

VUV studies of Gd-related energy transfer in Ce-doped mixed Lu, Gd aluminium perovskite

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Lutetium aluminium perovskite activated by Ce ($\text{LuAlO}_3\text{:Ce}$, abrr. LuAP:Ce) is a promising new addition to a group of scintillator materials considered for modern applications such as high energy and nuclear physics and nuclear medicine (PET) [1]. The Czochralski-grown monocrystals of LuAP:Ce were first evaluated in a garnet-free perovskite phase by Lempicki et al. in 1994 [2]. Although LuAP:Ce is reasonably efficient and fast scintillator (17 ns) 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 almost no loss in light yield or speed [3]. As a part of a larger effort at Superlumi station of HasyLab aimed at perovskite scintillator materials [4,5] we have conducted VUV studies of mixed Lu, Y and Gd aluminium perovskite crystals. Here we report some of our recent results in this area.

In Fig. 1 we show the emission and excitation spectra of $\text{Lu}_{0.65}\text{Gd}_{0.35}\text{AP:Ce}$, $\text{Lu}_{0.2}\text{Y}_{0.8}\text{AP:Ce}$ (Crytur, Czech Republic) and, for comparison, LuAP:Ce (Litton Airtron, USA). Although the emission spectra of these three crystals are nearly the same (only the (Lu,Gd)AP spectrum is shown in the figure) the excitation spectra show some variations that may be indicative of different host-to-ion energy transfer processes.

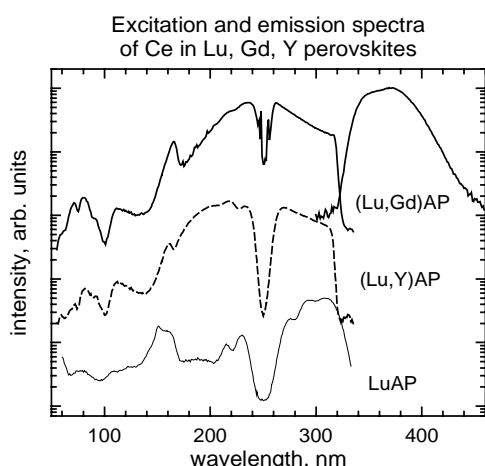


Figure 1: Uncorrected emission (resolution 3 nm) and excitation spectra (resolution 1.6 nm) of Ce-doped Lu/Gd, Lu/Y and Lu aluminium perovskite crystals at 8 K. The emission spectrum was measured with the excitation wavelength set at 255 nm. The excitation spectra were measured with the emission wavelength set at 370 nm. Large distortions of the (Lu,Gd)AP and (Lu,Y)AP excitation spectra are due to higher concentrations of Ce in mixed crystals.

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 [6]. Also 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 [4,5]. In this note, 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 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 solid 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.

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 (LuGd):AP:Ce crystals [3]. Clearly, all these features can be associated with the Gd f-f transitions starting at $^8\text{S}_{7/2}$ and terminating at various levels of the ^6P , ^6I , ^6D , ^6G , and ^6F terms of the Gd^{3+} ion [3,7-9]. Note that energy levels of the lanthanide 3+ ions in VUV have only recently been measured and calculated theoretically [9]. 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.

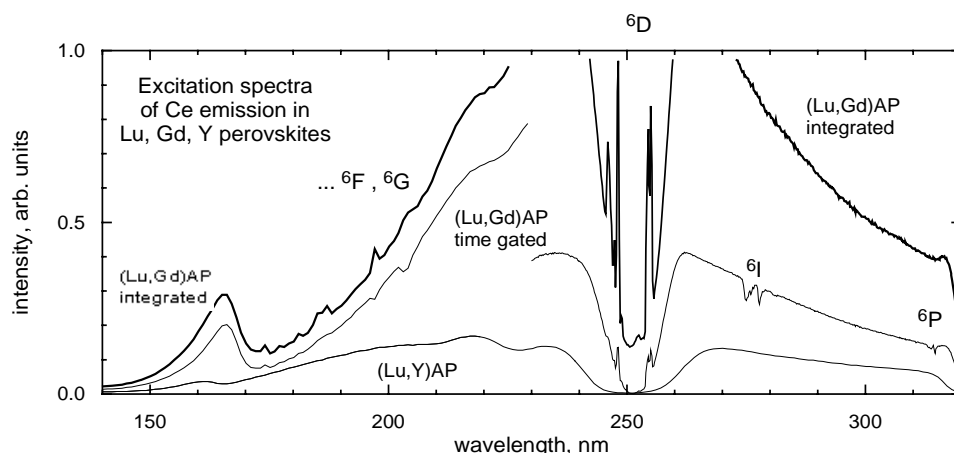


Figure 2: Uncorrected excitation spectra of the Ce-doped Lu, Gd and Y aluminium perovskite crystals at 8 K. The spectral resolution is about 0.3 nm. For designation of the curves see text.

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

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

The appearance of the 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 [3]. 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, although poorly resolved, Ce^{3+} bands (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. 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 delay introduced by Gd^{3+} ions can be estimated to be between 40 and 180 ns in agreement with previous studies [3] and that efficiency of the Gd-Ce transfer must be very high.

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