALS AND EXPERIMENTAL SET-UPS

The reference $LuAlO_3$:Ce sample was cut from the boule provided by M. Randles (Synoptics Div., Litton Airtron Corp., Charlotte, NC). The crystals were pulled from the melt (Czochralski method) on iridium wire in an atmosphere of N_2. The Ce-concentration in the melt was 0.25 mole% but the actual concentration found by mass spectroscopy analysis was only 200 ppmw.

The mixed $Lu_xY_{1-x}AlO_3$:Ce and $Lu_xGd_{1-x}AlO_3$:Ce crystals were grown by Crytur Ltd (Palackého 175, 51119 Turnov, Czech Republic) by Czochralski method. The Ce-concentration in these crystals was much higher than in the reference LuAP sample at 0.1 to 0.3 at.%. More details about these crystals and their basic properties was given by Chval et al.[9]

The VUV experiments presented in this paper include measurements of luminescence spectra, excitation spectra and emission time profiles obtained under pulsed VUV excitation from the synchrotron radiation have been conducted at Superlumi station of Hasylab, Hamburg, Germany. A detailed description of Superlumi's experimental facilities given by Zimmerer [12] is also available on-line.[13]

3. EXPERIMENTAL RESULTS

In Fig. 1 we show uncorrected emission (resolution 3 nm) and excitation (resolution 1.6 nm) spectra of two samples of mixed crystals, $Lu_{0.65}Gd_{0.35}$AP:Ce and $Lu_{0.2}Y_{0.8}$AP:Ce. For comparison we have also included the spectrum measured for the reference sample (LuAP:Ce). Since the emission spectra of these three samples are nearly the same only the (Lu,Gd)AP spectrum is shown in the figure. Note that unlike the LuAP spectrum the spectra of mixed crystals show strong saturation distortions typical of highly doped samples. Nevertheless some variations observed in these spectra at the VUV wavelength range may be indicative of different host-to-ion energy transfer processes.

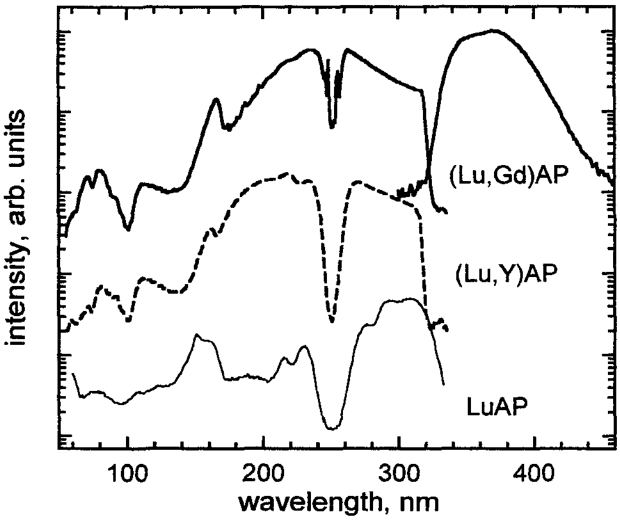

Fig. 1. Uncorrected emission and excitation spectra of Ce-doped Lu/Gd, Lu/Y and Lu aluminum perovskite crystals at 8 K. The emission spectrum was measured with the excitation wavelength set at 255 nm. The excitation spectra were measured with the emission wavelength set at 370 nm. Note the sharp features at about 250 nm in the (Lu,Gd)AP spectrum. The room temperature spectrum (not shown) displays almost no sharp line features because of thermal broadening.

The peaks in the vicinity of the bandgap energy (at 150 to 160 nm) have been previously associated with energy transfer mechanisms that enable the material to scintillate efficiently.[14] Although the structure in the VUV part of the spectra does not reflect any true physical processes of energy transfer (the spectra were not corrected) the short wavelength pulsed excitations below 100 nm have been demonstrated to produce luminescence time profiles modified by trap mediated recombination of charge carriers via the Ce^{3+} ions.[15,16] In this paper, however, we will concentrate on different processes that are responsible for some fine features clearly visible in the excitation spectrum of (Lu,Gd)AP:Ce (e.g. at about 250 nm, see Fig. 1) but are conspicuously absent in LuAP:Ce and (Lu,Y)AP:Ce.

In Fig. 2 we present two excitation spectra of the Ce^{3+} emission in (Lu,Gd)AP:Ce (thick and thin solid lines) designated "(Lu,Gd)AP integrated" and "(Lu,Gd)AP:Ce time gated" and, for comparison, the spectrum of (Lu,Y)AP:Ce (thin dashed line). The "integrated" spectrum was measured with the emission signal accumulated during the time between the consecutive synchrotron pulses (192 ns) while the "time gated" spectrum was measured within a 40 ns time window triggered by a synchrotron pulse with no delay.

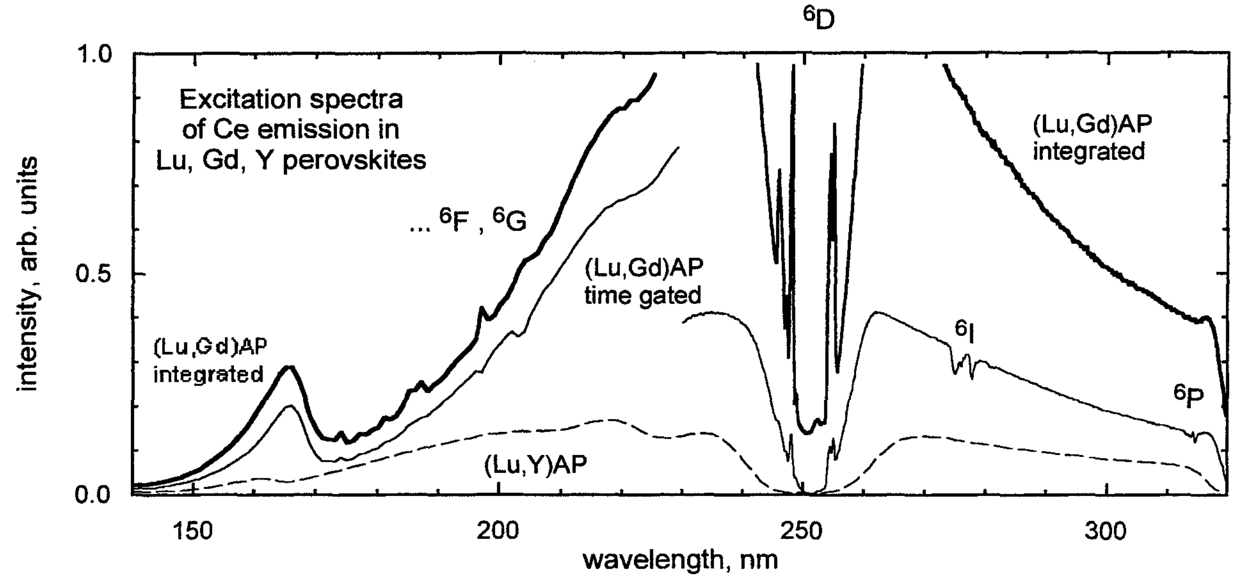

Fig. 2. Uncorrected excitation spectra of the Ce-doped Lu, Gd and Y aluminum perovskite crystals at 8 K. The emission wavelength was set at 370 nm. The spectral resolution was about 0.3 nm. Note the difference in appearance of sharp features between "time gated" and "integrated" curves. For designation of the curves see text.

The fine features observed in the spectra shown in Fig. 2 take a form of sharp lines (at about 245 and 255 nm) and/or "dents" (at 275 and 315 nm). Shorter wavelength features at about 203, 195, 185 nm take a form of lines (in the "integrated" spectrum) and/or "dents" (in the "time gated" spectrum). These lines were also observed in the absorption spectrum of (Lu,Gd):AP:Ce and GdAP:Ce crystals.[9,10] Clearly, all these features can be associated with the Gd *f-f* transitions starting at $^8S_{7/2}$ and terminating at various levels of the ^{6}P, ^{6}I, ^{6}D, ^{6}G, and ^{6}F terms of the Gd^{3+} ion.[9,10,,17,18] Note that energy levels of the lanthanide 3+ ions in VUV have only recently been measured and calculated theoretically.[18] In Table 1 we summarize the energies of all the Gd-related spectral features that we were able to resolve in the excitation spectra of the Ce emission in (Lu,Gd)AP.

Table 1.
Summary of Gd^{3+} transition energies in (Lu,Gd)AP.

Terms	^{6}P	^{6}I	^{6}D	^{6}G, ^{6}F...
Observed energies (cm^{-1})	31,780 31,870	36,000 36,360	39,200 39,300 39,600 40,200 40,300 40,400 40,600	49,100 50,800 53,500 54,000 55,200 56,500

Finally in Fig. 3 we show time profiles of Ce^{3+} emission from (Lu,Gd)AP:Ce under pulsed synchrotron excitation of two different wavelengths; 255 nm (coincident with the wavelength of the sharp line in the excitation spectrum, see Fig. 2) and 260 nm. The temperature was 10 K. Note much larger contribution of slow components in the time profile obtained under the 255 nm excitation (into the Gd^{3+} line).

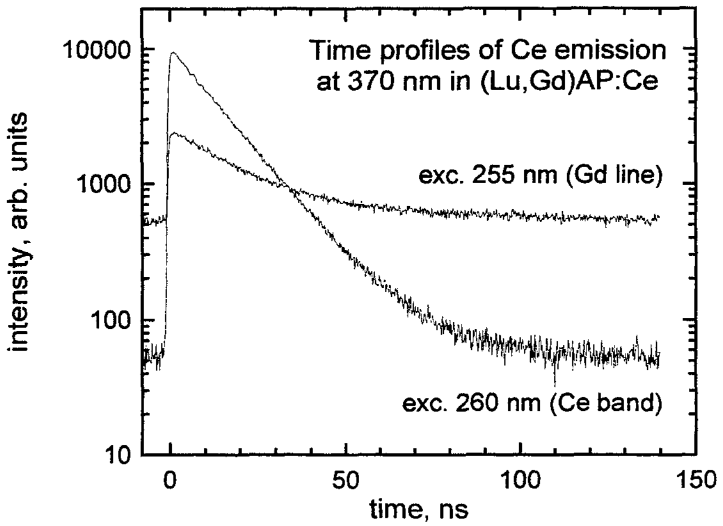

Fig. 3. Time profiles of Ce-emission in (Lu,Gd)AP:Ce under pulsed synchrotron excitations of 255 and 260 nm at 10 K. The emission wavelength was set at 370 nm.

It is interesting to note that larger contributions of slower components in the scintillation time profile (gamma excitation) in GdAP:Ce in comparison to YAP:Ce and (Lu,Y)AP:Ce have been reported earlier by Mares et al.[11] This suggests that direct excitation into Gd absorption lines mimicks processes that are active in the Gd-containing material excited by ionizing radiation such as gamma or x-rays.

4. DISCUSSION

The appearance of Gd-related features in the excitation spectra of Ce-emission in (Lu,Gd)AP:Ce (lines and dents) can easily be explained by assuming that energy absorbed by Gd^{3+} ions is transferred, with some delay, to Ce^{3+} ions.[9] Note that the emission spectrum under the 255 nm (39,200 cm-1) excitation into one of the well resolved Gd^{3+} peaks shows exclusively the well known poorly resolved double band characteristic of the spin-orbit split *d-f* transition at Ce^{3+} ion (see Fig. 1). For excitation wavelengths, for which direct Ce^{3+} excitation is weak (240 to 260 nm), the Gd^{3+} ions provide additional channels by which energy (otherwise lost) is collected and transferred to Ce^{3+} ions (hence "lines"). On the contrary, for excitation wavelengths for which direct Ce^{3+} excitation is efficient (e.g. 265 to 320 nm), Gd^{3+} ions compete with Ce^{3+} ions changing the distribution of intensity between slower and faster components in the time profiles of the Ce^{3+} emission (see Fig. 3). In the short (40 ns) time window this process effectively lowers the intensity of the Ce^{3+} emission (hence "dents" in the "time gated" spectrum). Since no "dents" are observed in the "integrated" spectrum we conclude that efficiency of the Gd-Ce transfer must be very high.

5. CONCLUSION

The resonant excitation into Gd^{3+} absorption lines by synchrotron radiation in mixed (Lu,Gd)AP:Ce reveals the existence of additional channel by which the energy can be transferred to Ce^{3+} ions. Since the Gd-subsystem provides significant fraction of the stopping power of the mixed (Lu,Gd)AP crystal this channel must be important for scintillation performance of the material. Despite the prominence of the direct charge carrier capture and recombination at Ce^{3+} ions in perovskites other processes, such as the one studied in this paper, may prove important in these systems.

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