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Background

Trivalent Praseodymium is widely applied as an activator in UV emitting phosphors, cascade emitting luminescent materials, and scintillators. The doping level is usually rather low, viz. between 0.1 and 1.0%, since Pr³⁺ exhibits efficient concentration quenching due to cross-relaxation processes. Therefore, most commonly a low quantum efficiency for doping levels larger than 1% is observed. The emission spectrum of Pr³⁺ is a very sensitive function of the host lattice properties and can show 4f-5d band emission in the UV range, or 4f-4f line emission in the UV and visible range.

Host lattice	NaPrF ₄	KPrF ₄	RbPrF ₄
crystal system	hexagonal	orthorhombic	orthorhombic
space group	P-6 (174)	Pnma (62)	Pnma (62)
coordination number	2 Ln places both CN 9	9	9
Ln – F distance [nm]	0.2380- 0.2517	0.2316- 0.2526	0.2410- 0.2583
Phonon frequency [cm ⁻¹]	441		

Fig. 1 Crystallographic data of the different fluorides

Synthesis

Sample preparation was performed by the so called “Mix and Fire” method. As starting materials high purity NaF, KF, RbF, LaF₃, and PrF₃ were used. Appropriate blends were sintered for 6 h at various temperatures (750 °C for NaPrF₄ and 650 °C for KPrF₄ and RbPrF₄) in a thoroughly dried Nitrogen stream.

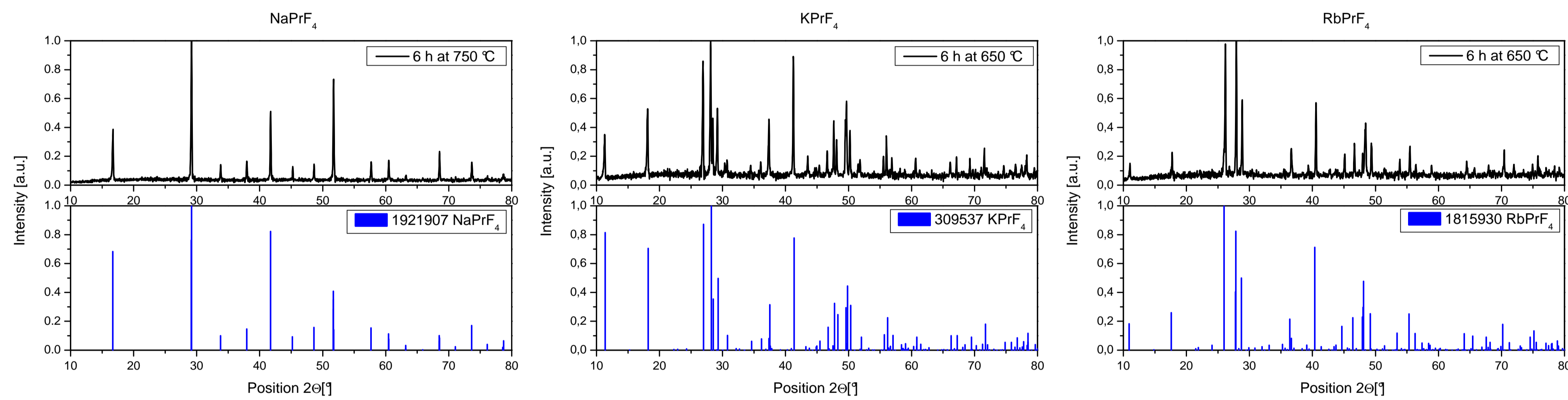


Fig. 2 Powder diffraction pattern of the different fluorides

Obtained luminescent materials were characterised by optical spectroscopy, viz. emission, excitation, and reflection scans. To this end, the phosphors were excited at 160 nm in a VUV spectrometer and emission spectra were recorded between 200 and 800 nm. Excitation scans were monitored for the most intense emission line at around 406 nm (¹S₀ – ¹I₆) between 120 and 350 nm.

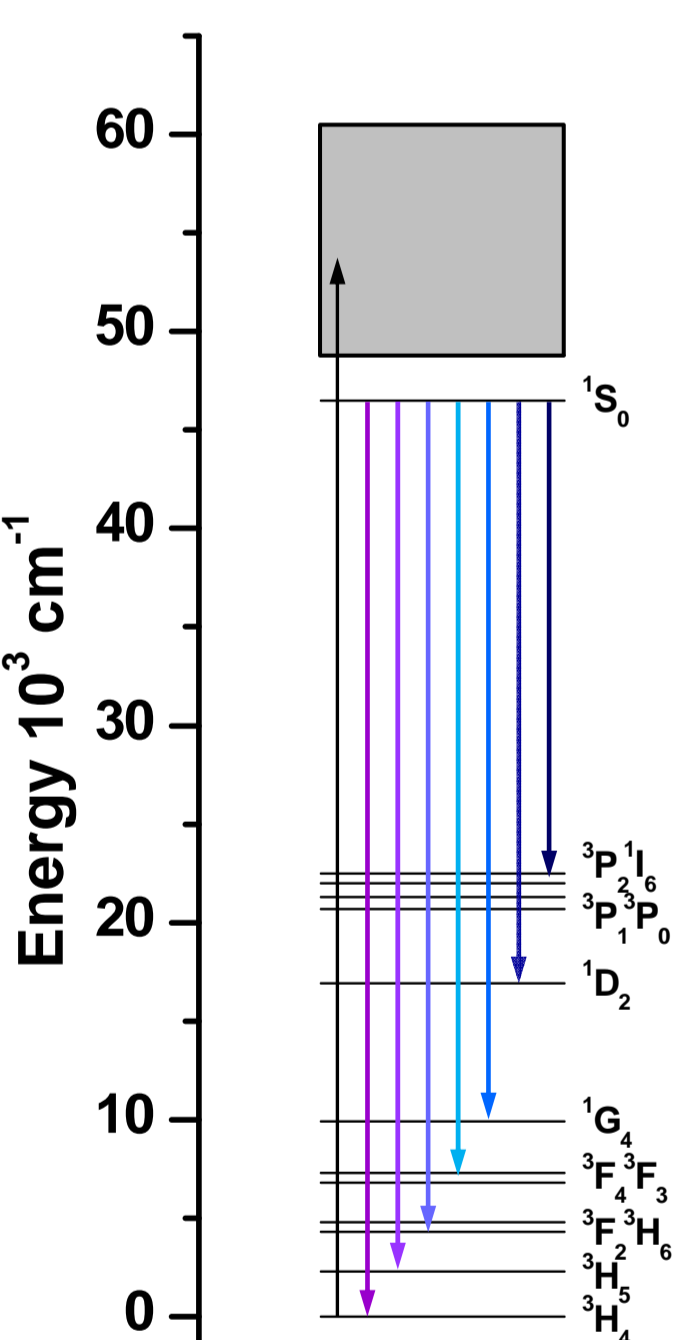


Fig. 3 Energy diagram of Pr³⁺

In all cases absorption in the visible range of the spectra of trivalent Praseodymium is quite intense. Excitation is possible into the 5d band or the ¹S₀ energy level of Praseodymium. Emission occurs from the ¹S₀ energy level to the lower 4f levels which results in UV emission. All other emission lines in the visible range of the spectra are quenched due to cross relaxation.

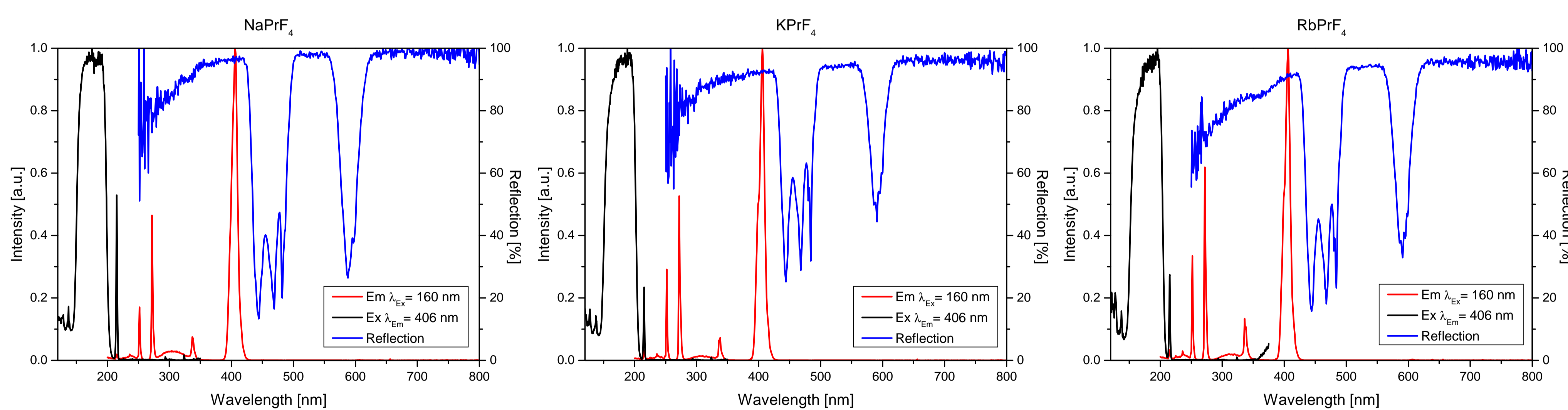


Fig. 4 Luminescence spectra of the different fluorides

For reference purposes BAM:Eu²⁺ was used. It turned out that the quantum efficiency of the best samples is equal to that of the reference. An explanation for this extraordinary finding can be given in the framework of the energy level scheme of trivalent Praseodymium.

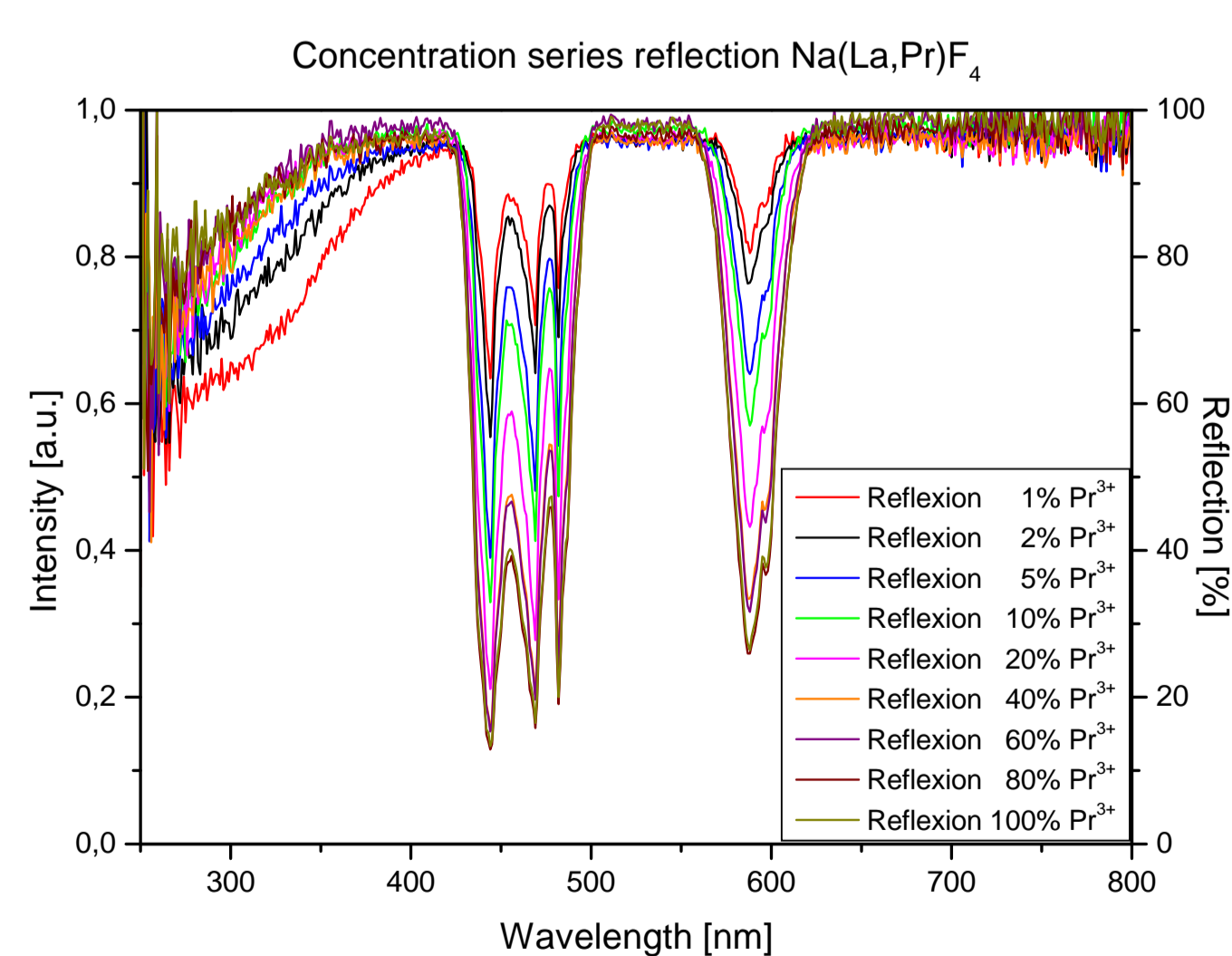


Fig. 5 Reflection spectra of concentration series of Na(La,Pr)F₄

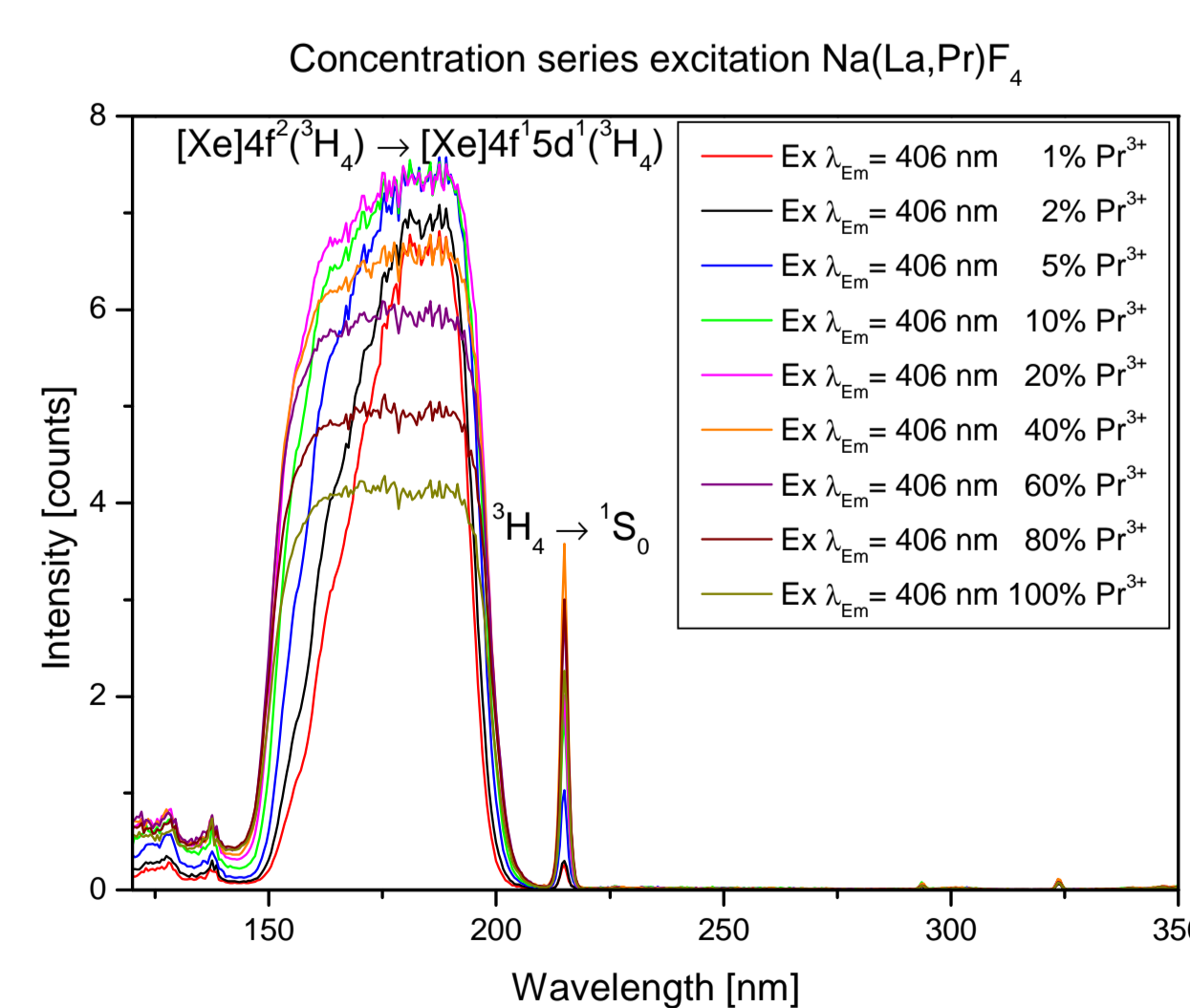


Fig. 6 Excitation spectra of concentration series of Na(La,Pr)F₄

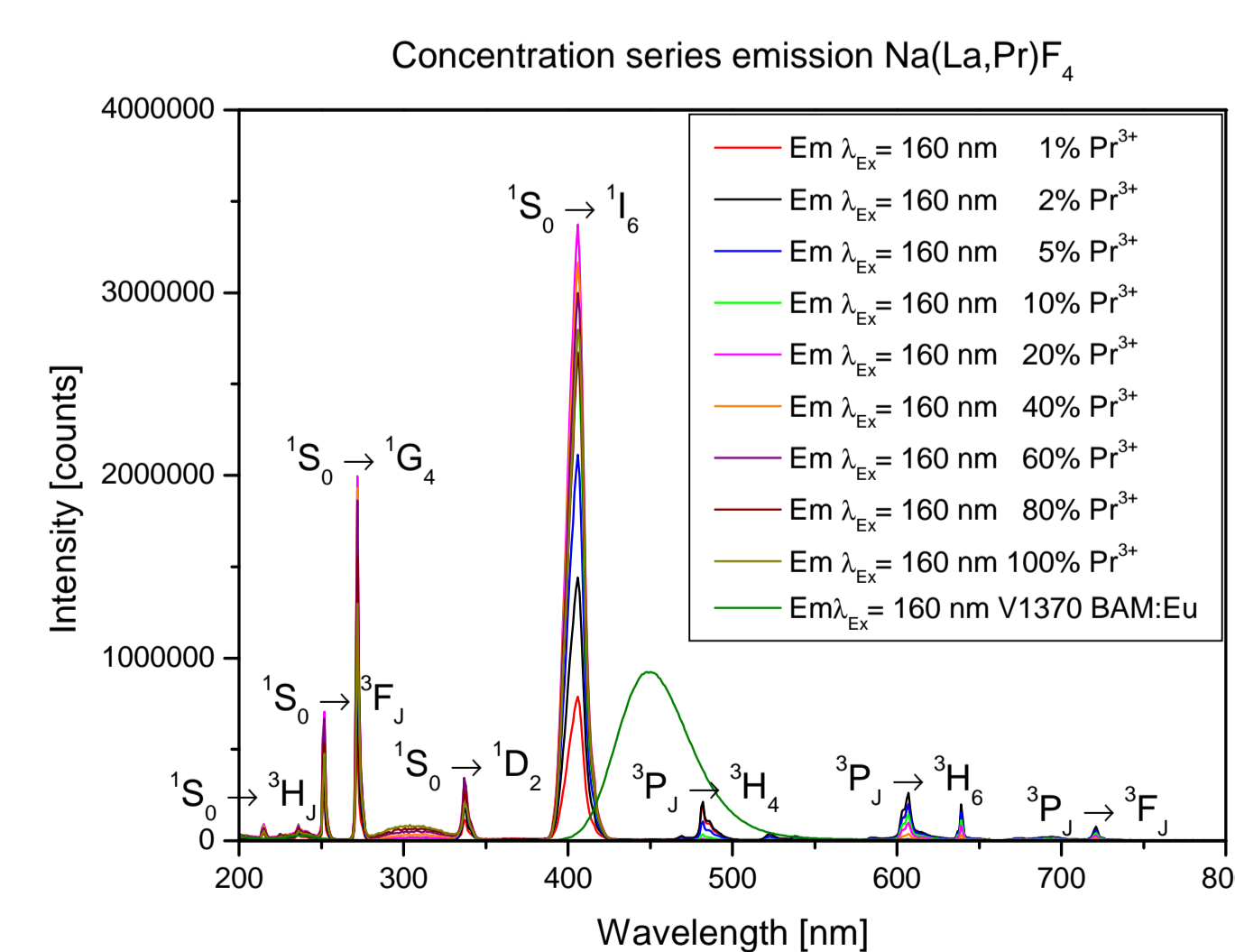


Fig. 7 Emission spectra of concentration series of Na(La,Pr)F₄

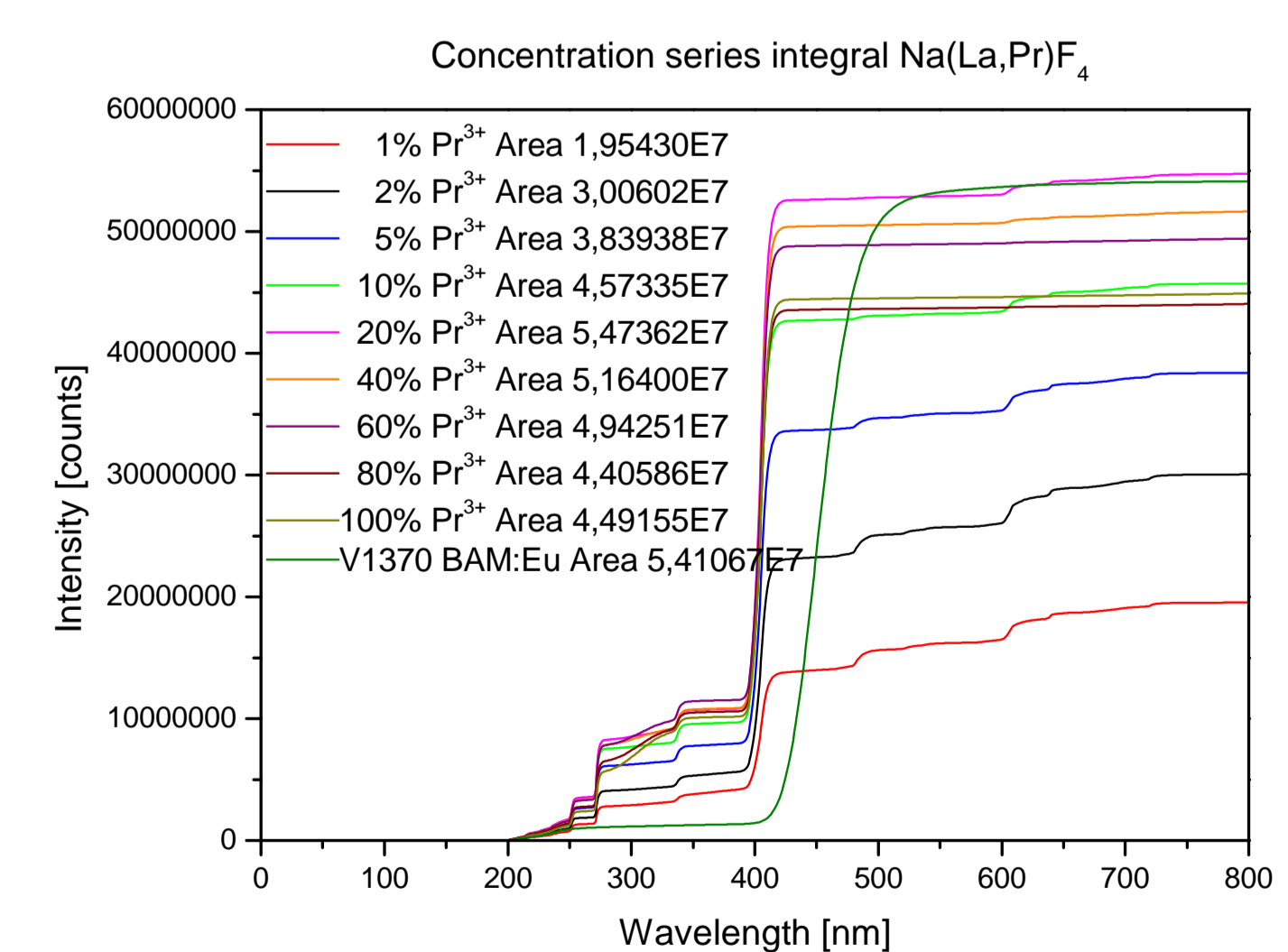


Fig. 8 Integral of the emission of concentration series of Na(La,Pr)F₄

Conclusions

Single phase fluorides could be prepared by sintering in a dried Nitrogen stream. All samples exhibit a green body colour due to rather strong 4f-4f absorption of the trivalent Praseodymium in the visible range. Emission could be observed exclusively in the UV range of the spectrum while the visible emission is quenched by cross relaxation. The concentration series exhibits an increase of the emission intensities upon a concentration of 20% Pr³⁺, which is comparable to the reference standard BAM:Eu²⁺. For even higher Pr³⁺ concentrations luminescence quenching is observed.