

Diaz Research Group: Using Vacuum Ultraviolet Spectroscopy to Study Electron Migration and Trapping in Luminescent Materials

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Introduction:

Phosphors are materials that emit visible light when exposed to some excitation source, such as ultraviolet (UV) or vacuum ultraviolet (VUV) radiation. Phosphors absorb the excitation energy and then emit light at some longer wavelength in the visible spectrum. Such phosphors are used in everyday fluorescent lighting, which include a combination of red, green, and blue phosphors (**Figure 1**). These phosphors are comprised of a solid-state host into which a small amount of dopant is added. For example, the red phosphor in Figure 1 is $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$ - a small amount of Eu^{3+} in an yttrium oxide host lattice. The red emission comes from the Eu^{3+} .

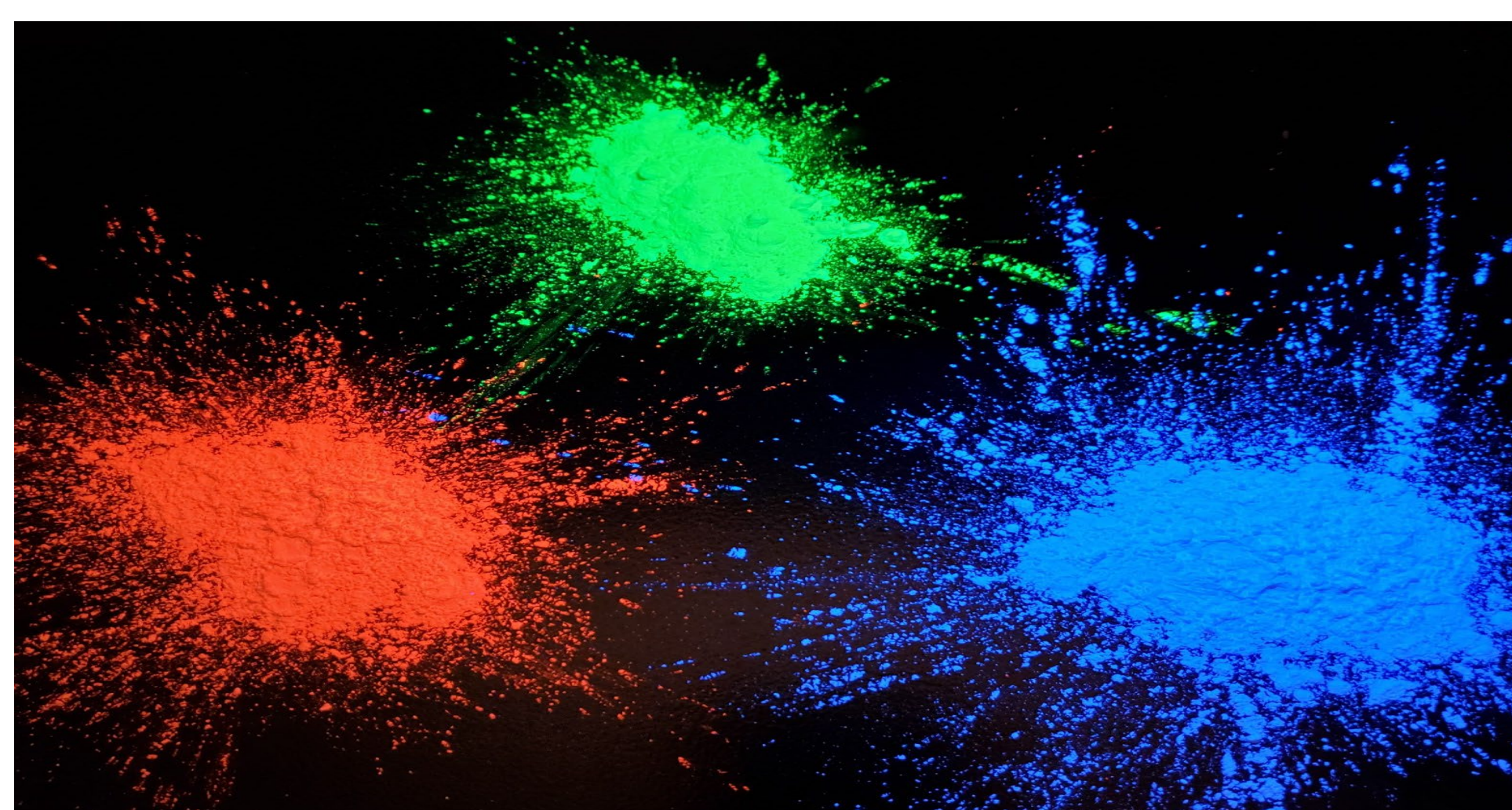


Figure 1: Common fluorescent lamp phosphors.

For solid-state materials, the photons are absorbed either by the host lattice or the dopant atoms, depending on the energy. When the material is exposed to energies greater than the band gap and excitation occurs, an electron-hole (e-h) pair is produced in the host. This electron hole pair can migrate to the surface of the material and revert to the ground state, or it can be trapped by the dopant or by defects (**Figure 2**). **The fraction of e-h pairs that are captured by the dopant is called the transfer efficiency, η_t .**

The overall goal of this research is to further our understanding of structure property relationships in luminescent materials such that accurate predictions can be made about a material's optical properties based on its composition and its electronic and crystal structure. Areas of interest are:

1. What are the important relationships between the crystal and electronic structure of a phosphor and the resulting efficiency under VUV excitation?
2. How can we estimate the amount of energy lost to the particle surface? And
3. How do different kinds of defects impact the phosphor efficiency?

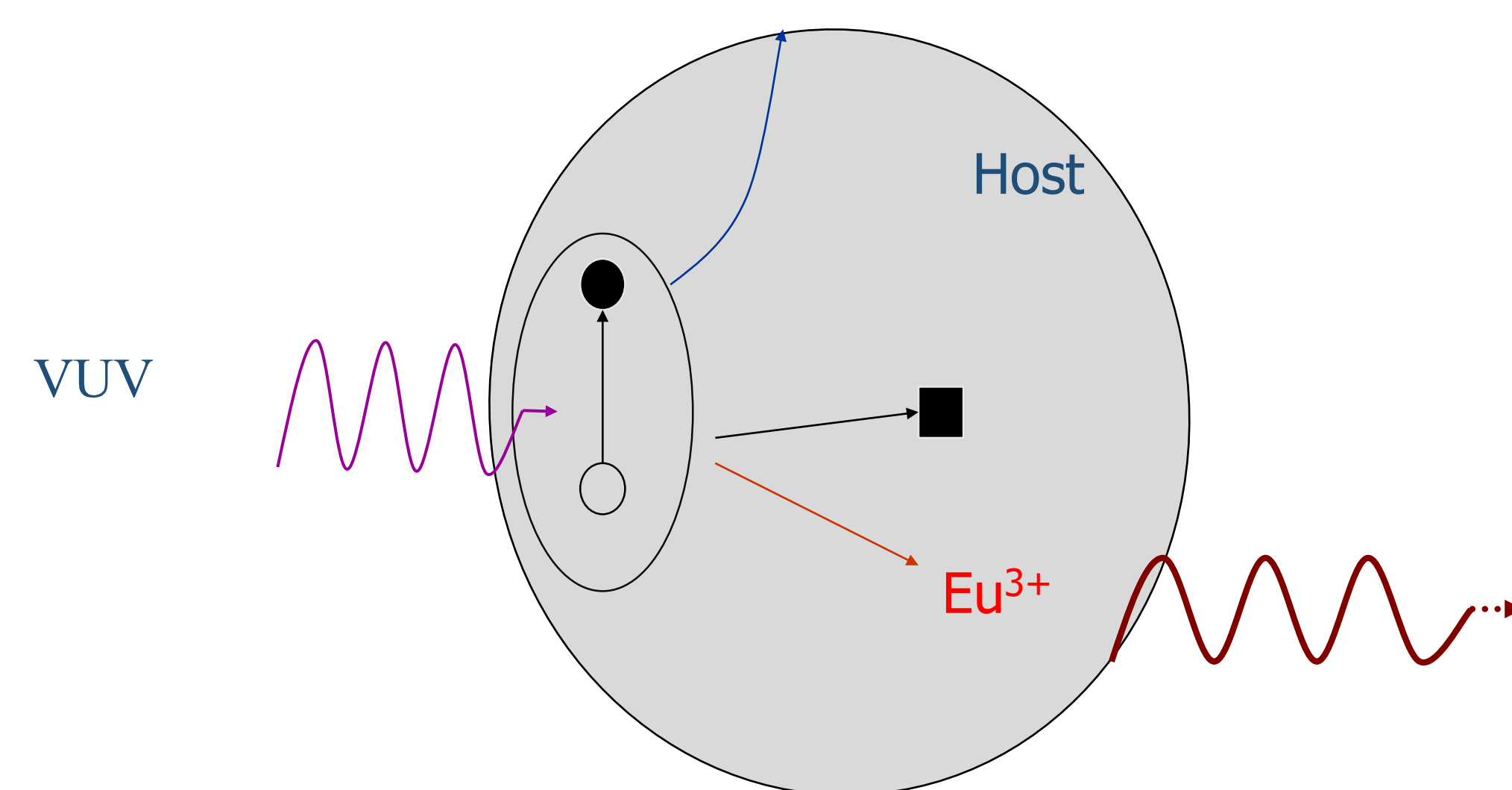


Figure 2: Diagram of energy transfer through a doped phosphor. An electron-hole pair created in the host can be trapped by a luminescent dopant (Eu^{3+}), trapped by defects, \square , or lost to the particle surface.

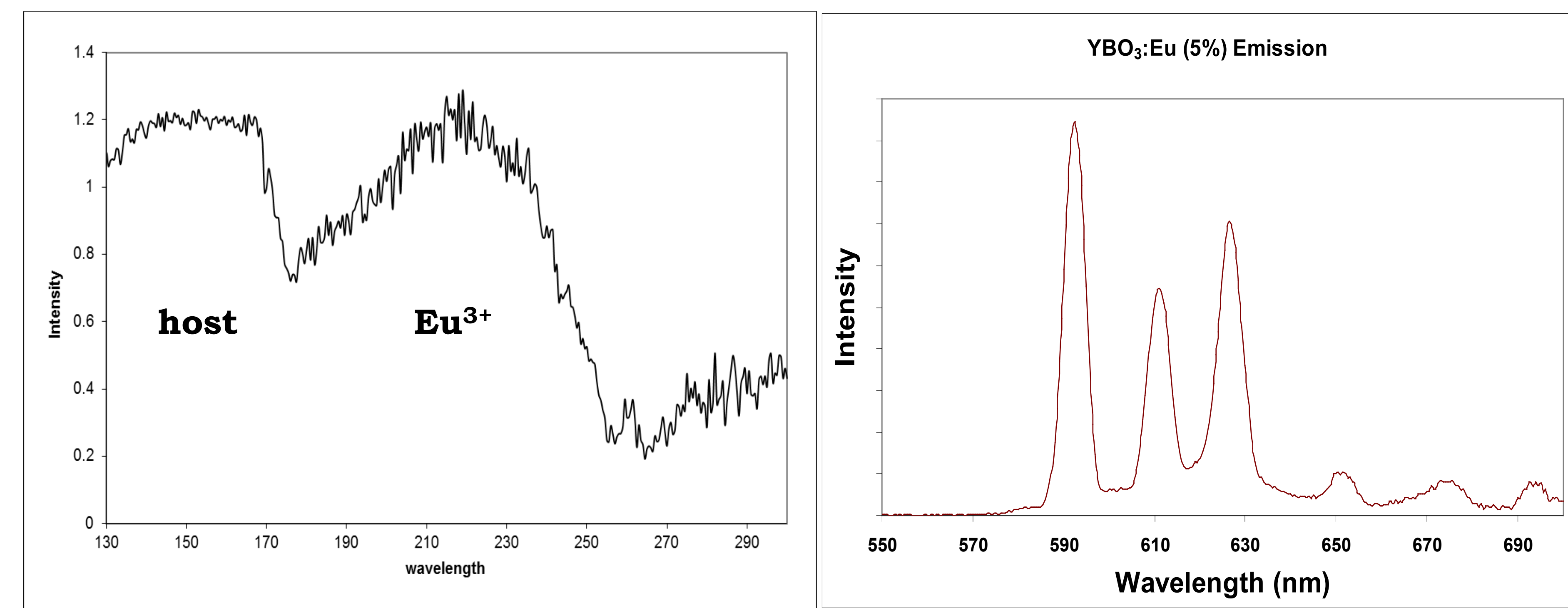


Figure 3: Excitation and Emission spectra of Eu^{3+} doped YBO_3 . Excitation at wavelengths shorter than 165 nm occurs via the host, while excitation at longer wavelengths occurs directly at the dopant.

Example Studies

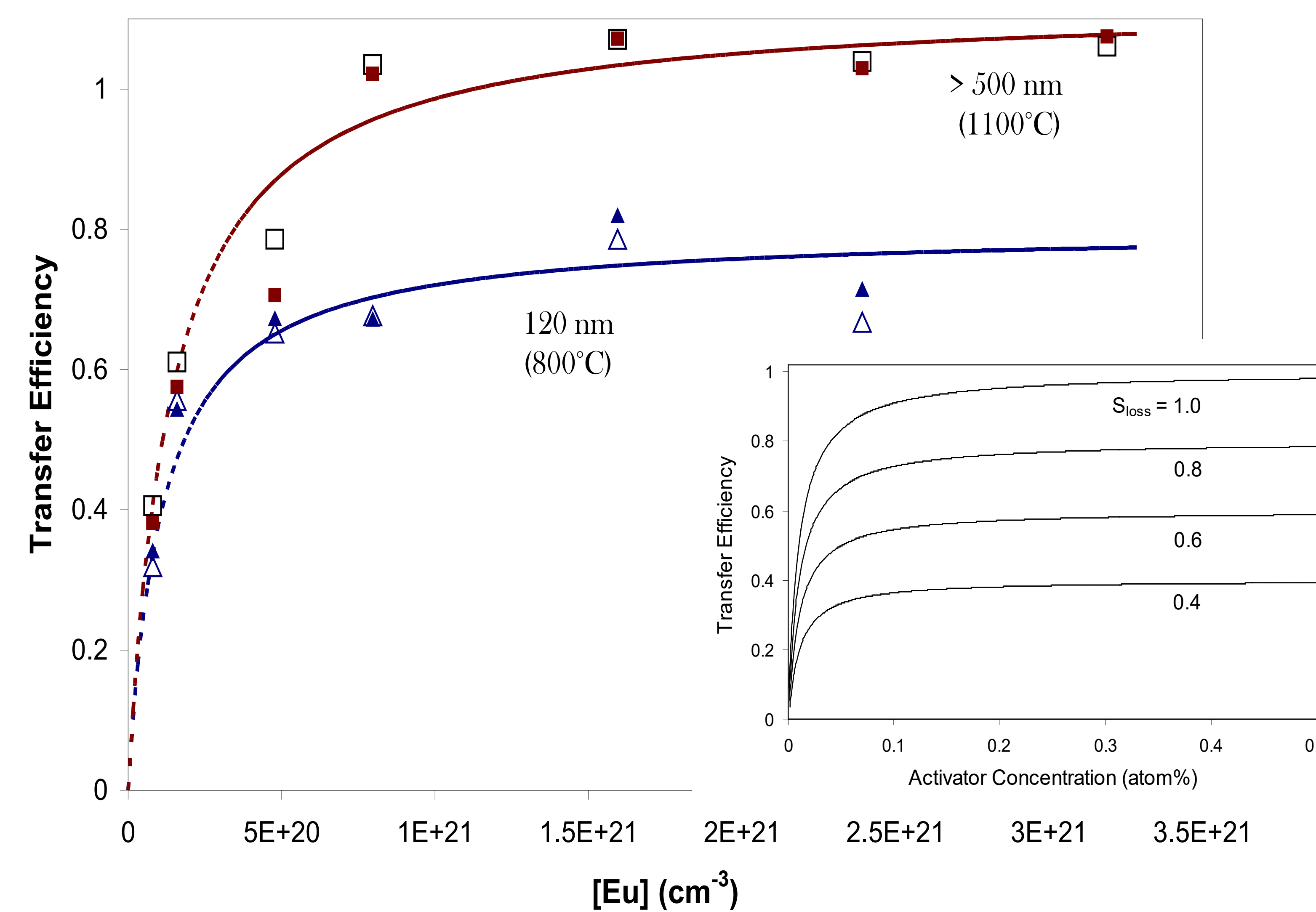


Figure 4: Transfer efficiency in Eu^{3+} doped YBO_3 with different particle sizes. **Inset:** theoretical models of the affect of surface losses on ht. The “flattening out” of the curve is due to about 25% of the energy being lost to the surface.

Selected References:

- M. Swinhart, A. DeLarme, A. Diaz., “A study of the impact of oxygen vacancies on the VUV efficiency of rare-earth doped YBO_3 via Ca^{2+} co-doping,” *Optical Materials* **127** 112261 (2022).
- A. L. Diaz, “Review – Progress in Understanding Host-Sensitized Excitation Processes in Luminescent Materials,” *Invited. ECS Journal of Solid State Science and Technology* **8** R14 (2019).
- M. Wallace and A. L. Diaz, “Systematic trends in electron-hole pair trapping efficiency of rare earth doped YBO_3 under vacuum ultraviolet excitation,” *Journal of Luminescence* **161** 403 (2015).

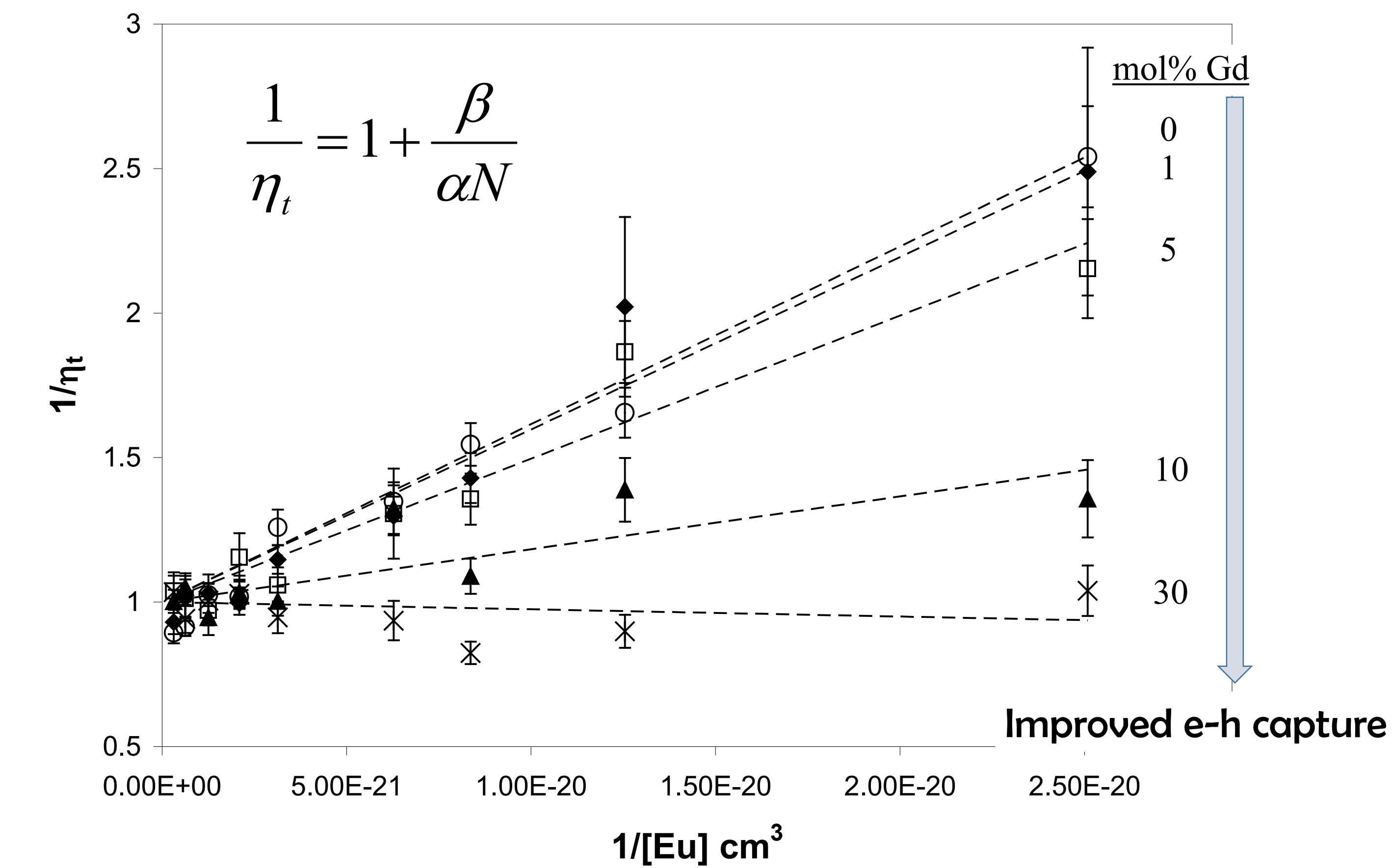


Figure 5: $\text{YBO}_3:\text{Gd},\text{Eu}$. Theoretical models predict that a plot of $1/\eta_t$ vs. $1/[\text{Eu}]$ will be linear with a slope of β/α , where β represents trapping by killers and α represents trapping by the dopant. A shallower slope implies more efficient trapping. In this case the addition of Gd^{3+} to the YBO_3 lattice greatly improves the migration and trapping of e-h pairs to the Eu^{3+} dopant.

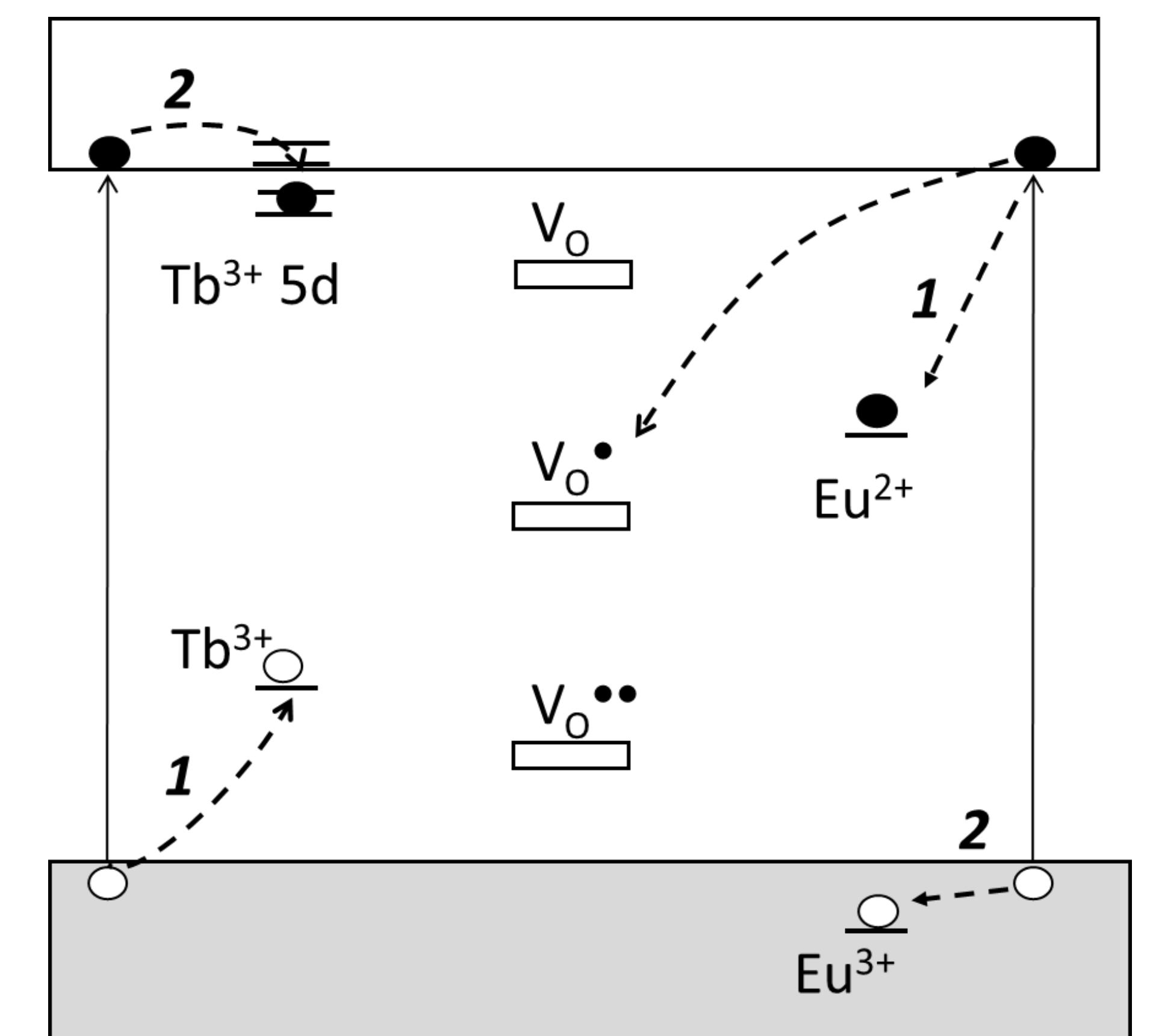


Figure 6: Energy level diagram showing how oxygen vacancies (V_O) compete with dopants to trap e-h pairs. The trapping mechanisms of Tb^{3+} and Eu^{3+} are different, leading to differences in the impact of the vacancies.

K. Olsen, A. Lawler, and A. L. Diaz, “Quantitative Assessment of Surface Loss in Nanocrystalline $\text{YBO}_3:\text{Eu}^{3+}$ from Measurements of Host-to-Activator Transfer Efficiency,” *Journal of Physical Chemistry C* **115** 17136 (2011).

R. L. Rabinovitz, K. J. Johnston, and A. L. Diaz, “Investigation of the Effect of Gd^{3+} on Host-to-Europium Transfer Efficiency in $(\text{Y},\text{Gd})\text{BO}_3:\text{Eu}^{3+}$ Under VUV Excitation,” *Journal of Physical Chemistry C*, **114** 13884 (2010).