

Pr³⁺ - The Multitasking Ion

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Introduction

Garnet is the common name of a group of cubic minerals belonging to the orthosilicates, which contain solely isolated tetrahedral [SiO₄]⁴⁻ units. The general formula of garnets is C₃A₂D₃O₁₂, which, in case of natural garnets, can be written as C₃A₂(SiO₄)₃, where C = Fe²⁺, Mg²⁺, Ca²⁺ and A = Al³⁺, Fe³⁺, Cr³⁺ and V³⁺. In the general formula, O denotes oxygen and C, A, D symbolize cations occupying the dodecahedral, octahedral and tetrahedral sites, respectively. Artificial garnets according to the formula (Y_{1-x}Lu_x)₃(Al_{1-y}Ga_y)₅O₁₂ are applied as hosts for laser gain media, scintillators, and LED phosphors.

In the present study, the luminescent properties of Pr³⁺ doped garnet type host lattices, namely Lu₃(Al_{1-y}Ga_y)₅O₁₂, (Y_{1-x}Lu_x)₃Al₃MgSiO₁₂ and (Y_{1-x}Lu_x)₃AlMg₂Si₂O₁₂ are discussed as a function of their composition.

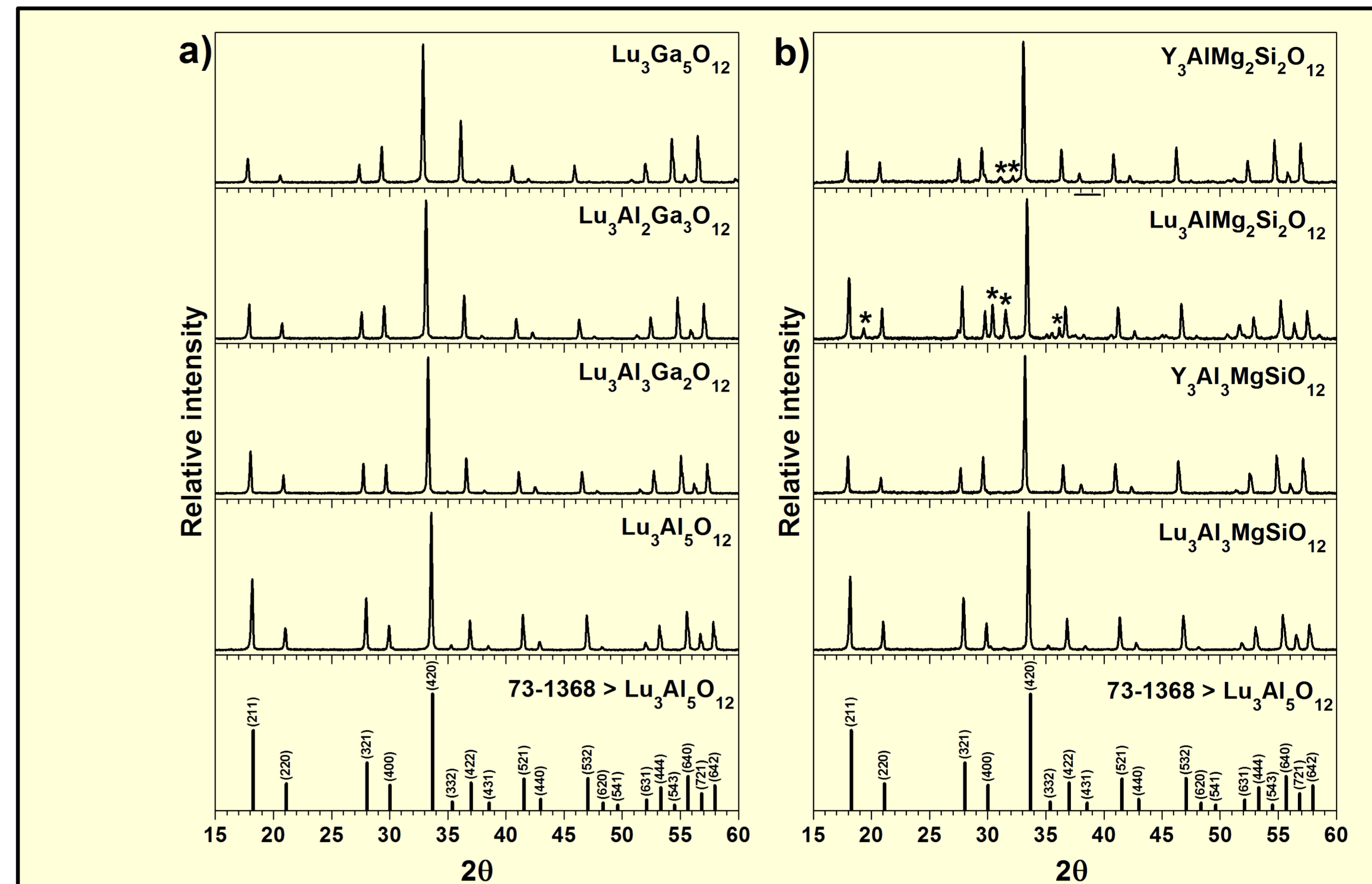


Fig. 1. XRD patterns of Lu₃(Al,Ga)₅O₁₂ (a) and (Y,Lu)₃(Al,Mg,Si)₅O₁₂ (b) doped with 1% Pr³⁺.

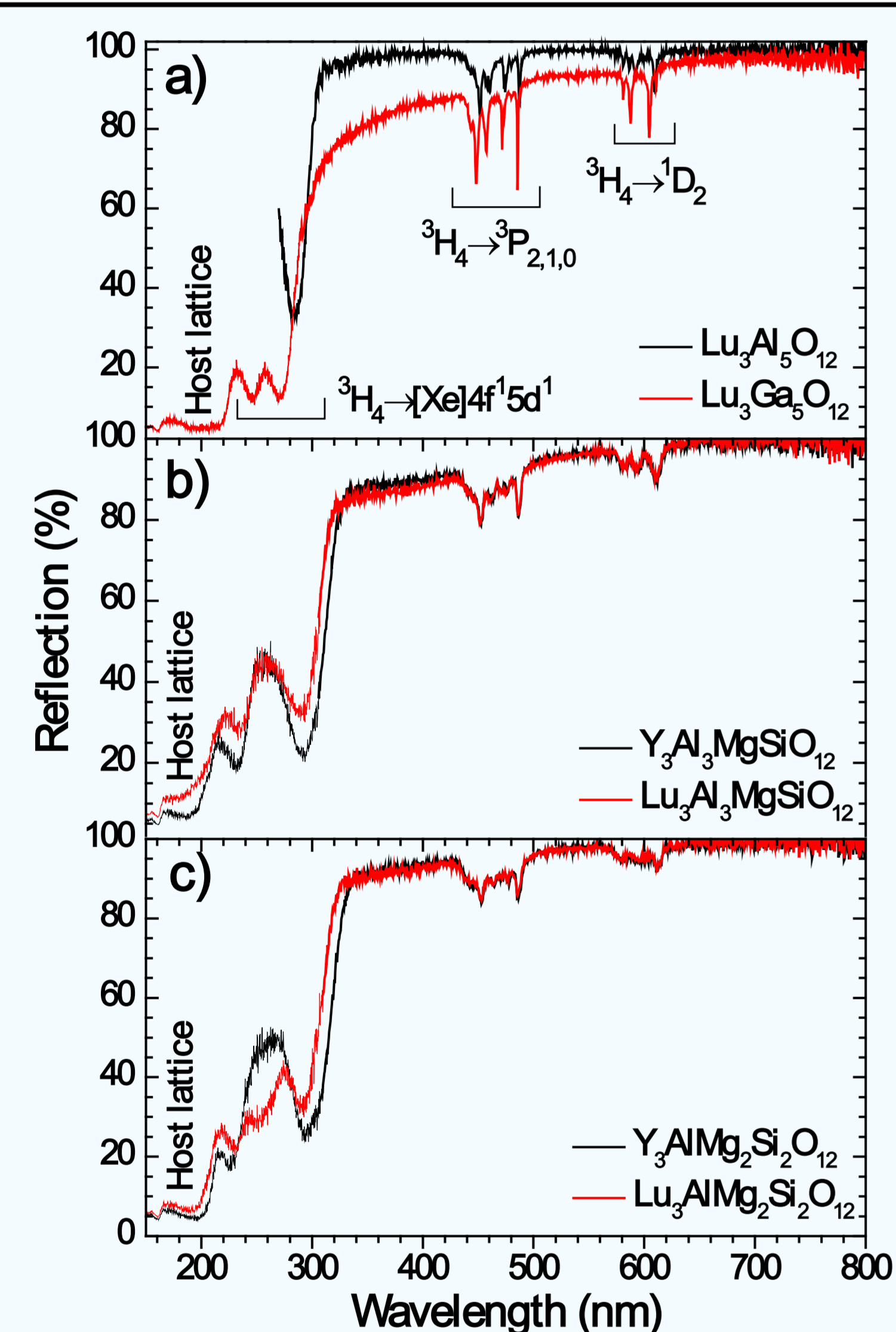


Fig. 2. Reflection spectra of samples doped with 1% Pr³⁺.

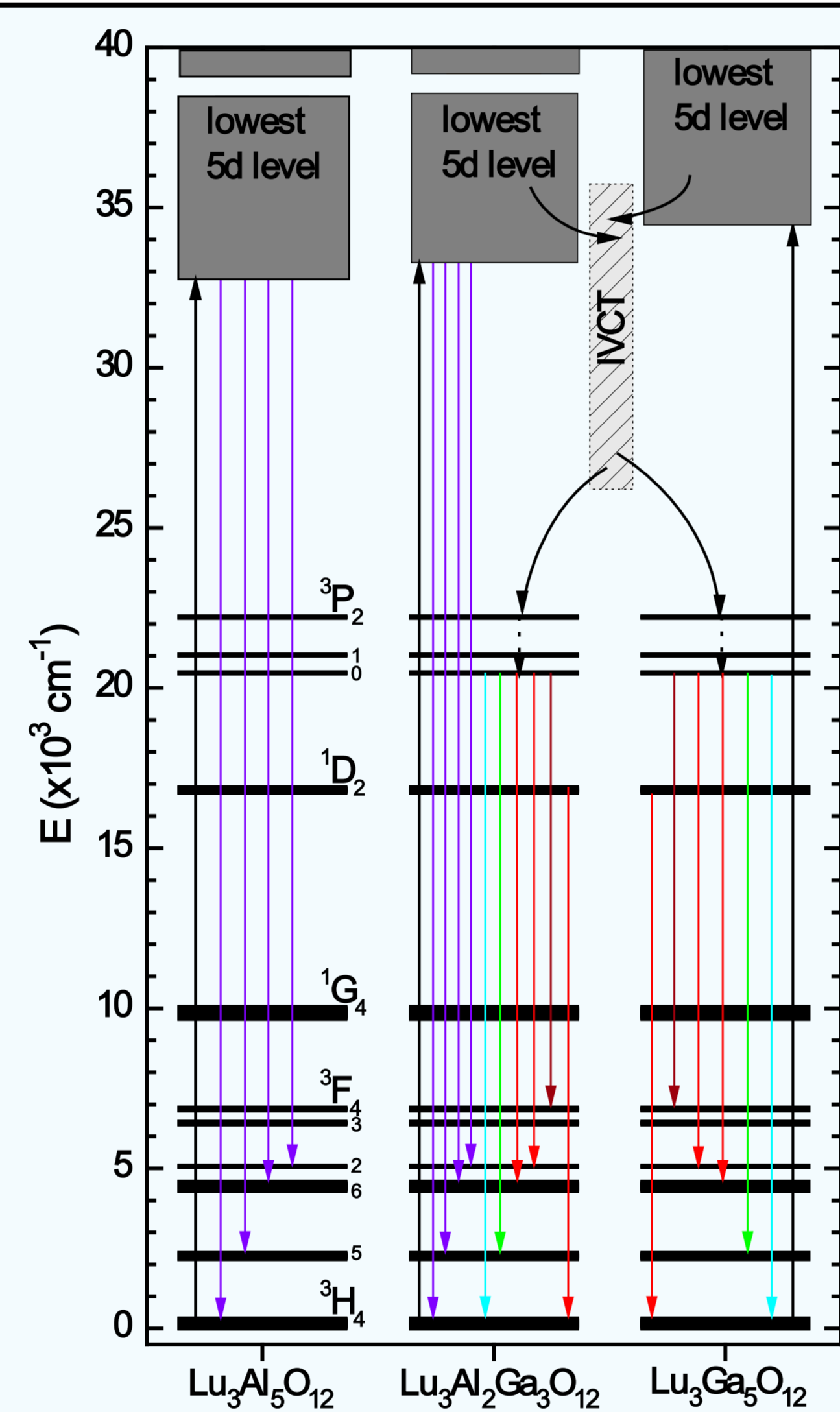


Fig. 4. Simplified Dieke diagram for Pr³⁺.

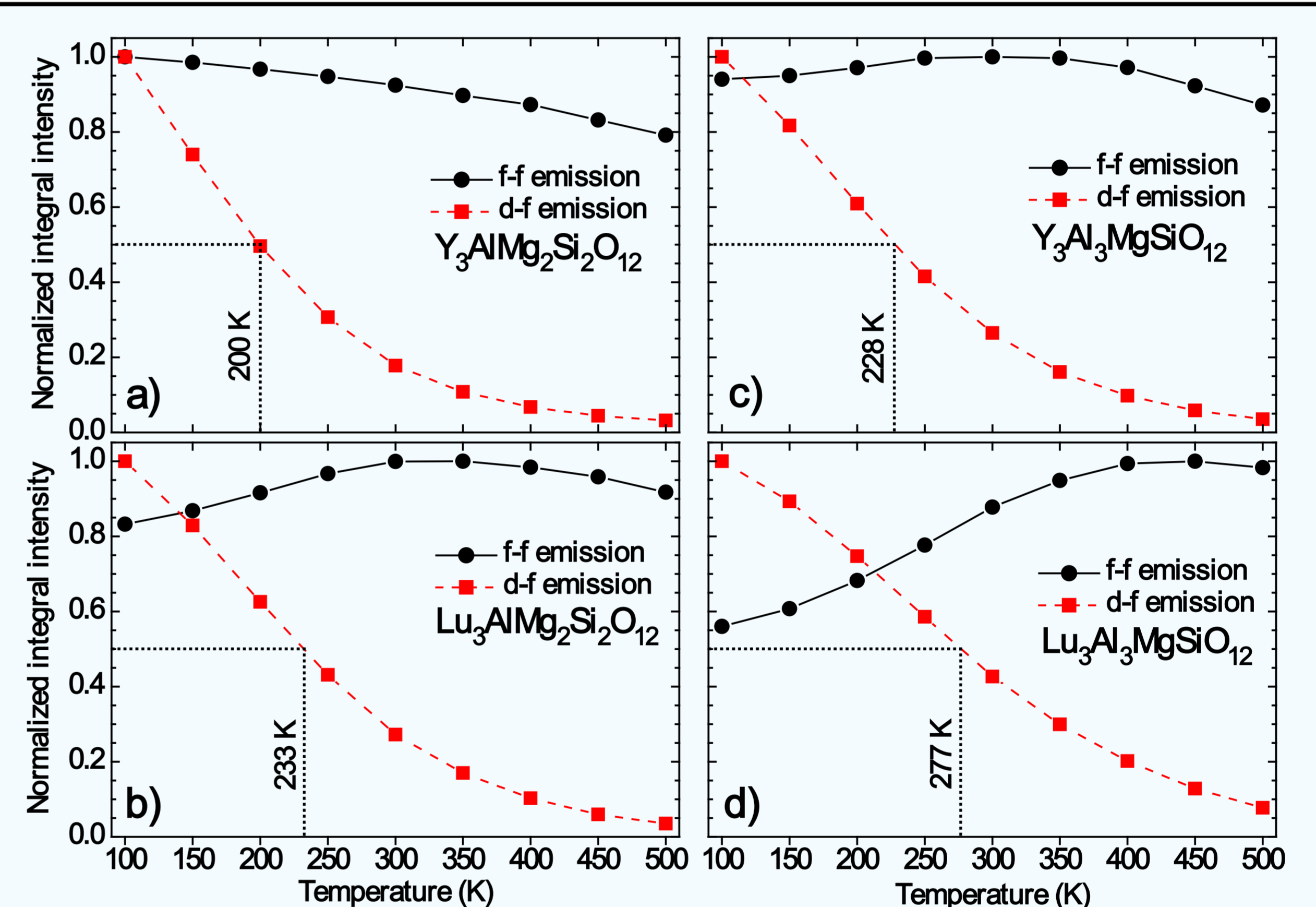


Fig. 5. Thermal quenching of (Y,Lu)₃(Al,Mg,Si)₅O₁₂:1%Pr³⁺ samples (λ_{ex} = 280nm).



Fig. 6. Y₃AlMg₂Si₂O₁₂:1%Pr³⁺ at daylight (left) and UV (254nm) excitation (right).

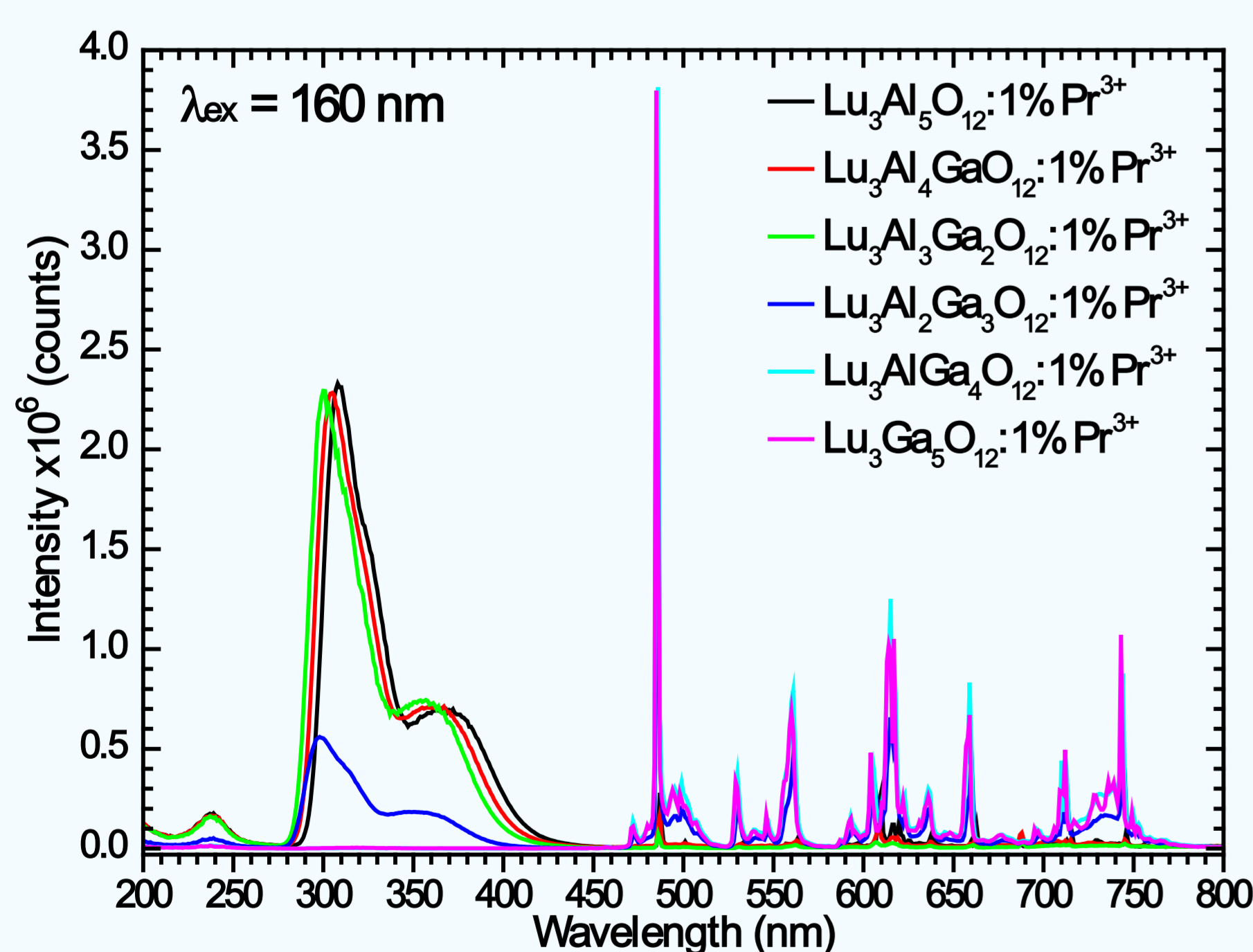


Fig. 3. Emission spectra of Lu₃(Al,Ga)₅O₁₂:1%Pr³⁺.

Material	Band gap	
	nm	cm ⁻¹
Lu ₃ Al ₅ O ₁₂	177	56497
Lu ₃ Al ₄ GaO ₁₂	184	54348
Lu ₃ Al ₃ Ga ₂ O ₁₂	192	52083
Lu ₃ Al ₂ Ga ₃ O ₁₂	197	50761
Lu ₃ AlGa ₄ O ₁₂	207	48309
Lu ₃ Ga ₅ O ₁₂	215	46511
Y ₃ Al ₃ MgSiO ₁₂	201	49751
Y ₂ LuAl ₃ MgSiO ₁₂	198	50505
YLu ₂ Al ₃ MgSiO ₁₂	195	51282
Lu ₃ Al ₃ MgSiO ₁₂	190	52632
Y ₃ AlMg ₂ Si ₂ O ₁₂	210	47619
Y ₂ LuAlMg ₂ Si ₂ O ₁₂	206	48544
YLu ₂ AlMg ₂ Si ₂ O ₁₂	204	49020
Lu ₃ AlMg ₂ Si ₂ O ₁₂	195	51282

Table 1. Optical band gaps of synthesized samples.

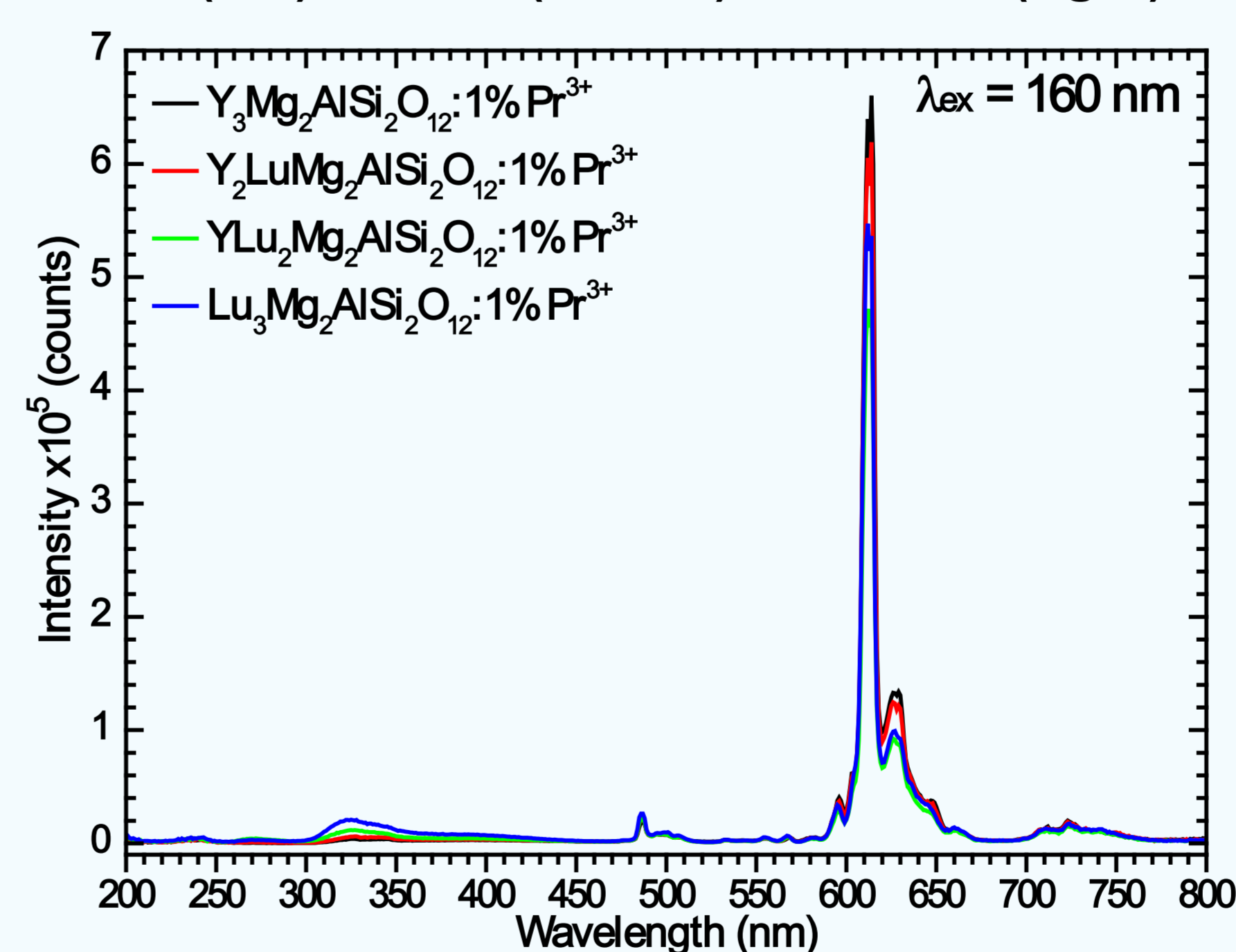


Fig. 7. Emission spectra of (Y,Lu)₃AlMg₂Si₂O₁₂:1%Pr³⁺

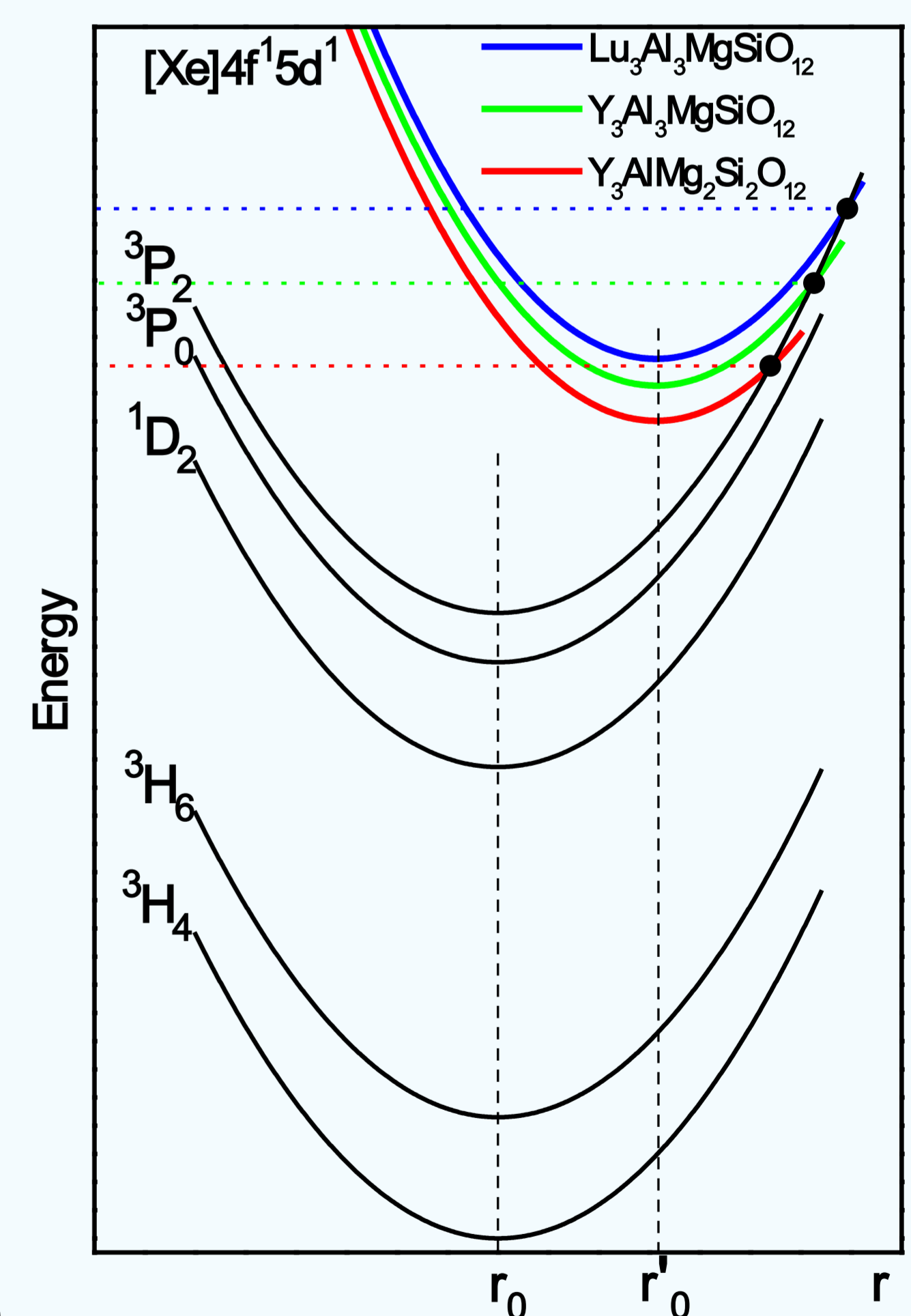


Fig. 8. Simplified coordination diagram of (Y,Lu)₃(Al,Mg,Si)₅O₁₂:1%Pr³⁺

Conclusions

In this work, we demonstrated that a modification of the LuAG host by Ga, Y, or Si and Mg results in strong changes with respect to the optical spectra of Pr³⁺ located into the dodecahedral garnet site. Pr³⁺ in LuAG:Pr emits at around 310 nm. Replacement of Al by Ga resulted in emission maximum shift to higher energy. 5d-4f band emission of Pr³⁺ was completely quenched if more than 60% of Al³⁺ was substituted by Ga³⁺. The replacement of Al³⁺ by Ga³⁺ results in a band gap shift from 177 to 215 nm. Samples with incorporated Mg²⁺-Si⁴⁺ pairs generated stronger crystal fields, which strength increased with higher content of Mg²⁺-Si⁴⁺ and Y³⁺. Moreover, the strong energy transfer from 5d to 4f states was observed. It was also figured out that this energy transfer depends strongly on the crystal field strength and temperature. This can be explained by the configurational coordinate diagram. The stronger crystal field shifts 5d orbitals to lower energies, therefore electron can easier reach crossing point of [Xe]4f¹⁵d¹ and ³P₂ level by gaining thermal energy. Then it relaxes from ³P_J to ¹D₂ level, from which radiative transition occurs.