Two-Photon Emission in $NaLaF_4$:Pr and $NaPrF_4$ Revisited

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Background

Trivalent Praseodymium is widely applied as an activator ion in luminescent materials, laser gain media, and scintillator crystals/ceramics. The applied doping level is usually rather low, viz. between 0.1 and 1.0%, since Pr^{3+} exhibit efficient concentration quenching due to cross-relaxation processes. In other words, low quantum efficiency for a doping level larger than 1% is observed. The emission spectrum of Pr^{3+} is a very sensitive function of the host structure and can show $[Xe]4f^15d^1$–$[Xe]4f^2$ band emission solely in the UV range, or $[Xe]4f^2$–$[Xe]4f^2$ line emission ranging from the UV-C to the NIR.

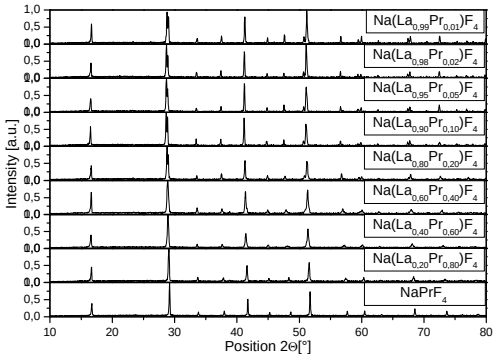

Fig. 1 Powder diffraction pattern of $Na(La,Pr)F_4$

Host lattice	$NaLaF_4$	$NaPrF_4$
Crystal system	hexagonal	hexagonal
Space group	P-6 (174)	P-6 (174)
Coordination number	2 Ln sites both CN 9	2 Ln sites both CN 9
a = b [Å]	6.186	6.123
c [Å]	3.834	3.744
Phonon frequency [cm^{-1}]	430	440

Table 1 Crystallographic data of $NaLnF_4$

This work deals with the synthesis and optical properties of β-$NaLaF_4$ doped by Pr^{3+} as a function of the Pr^{3+} concentration. The structure exhibits three different cation sites whereby the first site is fully occupied by Ln^{3+}, the second one is randomly occupied either by Ln^{3+} or Na^+, and the third one is fully occupied by Na^+. Both sites containing Ln^{3+} ions display C_{3h} symmetry and a nine-fold coordination of the ion.
Sample preparation was performed by the so called "Mix and Fire" method. As starting materials high purity NaF, LaF_3, and PrF_3 were used. Appropriate blends were sintered for 6 h at 700 °C in a Nitrogen stream.

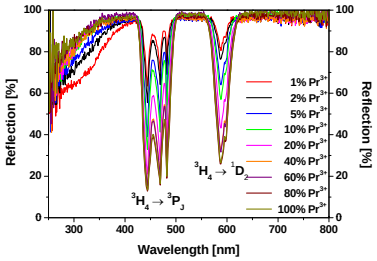

Fig. 2 Reflection spectra of concentration series of $Na(La,Pr)F_4$

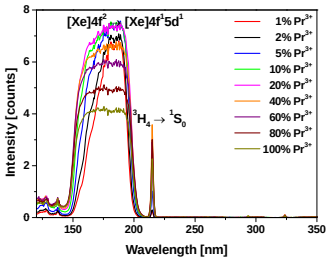

Fig. 3 Excitation spectra of concentration series of $Na(La,Pr)F_4$

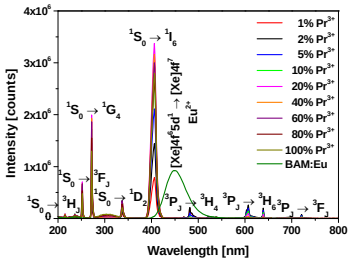

Fig. 4 Emission spectra of concentration series of $Na(La,Pr)F_4$

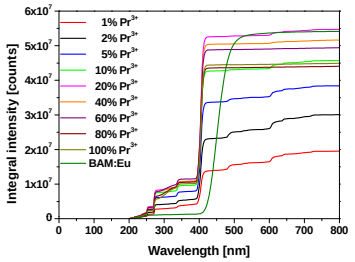

Fig. 5 Integral of the emission of concentration series of $Na(La,Pr)F_4$

Host matrices based on fluorides exhibit a low covalent character for the metal fluoride bonds because of the high electronegativity of fluoride. For this reason, the position of the lowest energy level of the $[Xe]4f^15d^1$-band depends mainly on crystal field splitting. The crystal field splitting is related to the size, coordination geometry, and number of the crystallographic sites whereat the trivalent Praseodymium is located.
Obtained luminescent materials were characterised by luminescence and reflection spectroscopy to investigate the luminescence process of $Na(La,Pr)F_4$. The excitation of Pr^{3+} takes place via the 5d band, whereas emission occurs in all cases exclusively from the different 4f states of the ion.

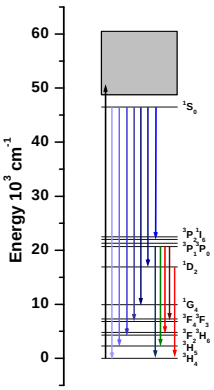

Fig. 6 Energy diagram of Pr^{3+}

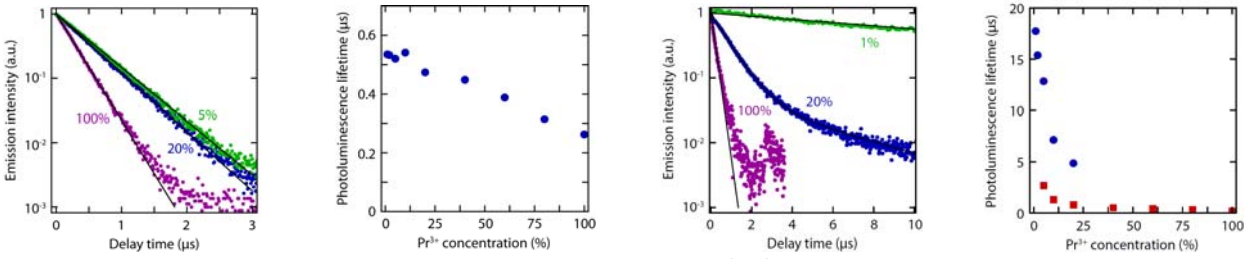

Fig. 7 Decay time measurements of the $^1S_0$-$^1I_6$ emission at 406 nm and the $^3P_0$-$^3H_6$ emission at 609 nm of $Na(La,Pr)F_4$

Decay curves of all samples were recorded to elucidate the Pr^{3+} concentration at which quenching sets in. From the obtained spectra and decay data, the internal quantum efficiency of all samples were calculated, which results in values larger than 100% if the Pr^{3+} concentration does not exceed 10%. For higher concentrations cross relaxation and concentration quenching is dominating the emission.

Pr^{3+} [%]	IQE of $^1S_0$ [%]	IQE of $^3P_0$ [%]	Total IQE [%]
1	100	40	140
2	100	29	129
5	100	14	114
10	100	7	107

Conclusions

Single phase ternary fluorides could be prepared by sintering the respective binary fluorides in a dried Nitrogen stream. All samples exhibit a green body colour due to rather strong $[Xe]4f^2$-$[Xe]4f^2$ absorption of the trivalent Praseodymium in the visible range. The concentration series exhibits an increase of the emission intensities upon a concentration of 20% Pr^{3+}, which is comparable to the reference standard BAM:Eu^{2+}. The overall internal quantum efficiency is derived from decay time measurements and found to be 140% for low doping concentrations.

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