Luminescence Properties of $K_3Lu(PO_4)_2$:Ce Crystals

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Ce^{3+} ion due to its efficient, relatively fast, short-wavelength emission is one of the most effective activators. Ce - activated $K_3Lu(PO_4)_2$ crystals have been studied under gamma, x-ray, VUV, and UV excitation and found as promising scintillators [1]. For all of the excitation forms, the luminescence of these materials is dominated by the *d-f* emission bands of Ce^{3+}. The shape and position of these bands, however, depends on temperature due to crystallographic structural phase changes [2] and multiple types of Lu^{3+} ions sites in the which the Ce^{3+} ion can substitute for Lu.

Figure 1 presents the luminescence excitation spectra for the Ce-emission. The structure in the band of wavelengths shorter than 150 nm is due to the spectral characteristics of the primary monochromator grating, and consequently, it does not reflect any true physical processes. However, since photons in this wavelength range have an energy greater than the energy bandgap of materials being investigated, a high signal level in this range indicates an efficient energy transfer from the host material to activator ions.

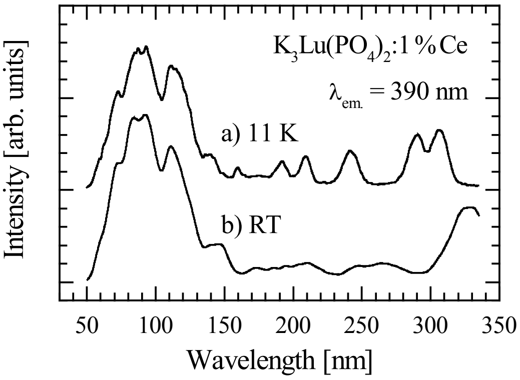

Figure 1: The excitation spectra of Ce^{3+} emission in $K_3Lu(PO_4)_{2:}$Ce.

At longer wavelengths, the spectral characteristics of the excitation path is quite smooth, so all of the features in that region are associated with the properties of the subject lattice-activator system. In the longer-wavelength range starting at about 180-200 nm, one can expect Ce^{3+} f-d transitions bands. Interestingly, the structure of these excitation bands (measured for the 390 nm emission) is quite distinct at low (a) and room (b) temperatures. A typical temperature-induced band broadening and shift are definitely not sufficient to explain observed differences. Since in $K_3Lu(PO_4)_2$ crystals, the Ce^{3+} substitutes only for the host Lu^{3+} ions, the observed effect has to be linked with the local lutetium coordination and symmetry changes. At the lowest temperatures, the material has a monoclinic symmetry and the Lu ions (and consequently also Ce ions) are seven-coordinated with the oxygen atoms. In the next figure we will label the luminescence corresponding to these temperatures as an emission I. As the temperature increases, at about 175 K, the material undergoes a transition that does not change the monoclinic structure, but that decreases the Lu coordination from seven to six. As will be shown, this rather drastic structural change, somewhat surprisingly, does not result in a correspondingly large change in the Ce emission. A second phase transition to a pseudo-hexagonal structure, occurs at about 240 K. Above this temperature, two non-equivalent (although both are six-coordinated) Lu sites persist. As a result, one can expect (and in fact we observe) two types of Ce emission – labeled as II and III.

The luminescence spectra measured at various temperatures are presented in Figure 2. The excitation wavelength in the VUV range [90 nm – spectra (a–d)] generates electron-hole (e-h) pairs that, to some extent, resemble excitation with ionizing radiation. The spectrum acquired at 11 K (a) is representative of emission I, and is practically identical to the corresponding x-ray-excited emission spectrum. Only slight changes occur up to 230 K (b). The only difference at this temperature is a constituent band broadening that is due to either a temperature-produced increase in the electron-phonon interaction, or the lower-temperature crystal structure transformation. After the second phase transition, the emission spectrum is completely altered. The spectra acquired at 260 K (c) and at RT (d) are virtually indistinguishable Gaussian-shaped bands centered at about 397 nm. – We label this emission as II. These spectra are also quite similar, but not identical to the x-ray excited luminescence spectrum.. The latest one seems to be a combination of emission II and much weaker "convexity" on its short-wavelength side, at around 360 nm. The excitation spectrum measured at this wavelength (not presented here) was almost identical to that measured at 390 nm, with only a slight difficult-to-discern modification of the specific f-d band relative intensities. An obvious conclusion is that this "convexity" also represents Ce emission - although characteristic of a Ce site other than the one associated with emission II. A proper selection of the excitation wavelength in the range below the bandgap allows one to "turn on" particular emissions. Trace (e) shows emission I excited by 305 nm synchrotron radiation at 11 K. This spectrum is practically identical to the spectra obtained under x-ray and VUV excitations at this temperature. While the 326 nm excitation at RT (f) produces mostly emission II, the 267 nm excitation leads to spectrum (g) with an evident admixture of emission III.

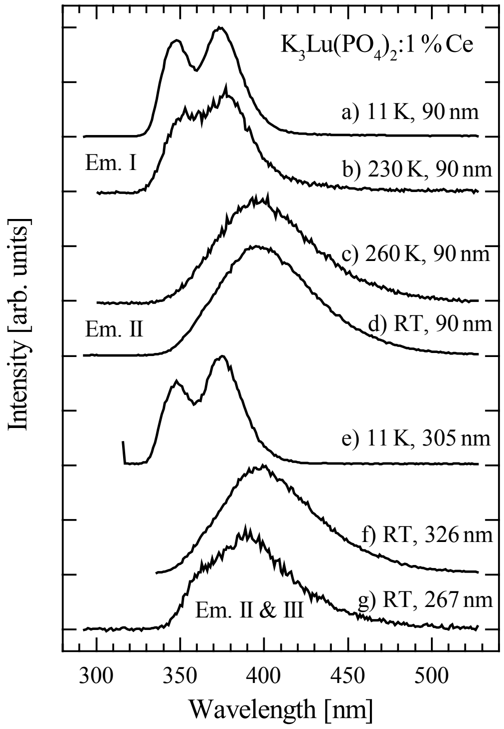

Figure 2: The luminescence spectra: (a), (b), (c), and (d) 90 nm excitation at 11, 230, 260 and 300 K, correspondingly; (e) 305 nm excitation at 11 K; (f) 326 nm excitation at RT; (g) 267 nm excitation at RT.

The presented spectroscopy of the Ce^{3+} *d-f* emission in $K_3Lu(PO_4)_2$ is a classic example of the influence of multiple sites and crystalline phase transitions on the behavior of luminescence centers in a host lattice. The subject materials clearly deserve more attention and further study involving an extended range of Ce-activation.

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References

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