Temperature effects in the VUV excitation spectra of Ce-activated LuAP

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Scintillation and spectroscopic properties of cerium activated lutetium orthoaluminate in a pure perovskite phase (LuAP:Ce, $LuAlO_3$:Ce) were reported for the first time more than a decade ago [1]. Although, since that time, the VUV excitation spectra of Ce emission in orthoaluminates have been published in a number of papers (see e.g. [2]), the peculiar temperature dependence of intensities of the peaks in these spectra, that will be the subject of this report, has never, as far as we know, been studied in details and explained.

In Fig. 1 we show the representative excitation spectra of the 360 nm Ce emission in LuAP measured at 12 and 298 K. In addition to the well known 5 *f-d* bands at 310, 295, 275, 230 and 215 nm, the spectra reveal also a shorter wavelength bands at 190 and 150 nm superimposed on the rising almost featureless tail extending far into VUV. The additional peak at 190 nm has been previously associated with the optically induced autoionization transition [2,3] while the bandgap peak at 150 nm and the VUV tail suggest strong response to over the bandgap excitation characteristic of the good scintillation material [2].

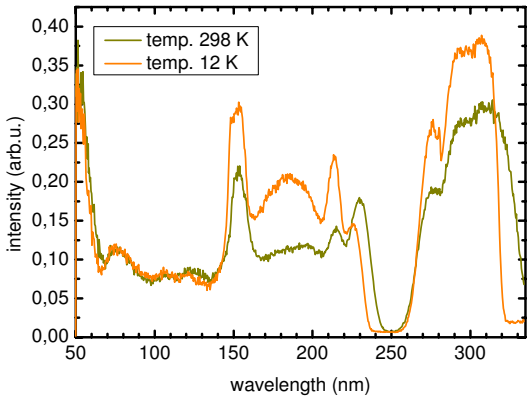

Figure 1: Corrected excitation spectra (resolution 0.32 nm) of LuAP:Ce. The spectra were measured with the emission wavelength set at 380 nm. Temperature was 298 and 12 K.

Although the spectra have been corrected using the salicylate standard, there are some remnant features at 60 to 80 nm due to spectral characteristics of the Al grating which do not reflect any real physical processes. The difference between the two spectra is presumably due to higher VUV sensitivity of the material at higher temperatures due to thermally induced detrapping of charge carriers.

The unexpected feature in these spectra is the thermally induced variation of the ratio between the two higher energy *f-d* peaks at 215 and 230 nm; while at low temperatures the peak at 230 nm is barely visible, for higher temperatures this peak shows much higher intensity than the 215 nm peak.

The temperature dependent variation of the intensity ratio of the peaks due to transitions to the two 5d(e) levels of the Ce^{3+} has been noted and studied in YAG:Ce [4]. Also, the "missing" *f-d* band in absorption spectra of CaF_2:Ce at low temperatures has been reported by Manthey [5]. In both cases the missing or weak bands have been attributed to forbidden transitions between the appropriate Kramer's doublets. The low symmetry crystal field component that would be responsible for splitting of the otherwise degenerate 5d(e) states was assumed, in both cases, to be tetragonal. Manthey's calculations yielded the value of 0.04 for the ratio of the forbidden and allowed band strengths (the missing band would have only 0.04 of the intensity of the observed band), while Robbins used Hoshina's et al calculations [6] to obtain theoretical values that he was able to compare with the experiment [4].

Before we proceed to adopt the Robbins' approach to the case of LuAP, we note that in YAG and CaF_2 the dominant cubic crystal field (8 nearest oxygen or fluorine ligands) sets the 5d(e) levels as the two lowest excited states of the Ce^{3+} ion. Since in LuAP the dominant crystal field term is octahedral (6 oxygen ligands) the lowest 5d levels are due to 5d(t) states and the effect is observed for the two highest, not the lowest, energy levels of the Ce^{3+} ion.

In Fig. 2 we present one of a number of excitation spectra measured at different temperatures between 12 and 300 K. As shown in the figure, the spectra have been decomposed into Gaussian components in order to evaluate the contribution of the two bands due to transitions to the low symmetry crystal field split 5d(e) states.

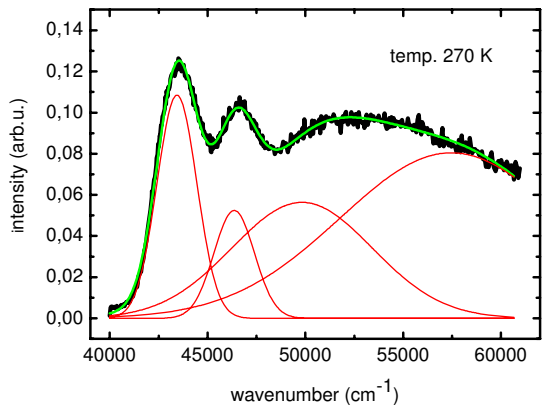

Figure 2: Corrected excitation spectrum of the Ce^{3+} emission at 270 K, presented against the wavenumber scale. The decomposition into four Gaussian components is shown.

The areas under the two lowest energy peaks have been taken to represent the relative strengths of transitions from the ground state to the tetragonal field split two 5d(e) excited states.

In Fig. 3 we present the ratio of the two 5d(e) band strengths (open circles) and a theoretical fit (solid line). The fit function, after Robbins, was taken as:

$$M_{230}/M_{215} = (p_A\exp(\Delta E/kT)+p_B)/ (p_B\exp(\Delta E/kT)+p_A) = (p_B/p_A +\exp(\Delta E/kT))/ (1+p_B/p_A \exp(\Delta E/kT))$$

where ΔE is the energy difference between the 4f $^2F_{5/2}$ ground state Kramer's doublets $E_{3/2}$, $E_{1/2}$ and p_B/p_A represents the ratio of transition probabilities between the two appropriate pairs of Kramer's doublets. The values obtained from the fit are shown in the figure.

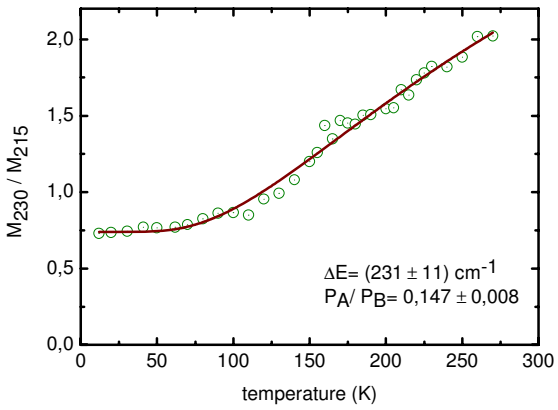

Figure 3: The ratio of band strengths (open circles) and theoretical fit (solid line).

It is interesting to note that the ground state 4f $^2F_{5/2}$ energy splitting in LuAP is clearly smaller than in YAG. Since for d-levels this energy will be much higher, both the cubic field (10Dq) and the tetragonal crystal field components in YAG will contribute to the red shift of the *d-f* emission in this material.

The most important observation is that by imposing the appropriate symmetry of the Ce site it is possible to tune the transition strength of the absorption band with the temperature. This observation may provide a tool to design better scintillation materials by reduction of self absorption; a serious problem in many Ce-doped scintillator materials.

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