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Luminescence Studies on Substituted (Y,Lu)(Al,Ga)$_3$(BO$_3$)$_4$

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Numerous types of borates for optical applications have long been studied, already. For instance, prominent phosphors for plasma displays on borate basis are (Y,Gd)BO$_3$:Eu^{3+} and (Y,Gd)BO$_3$:Tb^{3+}(Bi^{3+}).[1,2] More recently, borates have come into focus again, due to their possible use as laser gain media and their high band gap (≈5.7 eV).[3] Especially interesting are systems that feature self-frequency doubling and can thus be used to convert NIR radiation into visible light. Up to now, only a couple of materials seem suitable for that use. YAl$_3$(BO$_3$)$_4$ (YAB) doped by Nd or Yb is one of them. In the meantime, thorough investigations on the luminescence and electronic properties have been carried out on the material.[4,5] Interestingly enough though, investigations on the modified systems LuAl$_3$(BO$_3$)$_4$ and (Y,Lu)(Al,Ga)$_3$(BO$_3$)$_4$, respectively, are rare. In this study, we present the effects of Ga and/or Lu co-doping on the photoluminescence properties of YAB:Ce^{3+} as well as the influence of Gd^{3+} co-doping on YAB:Tb^{3+}. Therefore, excitation and emission spectra ranging from the VUV to the visible range of the spectrum were recorded. Additionally, studies on the thermal quenching behaviour were performed to determine possible energy transfer mechanisms and optimal temperature ranges for applications.

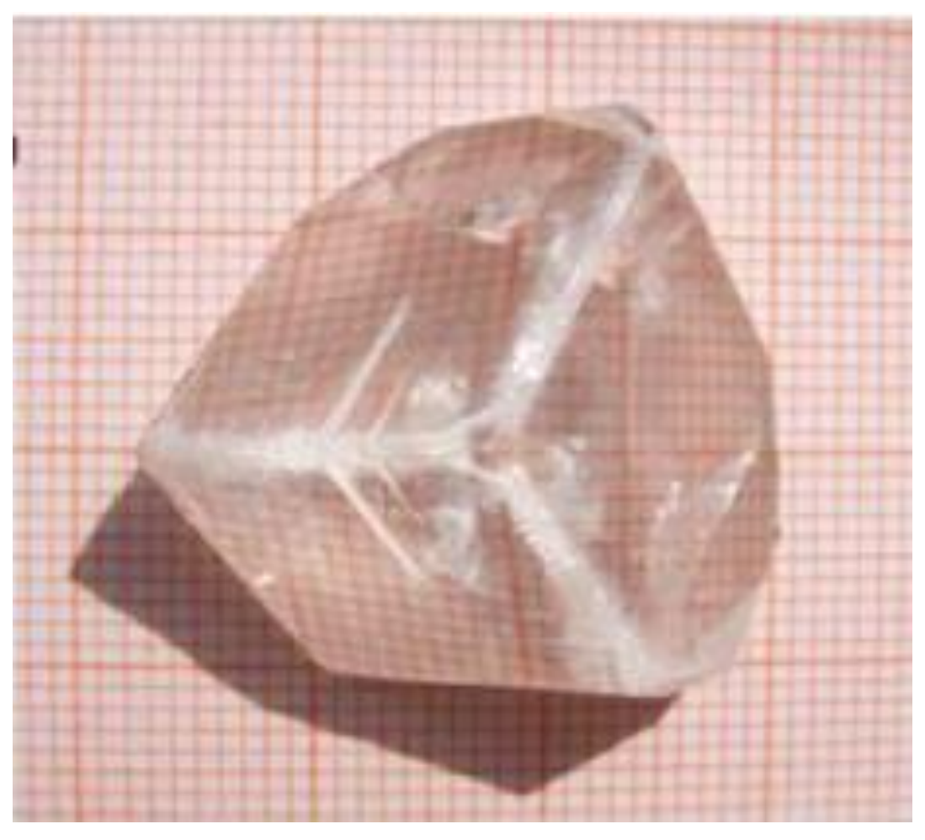

Fig. 1 LuAl$_3$(BO$_3$)$_4$ crystal [6]

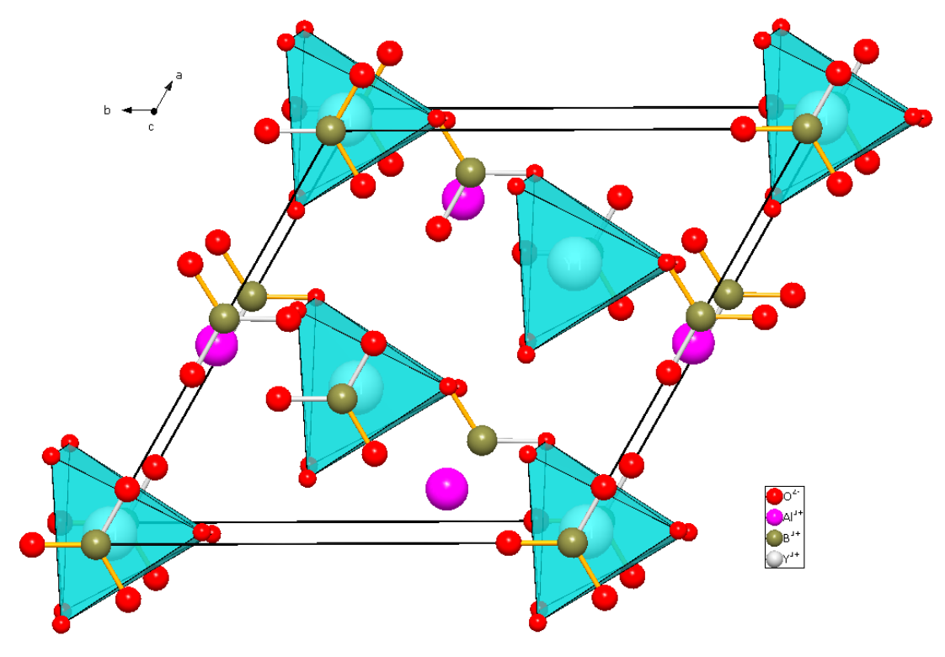

Fig. 2 Crystal structure of YAl$_3$(BO$_3$)$_4$ [7]

(Y,Lu)(Al,Ga)$_3$(BO$_3$)$_4$ crystallises in a huntite-like structure (CaMg$_3$(CO$_3$)$_4$), wherein the lanthanide ions are coordinated by two slightly rotated (≈8.3 °) oxygen triangles in a trigonal prismatic fashion leading to D$_3$ symmetry of the site. Further characteristics of the structure are layers of isolated alternating BO$_3^{3-}$ units and metal layers along <001> coinciding with the crystallographic c-axis. Relatively spacious aluminium octahedra lead to a large minimal distance between the individual lanthanide ions of around 5.9 Å. Finally, the minimal distance between aluminium and yttrium (≈3.6 Å) should be highlighted, since substitution of these ions is investigated in this study.

Crystallographic data of YAl$_3$(BO$_3$)$_4$ *[7]*

Crystal system	trigonal
Space group	R 32 (155)
Cell parameters	a = b = 9.29 Å c = 7.24 Å V = 541.13 Å^3 Z = 3

(Y,Lu)(Al,Ga)$_3$(BO$_3$)$_4$:Ce^{3+}

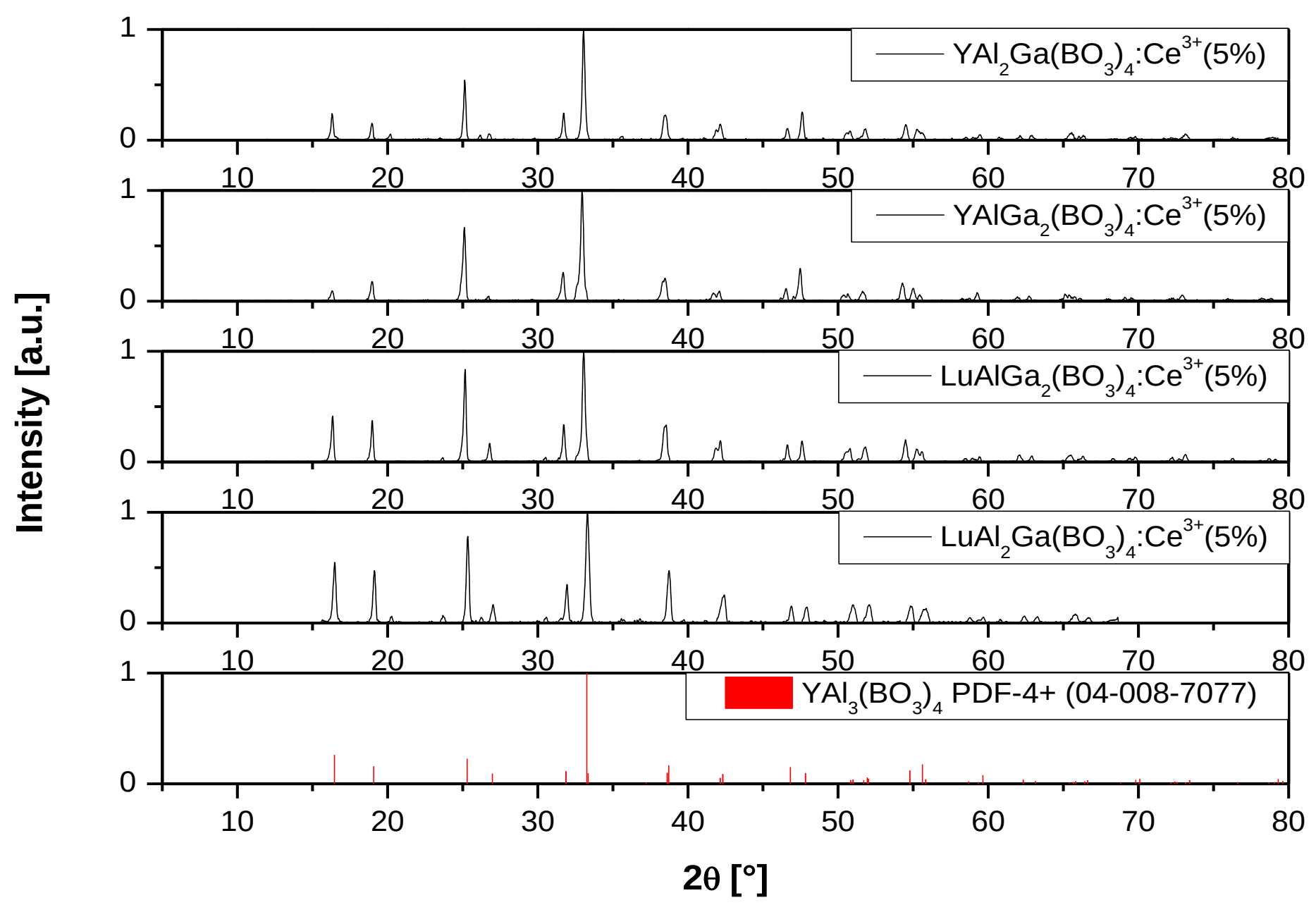

Fig. 3 Powder patterns of various substituted (Y,Lu)(Al,Ga)$_3$(BO$_3$)$_4$ compounds

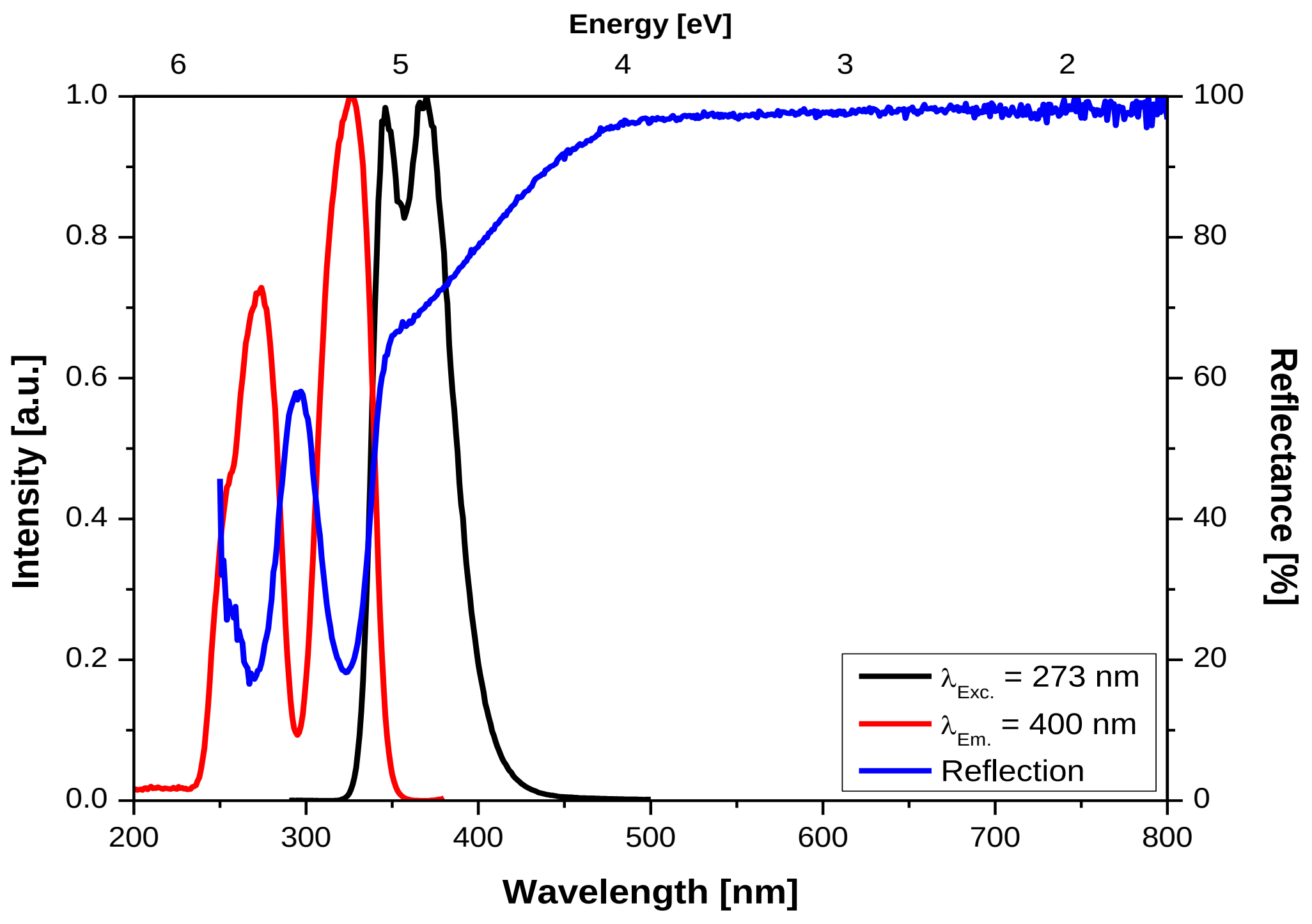

Fig. 4 Excitation, emission and reflection spectra of LuAl$_3$(BO$_3$)$_4$:Ce^{3+}(5%)

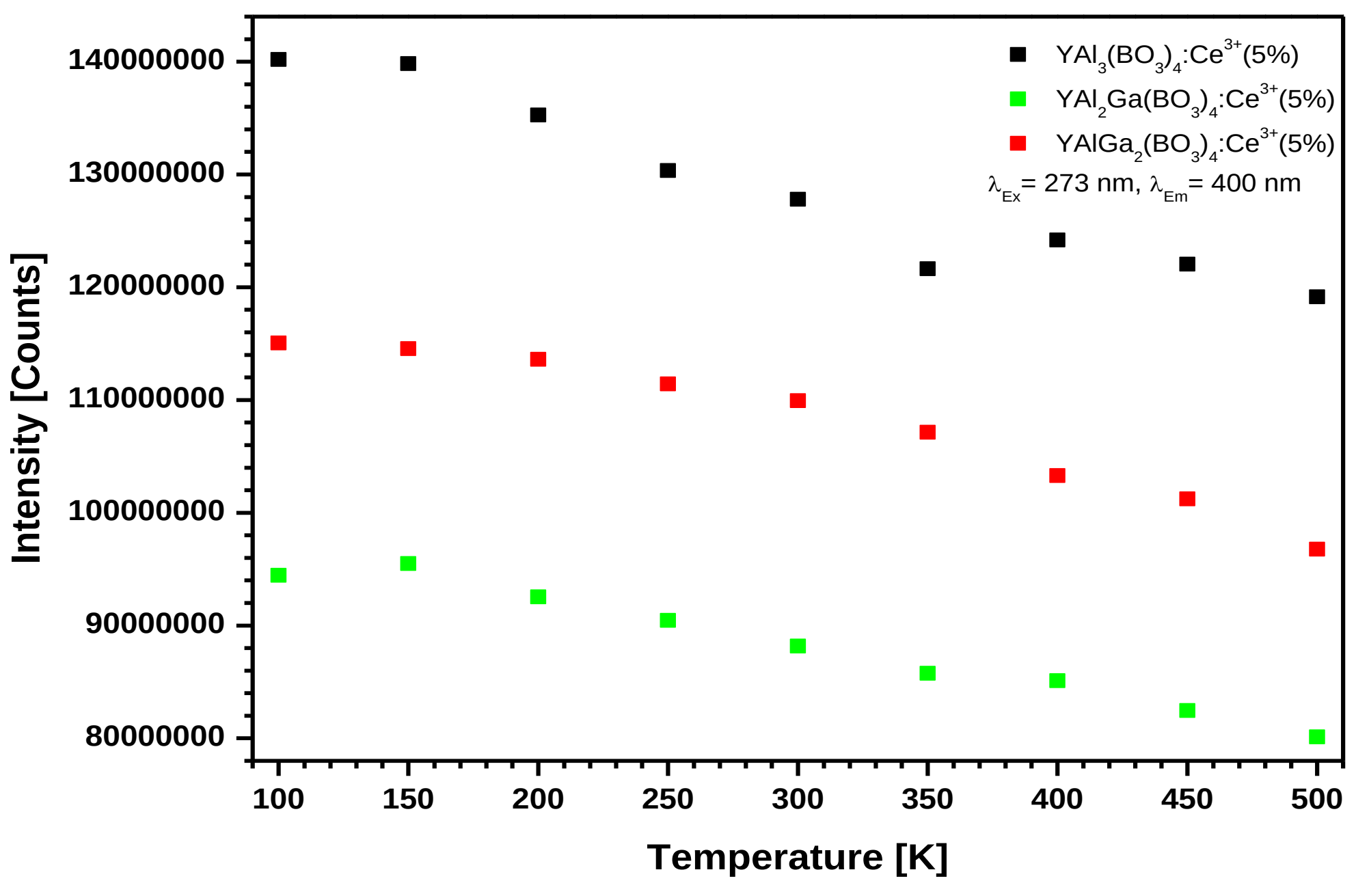

Fig. 5 Temperature dependant emission integrals of YAl$_3$(BO$_3$)$_4$:Ce^{3+}(5%), YAl$_2$Ga(BO$_3$)$_4$:Ce^{3+}(5%) and YAlGa$_2$ (BO$_3$)$_4$:Ce^{3+}(5%)

Acknowledgement

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Energy Transfer in YAl$_3$(BO$_3$)$_4$:Gd^{3+},Tb^{3+}

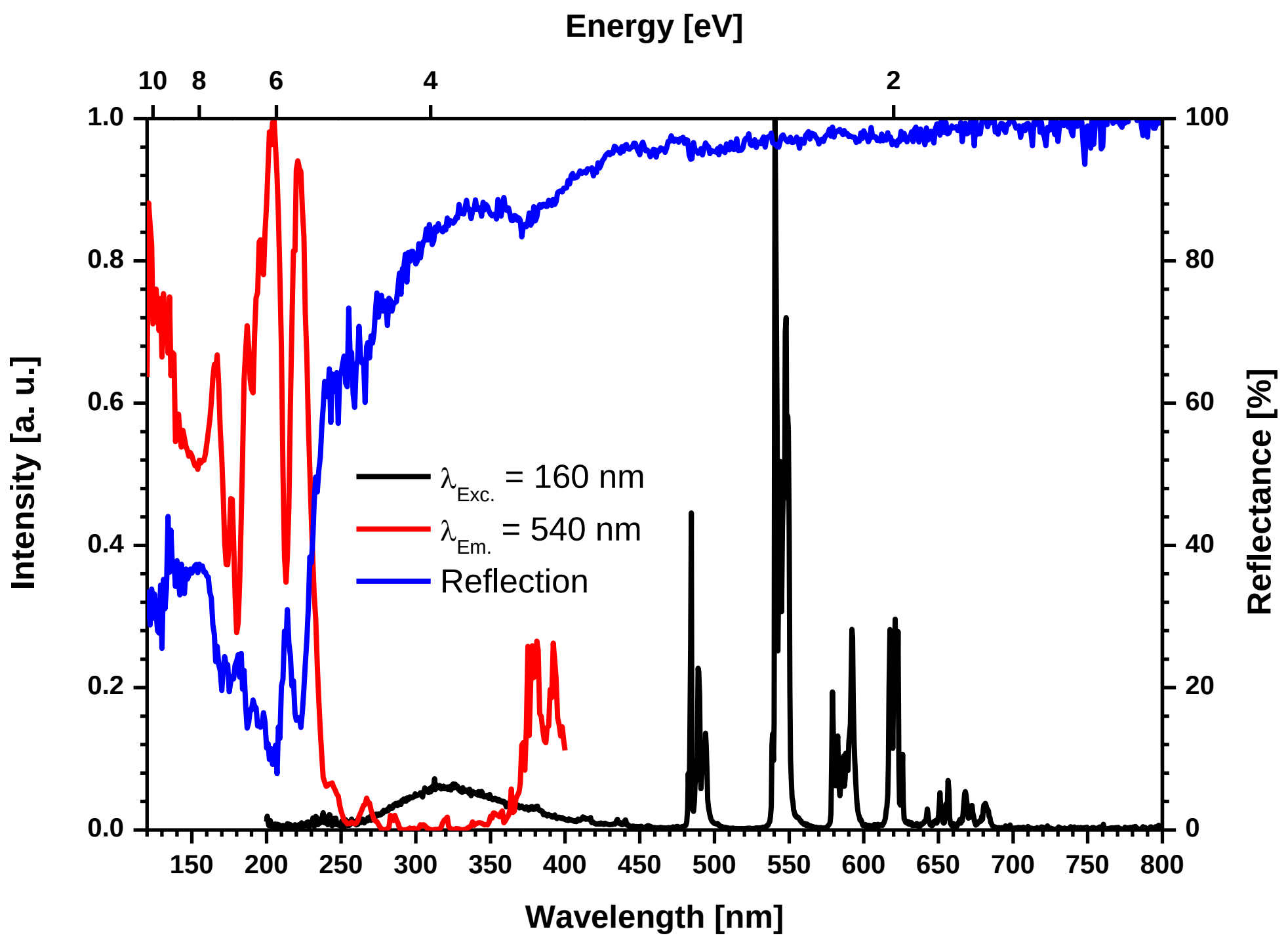

Fig. 6 VUV excitation, emission and reflection spectra of YAl$_3$(BO$_3$)$_4$:Tb^{3+}(5%)

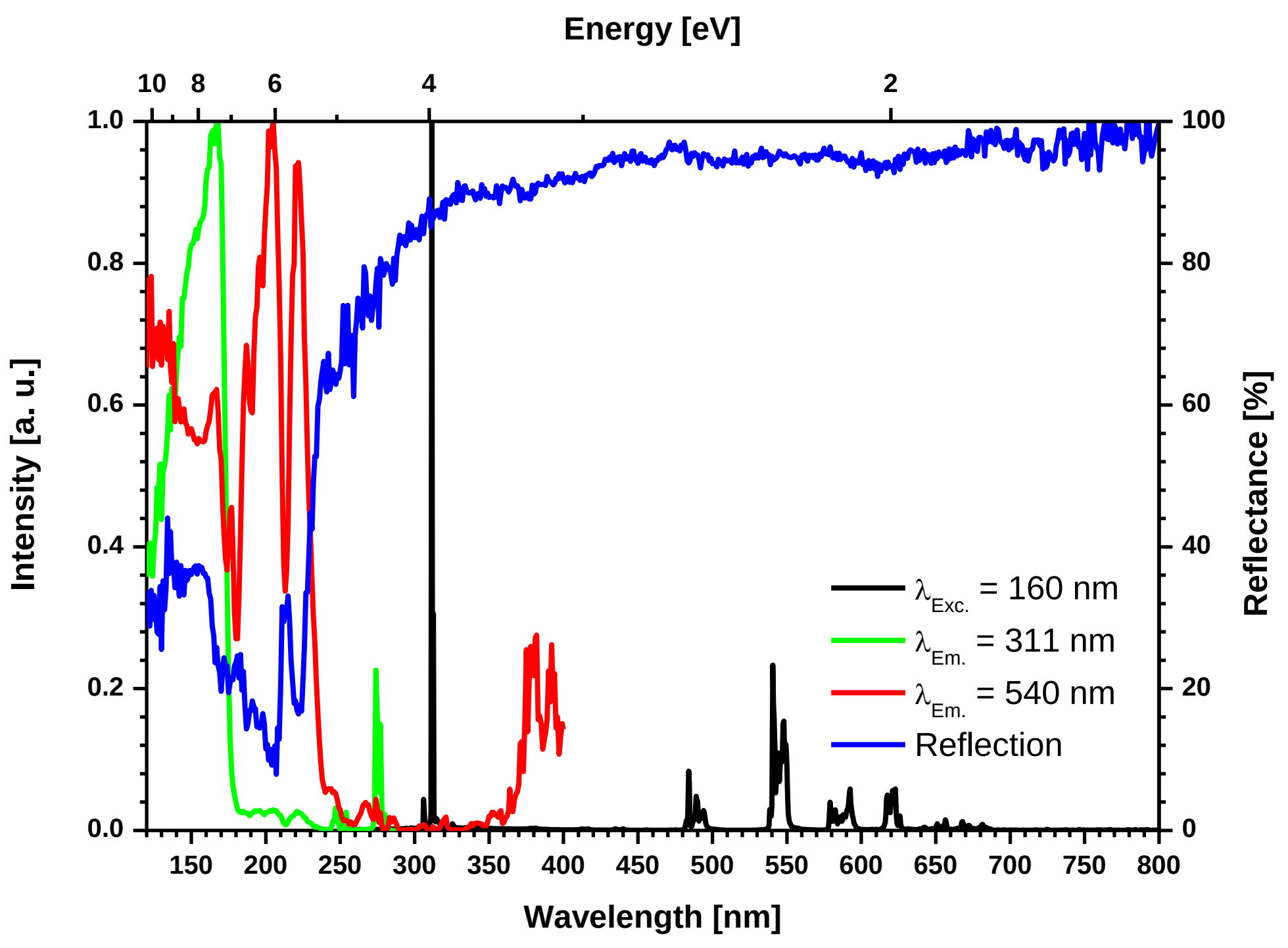

Fig. 7 VUV excitation, emission and reflection spectra of YAl$_3$(BO$_3$)$_4$:Gd^{3+},Tb^{3+}(10%, 5%)

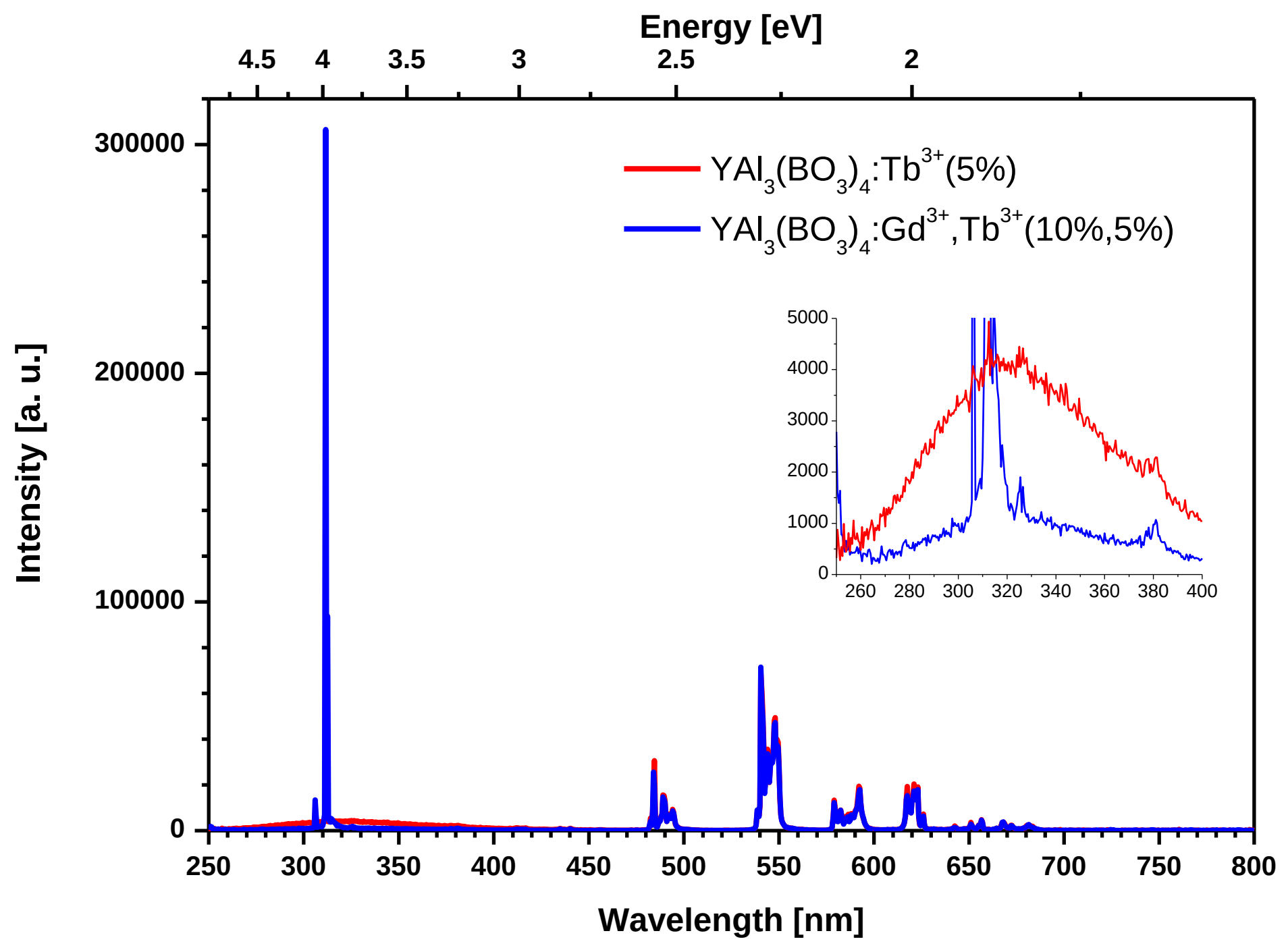

Fig. 8 Comparison of VUV emission spectra of YAl$_3$(BO$_3$)$_4$:Tb^{3+}(5%). and YAl$_3$(BO$_3$)$_4$:Gd^{3+},Tb^{3+}(10%, 5%)

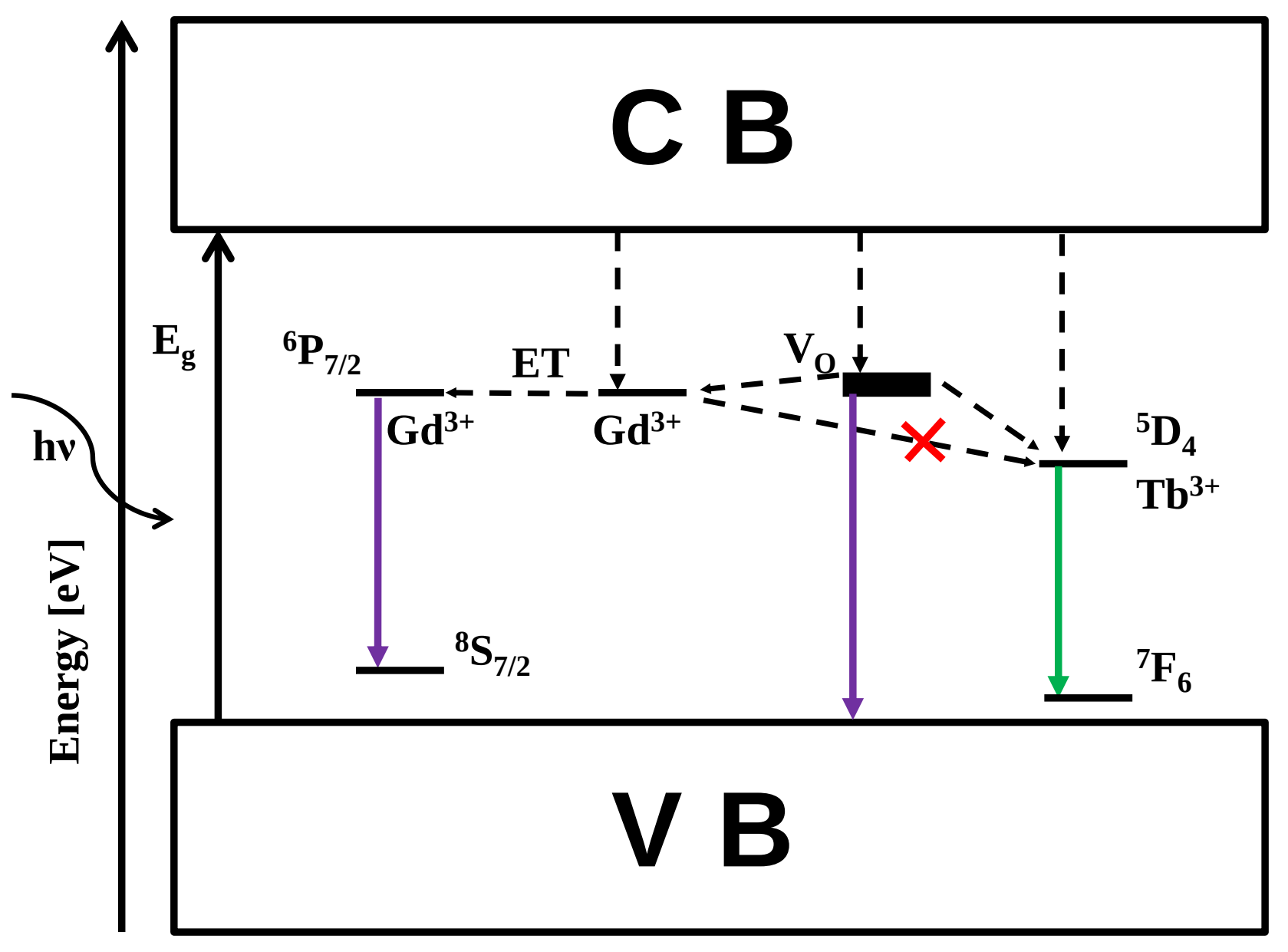

Fig. 9 Schematic energy transfer (ET) mechanisms in YAl$_3$(BO$_3$)$_4$:Gd^{3+},Tb^{3+}(10%, 5%)

Conclusion

The results of the present investigations on gallium/lutetium substituted YAl$_3$(BO$_3$)$_4$:Ce^{3+} and YAl$_3$(BO$_3$)$_4$:Gd^{3+},Tb^{3+} presented in this study, provide insights into the luminescence and energy transfer mechanisms within this host. Cerium doped samples showed characteristic excitation and emission spectra with three distinct excitation and two emission bands (Fig. 4). The excitation band at lowest energy was assigned to the band gap of the material, which fits well with literature values. The other two bands belong to the 4f → 5d excitation into split 5d-states. While the spectra of YAl$_3$(BO$_3$)$_4$:Ce^{3+} and LuAl$_3$(BO$_3$)$_4$:Ce^{3+} seem not to differ at all, the introduction of Ga did lead to significant changes. As expected, the band gap of the material decreased with increasing gallium content. That fits well with observations made with regard to other systems, viz. Lu$_3$(Al,Ga)$_5$O$_{12}$ or (Al,Ga)N. Finally, the most significant impact of substitution turned out to be on the temperature quenching behaviour. A rise in the gallium concentration lead to a more level drop in emission intensity compared to the pure Al compound (Fig. 5).
YAB:Tb^{3+} was co-doped by Gd^{3+} in order to enhance the absorption of Tb^{3+} via energy transfer and thus increase the emission intensity of Tb^{3+}. But in contrast to other known systems, such as ortho-phosphates or (Y,Gd)Ga$_3$(BO$_3$)$_4$, no energy transfer from Gd^{3+} to Tb^{3+} could be measured. Instead, VUV emission spectra indicate a significant reduction of defect luminescence, located at about 250 – 400 nm, if the system is co-doped by Gd^{3+}. Apparently, energy can be transferred efficiently from defects to Gd^{3+} but not to Tb^{3+} (Fig. 8). A proposed excitation/emission scheme is depicted in Fig. 9.

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