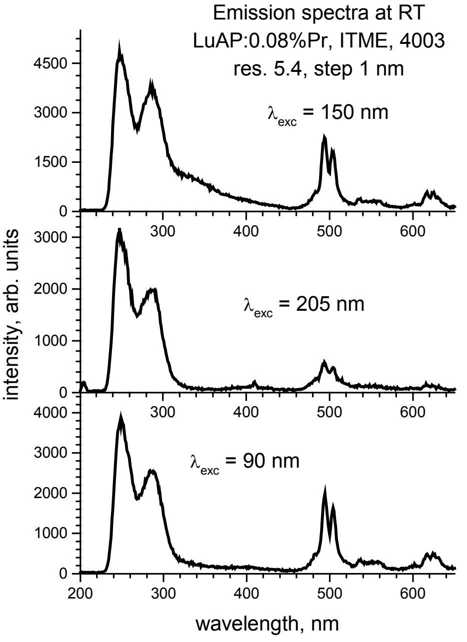
VUV spectroscopy of Pr-activated LuAP

A.J. Wojtowicz [1], K. Wiśniewski [1], M. Ptaszyk [1], T. Łukasiewicz [2)], and J. Kisielewski [2]

[1]Institute of Physics, N. Copernicus University, Grudziądzka 5, 87-100 Toruń, Poland
[2]Institute of Electronic Materials Technology, Wólczyńska 133, 01-919 Warsaw, Poland

Scintillation properties of cerium activated lutetium orthoaluminate (LuAP:Ce, $LuAlO_3$:Ce) in a pure perovskite form were studied and reported for the first time almost a decade ago [1]. Since the scintillation of LuAP:Ce, at 360 nm, decays with the fast component time constant of nearly 17 ns, it has been established as the fastest Ce-activated inorganic scintillator material. Shorter decay times can only be obtained from the Pr- and Nd-activated materials since the parity and spin-allowed $4f^{n-1}5d$-$4f^{n}$ emissions from these ions are characterized by even shorter wavelengths, peaking, in oxides, at about 250 and 190 nm. From the wavelength dependence of the electric dipole transition rate [2], the radiative lifetimes for Pr- and Nd-emissions can be estimated as 8 and 5 ns, respectively.

In this report we shall present some selected results of VUV studies on LuAP:Pr samples, performed at the Superlumi station of Hasylab at DESY. We will demonstrate that these studies, involving VUV synchrotron light, can be used to study various processes and channels of energy transfer from the host to activator ions in a scintillator material. The LuAP:Pr samples, in the form of 2x2x10 pixels, were cut from the larger boules grown at Institute of Electronic Materials Technology in Warsaw (ITME).



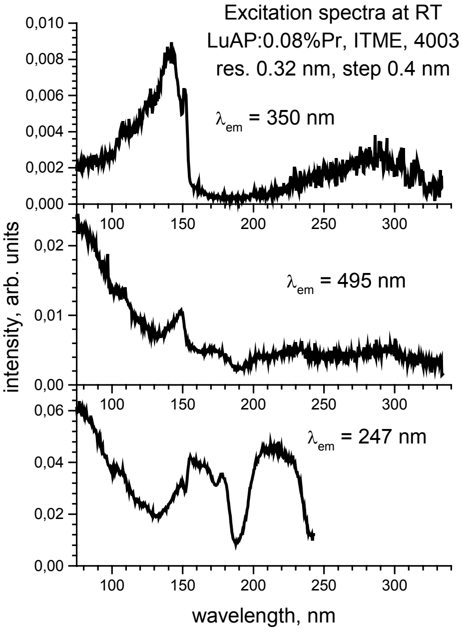


Figure 1: Uncorrected emission (resolution 5.4 nm) spectra of LuAP:Pr. The spectra were measured with the excitation wavelength set at 150, 205, and 90 nm, as indicated in the figure. For details see text. Temperature was 298 K.

Figure2: Corrected excitation spectra (resolution 0.32 nm) of LuAP:Pr. The spectra were measured with the emission wavelength set at 350, 495 and 247 nm, as indicated in the figure. For details see text. Temperature was 298 K.

In Fig. 1 we present the emission spectra of LuAP:0.08%Pr, under different excitation wavelengths. As demonstrated in Fig. 2, the 150 nm excitation corresponds to the "bandgap peak"responsible for efficient excitation of the "host" emission, characteristic of undoped LuAP, 205 nm excitation falls in the range of *f-d* transition energies ("direct excitation") and, finally, the 90 nm VUV excitation that is likely to mimick the X-or gamma ray excitation. Note that under "direct excitation" of 205 nm, the spectrum shows two well resolved *d-f* bands at 247 and 285 nm and also two sets of not particularly well resolved *f-f* emission lines, at about 500 nm ($^3P_0$) and 620 nm ($^1D_2$). This suggests that the $^3P_0$ and $^1D_2$ states are fed by some other processes involving *d*-levels of the Pr^{3+} ions. The relative intensities of *f-f* emission lines are, nevertheless, clearly higher in the other two spectra shown in Fig. 1, indicating that under 150 and 90 nm excitations there is an additional, direct channel of energy transfer from the host to $^3P_0$ and $^1D_2$ states bypassing *d*-levels. Note also that under 150 nm excitation there is an additional broad emission band at about 350 nm. This band is certainly absent in the 205 nm spectrum but it may be present, to a lesser degree, in the third spectrum, obtained under 90 nm excitation.

In Fig. 2 we present excitation spectra of LuAP:0.08%Pr. The spectra have been corrected using a sodium salicylate standard. The emission monochromator was set to select emissions typical of LuAP:0.08%Pr, namely, the *d-f* emission (at 247 nm), the *f-f* emission (at 495 nm) and "host emission" due to defect centers fed by excitonic mechanism of energy transfer (at 350 nm). The excitation spectrum of the *d-f* emission shows broad *f-d* bands (a single unresolved broad band peaking at 215 nm, and a complex band overlapping the bandgap range of energies, peaking at about 178 and 165 nm but extended toward energies over the bandgap), a weak excitonic origin bandgap peak at about 150 nm, and a featureless rising tail extending toward the VUV. The excitonic bandgap peak is much more pronounced in the "host emission" excitation spectrum while the rising VUV tail is also visible in the *f-f* emission excitation spectrum which is consistent with the relatively high contribution of the *f-f* emission to the total luminescence spectrum measured under the VUV excitation of 80 nm.

It is interesting to note the characteristic large Stokes shift in the excitation spectrum of the "host emission" suggesting the excitonic mechanism of energy trasnfer. Unlike the other two spectra this one shows a falling, not rising, tail extending into VUV pointing to strong competition between generation of excitons and consecutive hole and electron capture by Pr ions leading to Pr-emissions.

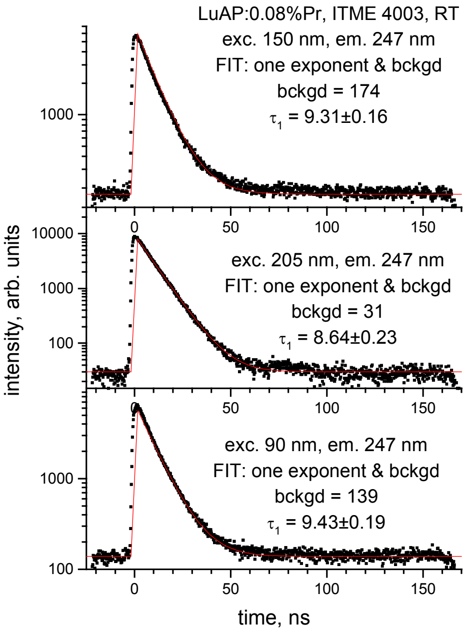


Figure 3: Emission time profiles of LuAP:Pr under direct f-d (205 nm) and indirect (150 and 90 nm) excitations. The emission monochromator was set to 247 nm, temperature was 298 K.

Finally, in Fig. 3, we show selected emission time profiles of LuAP:0.08%Pr under various excitations at 298 K. As expected, the direct excitation of Pr^{3+} ions leads to single exponential decays with the background and the decay time constant of 8.6 ns, consistent with decay times measured earlier [3]. Under indirect excitation the decay time of the Pr emission becomes slightly longer and there is also a higher background indicating more contribution from the slower components.

In this report we have presented evidence that indirect VUV excitation in LuAP:Pr provides an efficient and fast channel of energy transfer to the Pr^{3+} ions. Although the competition from the defect centers is negligible there is also, unfortunately, a preference of the $^3P_0$ and $^1D_2$ states over *d*-states under VUV excitation.

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