

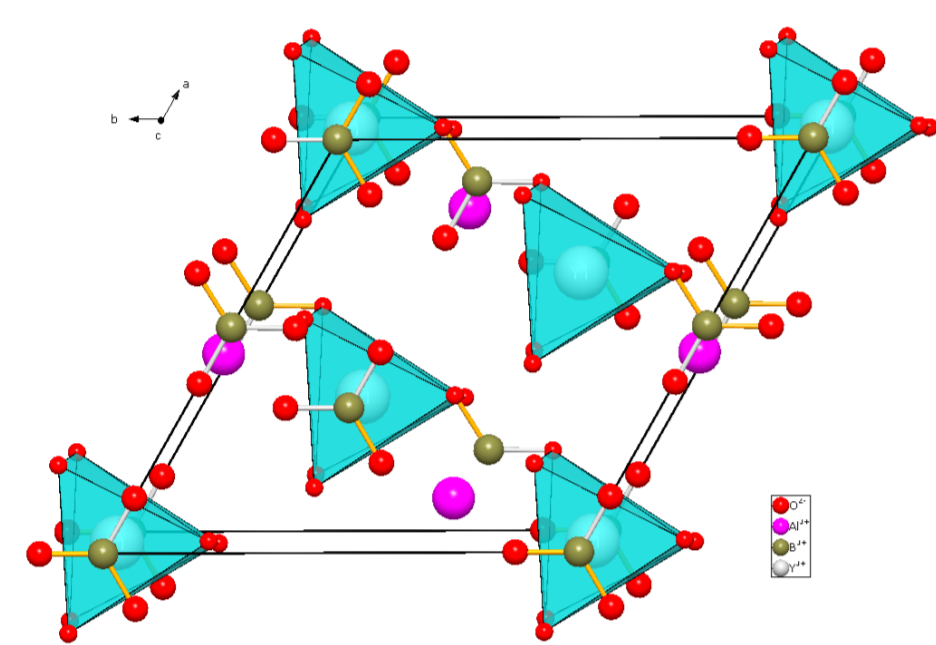

 T. Dierkes^{#,*}, P. Pues[#], R. Pöttgen[‡] and T. Jüstel[#]
[#]Department of Chemical Engineering, Münster University of Applied Sciences, Stegerwaldstraße 39, D-48565 Steinfurt, Germany

[‡]Institut für Anorganische und Analytische Chemie, Universität Münster, Corrensstrasse 30, D-48149 Münster, Germany

^{*}Corresponding author (t.dierkes@fh-muenster.de)

Introduction

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)BO₃:Eu³⁺ and (Y,Gd)BO₃:Tb³⁺(Bi³⁺). [1,2] More recently, borates have come into focus again, due to their possible use as laser gain media. [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. YAl₃(BO₃)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 LuAl₃(BO₃)₄ and (Y,Lu)(Al,Ga)₃(BO₃)₄, respectively, are rare. In this study, we present the effects of Ga and/or Lu co-doping on the photoluminescence properties of YAB. Therefore, excitation and emission spectra ranging from the VUV to the visible range of the spectrum were investigated. Additionally, studies on the thermal quenching behaviour were performed to determine possible energy transfer mechanisms and optimal temperature ranges for applications.

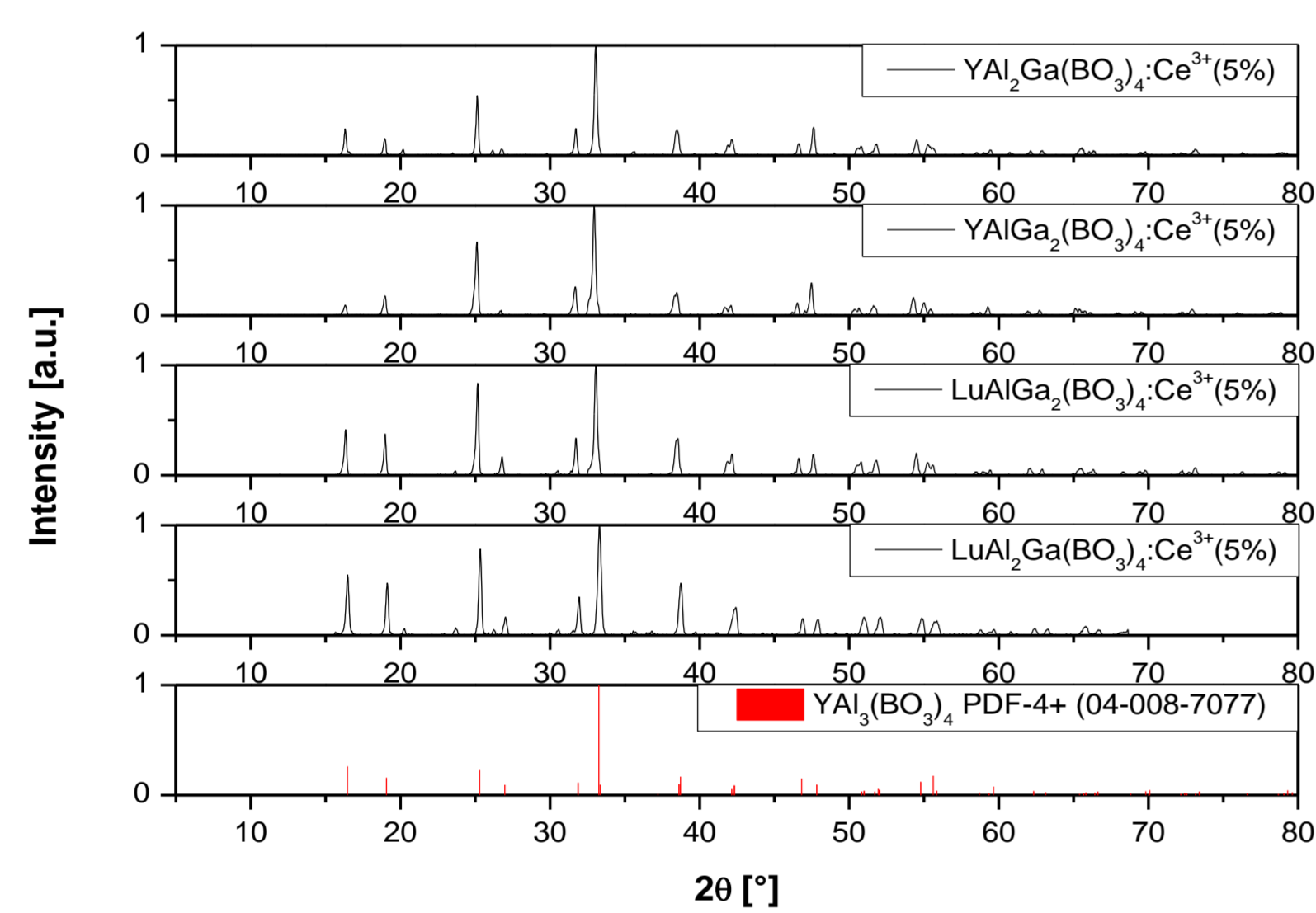
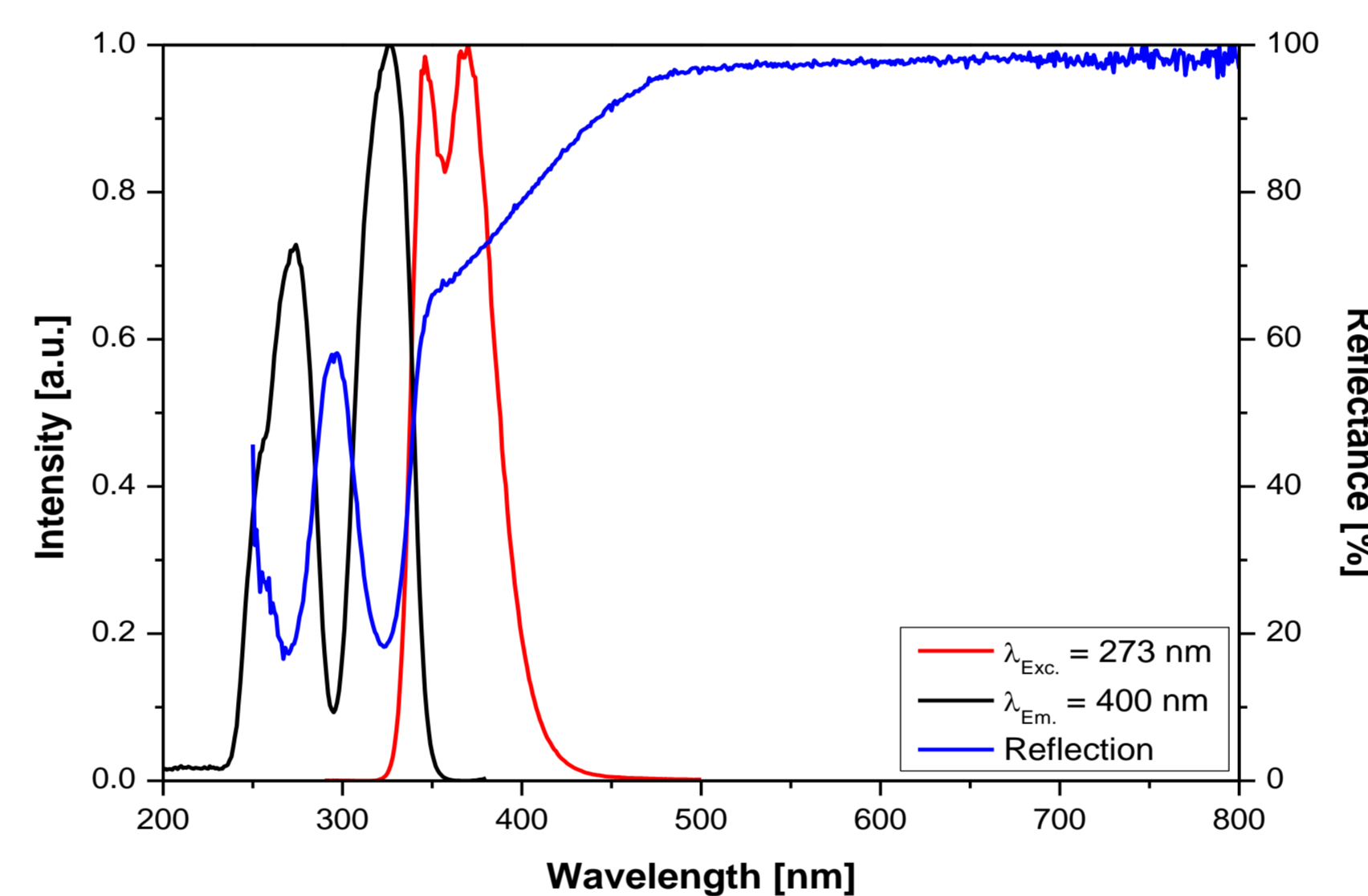
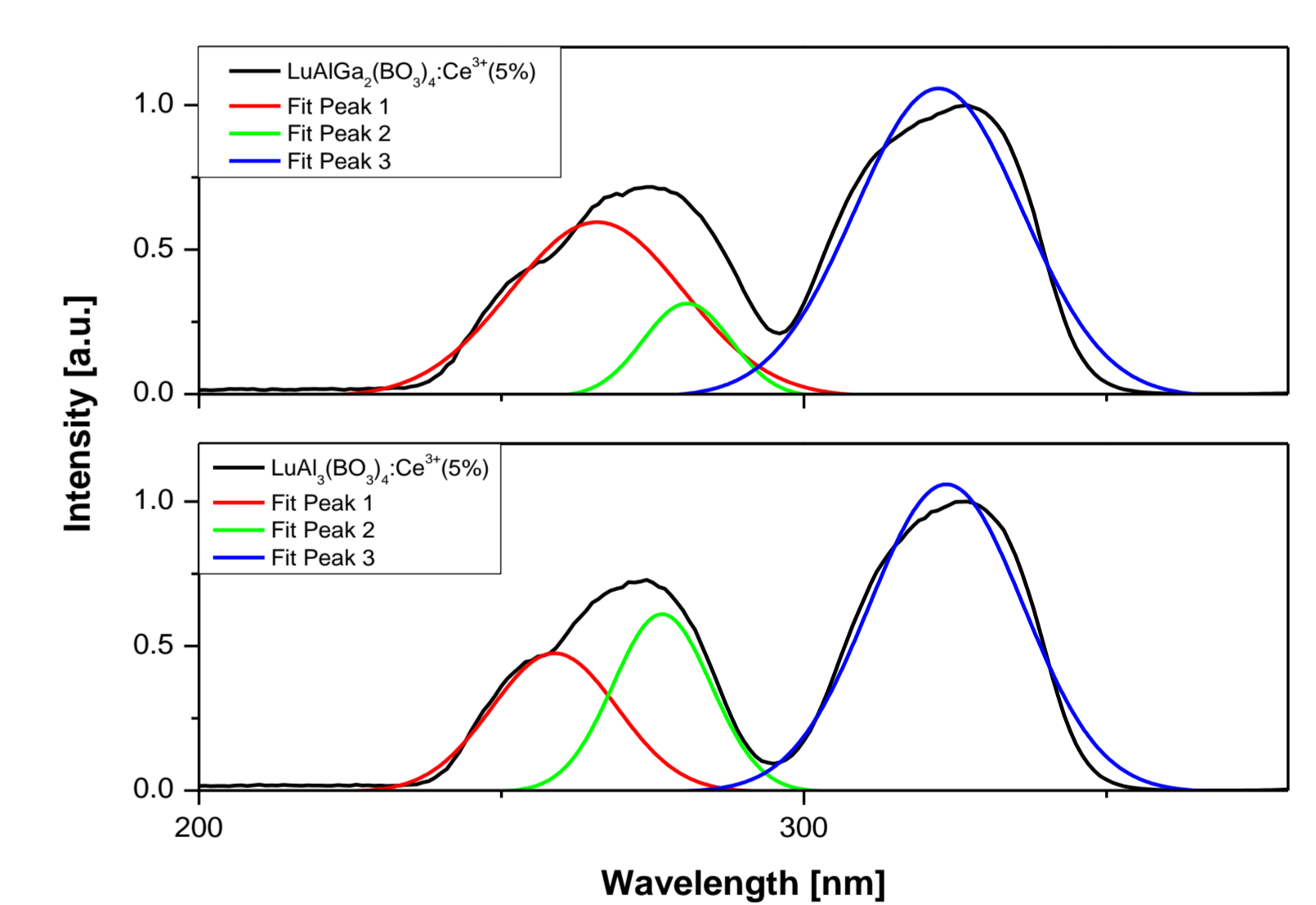
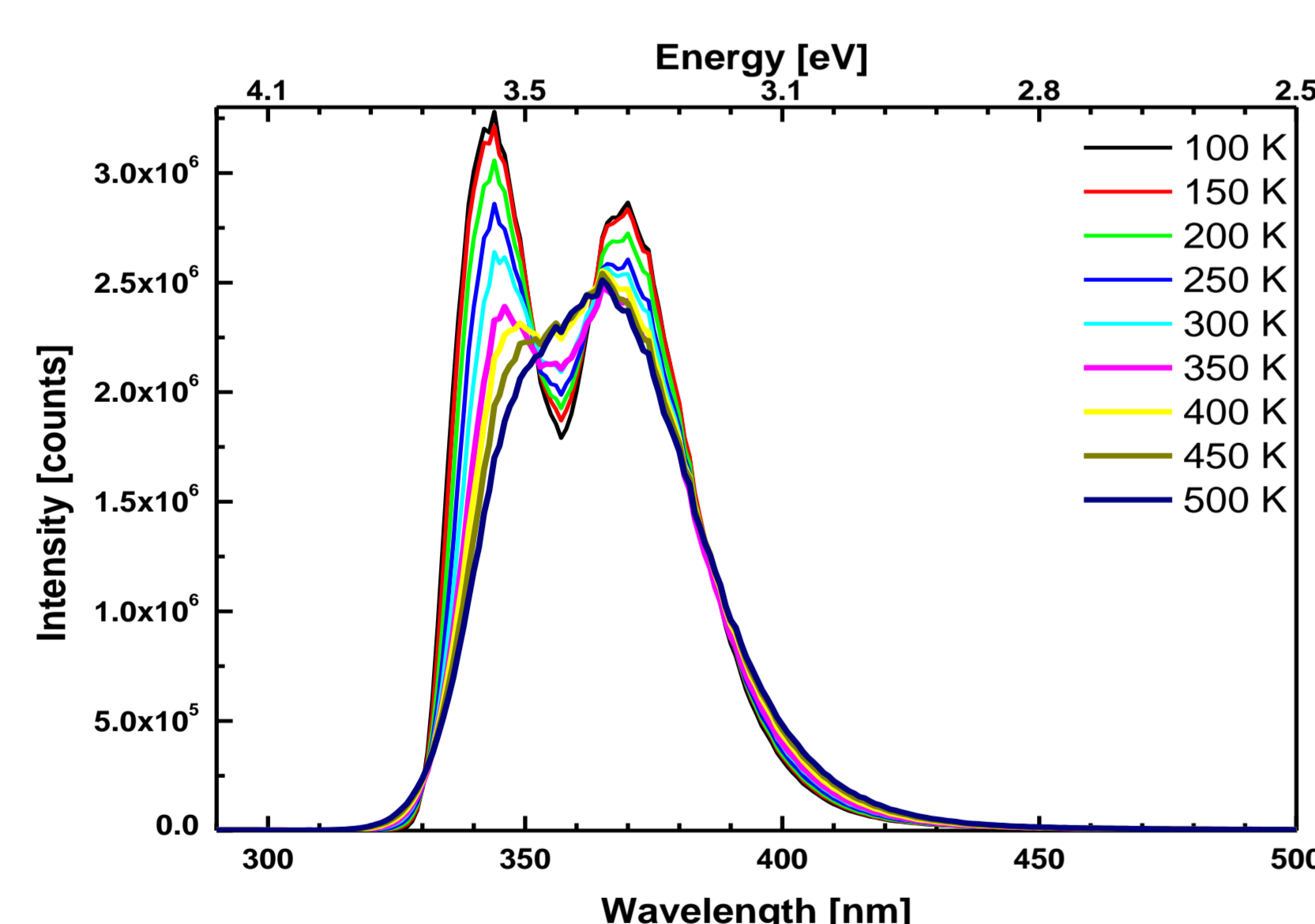
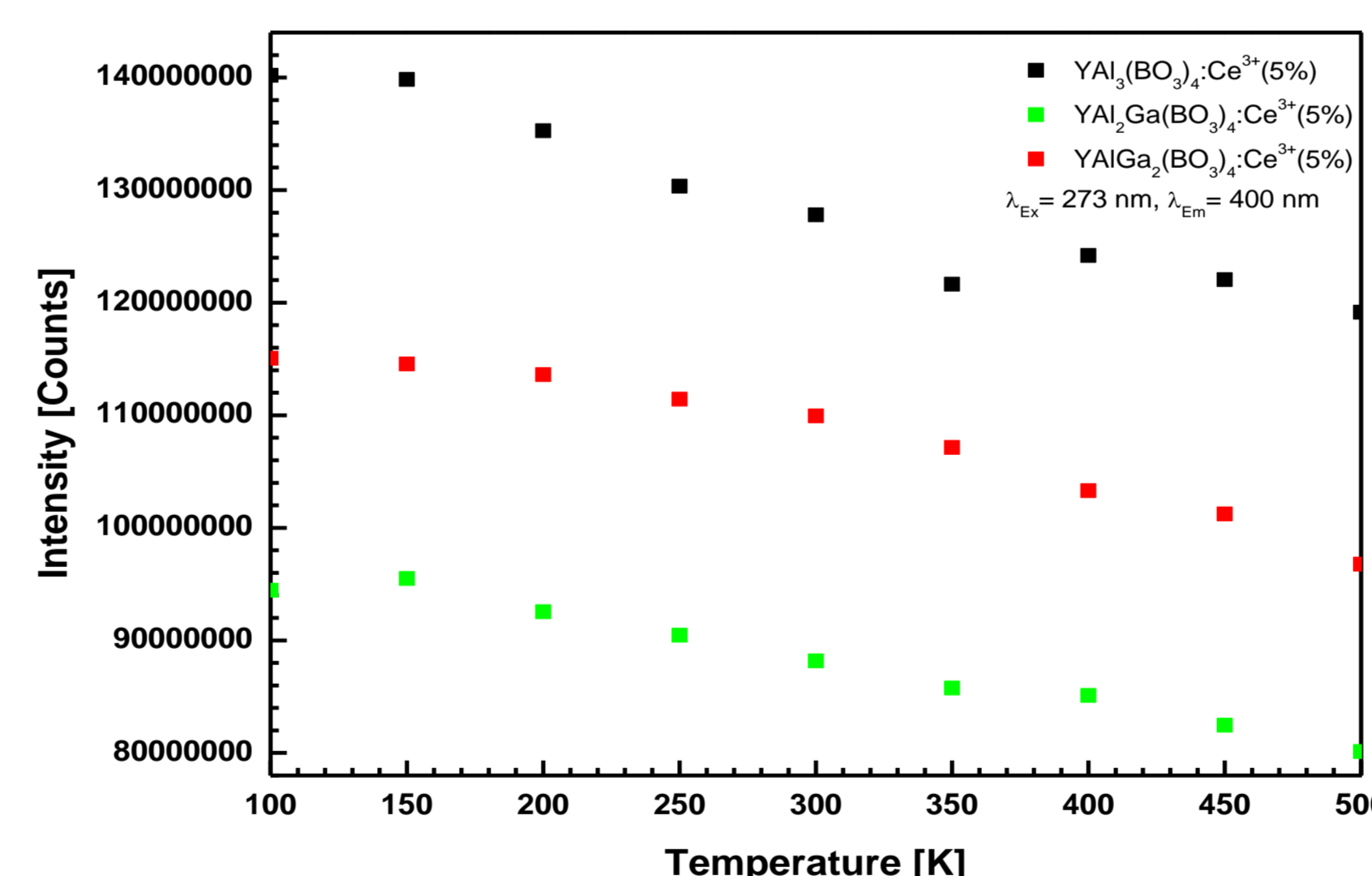
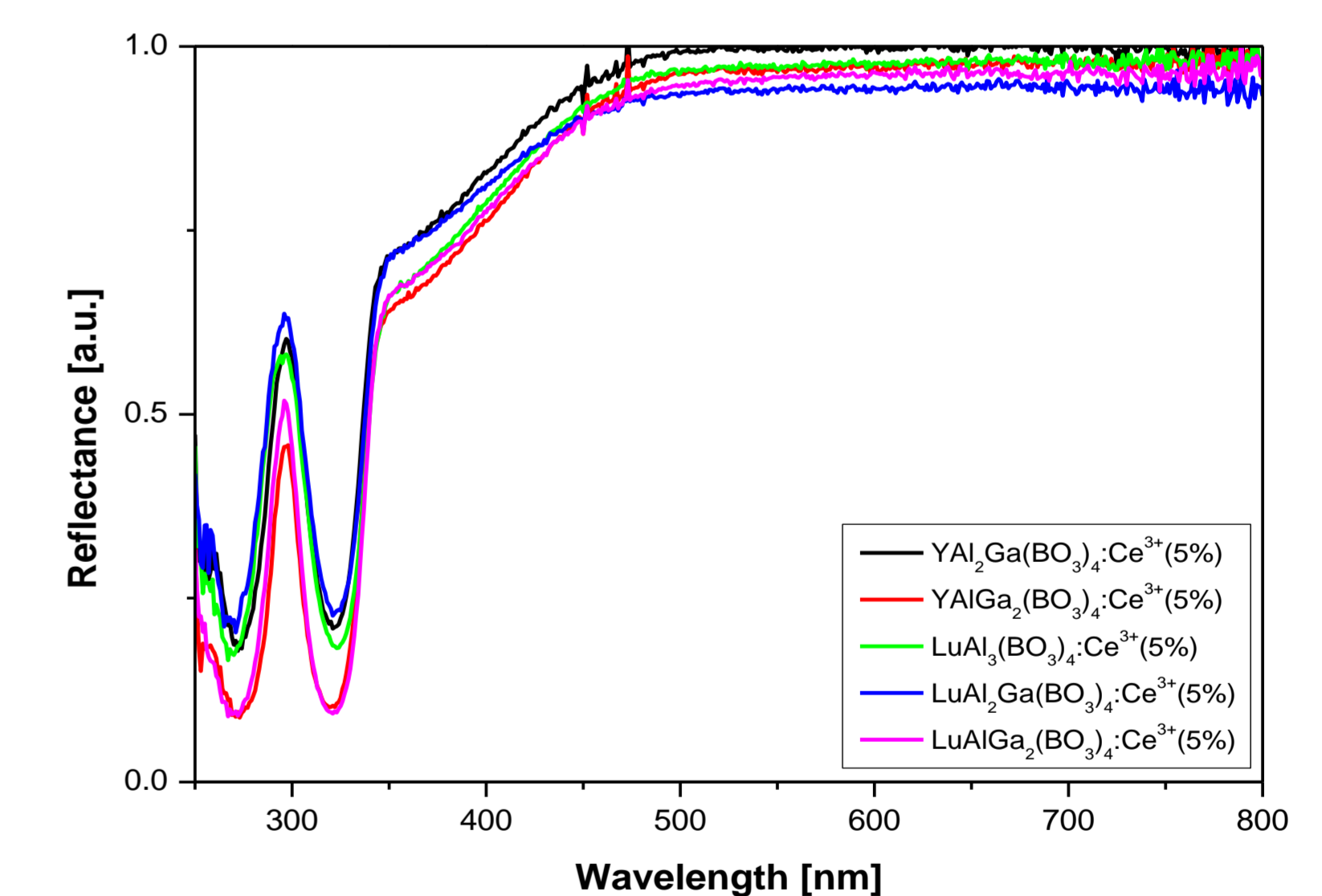

 Fig. 1 LuAl₃(BO₃)₄ crystal [6]

 Fig. 2 Crystal structure of YAl₃(BO₃)₄ [7]

(Y,Lu)(Al,Ga)₃(BO₃)₄ crystallises in a huntite-like structure (CaMg₃(CO₃)₄), where the lanthanide ions are coordinated by two slightly rotated (ca. 8.3 °) oxygen triangles in a trigonal prismatic fashion leading to D_{3h} symmetry of the site. Further characteristics of the structure are layers of isolated alternating BO₃³⁻ 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 YAl₃(BO₃)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

Effect of Al and Y Substitution on PL Spectra and Crystal Structure


 Fig. 3 Powder patterns of various substituted (Y,Lu)(Al,Ga)₃(BO₃)₄ compounds.

 Fig. 4 Excitation, emission and reflection spectra of LuAl₃(BO₃)₄:Ce³⁺(5%).

 Fig. 5 Excitation spectra of LuAl₃(BO₃)₄:Ce³⁺(5%) and LuAlGa₂(BO₃)₄:Ce³⁺(5%) and Gaussian fit thereof for three excitation maxima

 Fig. 6 Temperature dependent emission spectra of YAl₃(BO₃)₄:Ce³⁺(5%).

 Fig. 7 Temperature dependent emission integrals of YAl₃(BO₃)₄:Ce³⁺(5%), YAl₂Ga(BO₃)₄:Ce³⁺(5%) and YAlGa₂(BO₃)₄:Ce³⁺(5%).

 Fig. 8 Reflection spectra of selected (Y,Lu)(Al,Ga)₃(BO₃)₄ compounds.

Conclusions

The results of the present investigations on gallium/lutetium substituted YAl₃(BO₃)₄:Ce³⁺ presented in this study, provide insights in the precise luminescence of Ce³⁺. First of all, samples of single phase (Figure 3), wherein up to two aluminium atoms were substituted by gallium, could be prepared. But unlike in literature, it was found that the complete substitution of the entire aluminium could not be realised, due to an apparent phase transition for Ga concentrations higher than 67 mol-%. [8] The cerium doped samples showed characteristic excitation and emission spectra with three distinct excitation and two emission bands (Figure 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 the split 5d-states. The emission band is split into two due to relaxation into the two ground states of cerium, ²F_{5/2} and ²F_{7/2}, respectively. From low temperature measurements, the energy gap between these two states was calculated to about 2000 cm⁻¹, which corresponds well with the expected value. While the spectra of YAl₃(BO₃)₄:Ce and LuAl₃(BO₃)₄:Ce seem not to differ at all, which can probably be traced back to almost similar ionic radii and their large distance in the crystal system, the introduction of Ga did lead to significant changes. As expected, the band gap of the material decreased with increasing gallium content (Figure 5). That fits well with observations made with regard to other systems, viz. Lu₃(Al,Ga)₅O₁₂ or (Al,Ga)N. However, this finding must still be validated by VUV reflectance measurements. Finally, the most significant impact of substitution turned up to be on the temperature quenching behaviour. A rise in Ga concentration had as a result a more level drop in the emission intensity compared to the pure Al compound (Figure 7). However, the mechanism behind this kind of quenching behaviour and the role of Ga in it is still a subject of investigations.

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