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On the efficient luminescence of β-$Na(La_{1-x}Pr_x)F_4$

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ABSTRACT

This work describes the synthesis and the optical properties of β-$NaLaF_4$ and β-$NaLaF_4$ doped by Pr^{3+} as a function of the Pr^{3+} concentration. It is demonstrated that the emission spectrum is a strong function of the Pr^{3+} concentration and that the external PL efficiency increases with increasing Pr^{3+} doping level. An energy flow model involving cross-relaxation processes is given to explain this finding. The overall internal quantum efficiency is derived from decay time measurements and found to be 140% for low doping concentrations. Concentration quenching for emission from the $^1S_0$ level is suppressed for concentrations up to 20% of Pr^{3+} giving rise to strong absorption and highly efficient line emission around 406 nm.

1. Introduction

Trivalent praseodymium is widely applied as an activator ion in phosphors, laser gain media and scintillator crystals or ceramics. The doping level is usually rather low, viz. between 0.1 and 1.0%, since Pr^{3+} suffers from efficient concentration quenching due to cross-relaxation processes and thus low quantum efficiencies for a doping level higher than 1% [1–2]. Moreover, the emission spectrum of Pr^{3+} is a very sensitive function of the chemical properties of the host compound and can show $[Xe]4f^15d^1-[Xe]4f^2$ band emission in the UV range, or $[Xe]4f^2-[Xe]4f^2$ line emission in the UV and visible range [3].

Host matrices based on fluorides exhibit a low covalent character for the Pr–F bonds because of the high electronegativity of the fluoride anion. For this reason, the position of the lowest energy level of the $[Xe]4f^15d^1$ band depends mainly on the crystal field splitting. The crystal field splitting is related to the size, coordination geometry, and number of the crystallographic sites where the trivalent praseodymium is located [4]. As a general rule, the larger the cation site is, the smaller the crystal field splitting will be.

The hexagonal β-phase (P-6) is formed for all compounds according to $NaLnF_4$ (with Ln=Y, La–Lu) which was already reported by Thoma et al. in 1966 [5]. 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 [6–8].

In praseodymium doped $NaLnF_4$ (Ln=Y, La, Gd, Lu) the crystal field splitting is so small, that the energetic position of the $[Xe]4f^15d^1$ band is above the $^1S_0$ energy level of the ground state configuration $[Xe]4f^2$. Therefore, emission spectra solely show emission lines due to intraconfigurational $[Xe]4f^2-[Xe]4f^2$ transitions. The most intense emission line is located at 406 nm due to the rather strong $^1S_0$-$^1I_6$ transition. This wavelength is of particular interest, since solid state (In,Ga)N lasers, as e.g. applied in blue-ray DVD player or DLP projectors, emit at 405 nm [9].

Therefore, a luminescent material with intense line emission at this wavelength is of high interest for the development of laser gain media, if the quantum efficiency is large so that an efficient laser is in potential reach [10].

2. Experimental section

2.1. Synthesis

The solid state synthesis was performed by mixing the corresponding fluorides, viz. NaF (pro analysi, Merck), LaF_3 (99.9%, Chem Pur), and PrF_3 (99.9% Chem Pur) in stoichiometric amounts

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in an agate mortar. The homogeneous blends of the fluorides were filled in a glassy-carbon crucible and sintered for 6 h at 650 °C in a nitrogen stream to obtain single phase material. The nitrogen, which was used to avoid the reaction of the fluorides with oxygen, was further purified by drying with molecular sieve and KOH. 1% of $NaBF_4$ (97%, Alfa Aesar) was used as a flux agent. $NaBF_4$ decomposes thermally resulting in NaF and BF_3, whereby BF_3 evaporates over the gas phase. Therefore, no further purification steps of the achieved luminescent materials were necessary.

2.2. Characterisation

XRD data of powder samples were collected from $2\Theta=10$–80° (step size 0.02° and integration time 0.1 s) using CuK_α radiation on Rigaku MiniFlex II diffractometer working in Bragg–Brentano ($\Theta/2\Theta$) geometry.

Reflection spectra were recorded on Edinburgh Instruments FS900 spectrometer equipped with a 450 W Xe arc lamp, cooled single-photon counting photomultiplier (Hamamatsu R928) and an integration sphere coated with barium sulphate. $BaSO_4$ (99%, Sigma-Aldrich) was used as a reflectance standard.

The VUV spectrometer (Edinburgh Instruments FS920) was used for exciting phosphor samples at 160 nm. The spectrometer was equipped with a VUV monochromator VM504 from Acton Research Corporation (ARC) and a deuterium lamp as an excitation source. The sample chamber was flushed with dried Nitrogen in order to prevent absorption of VUV radiation by water and oxygen. Excitation and emission spectra were recorded in the ranges of 120–350 nm and 200–800 nm, respectively. The emission spectra were corrected by a correction file obtained from tungsten incandescent lamp certified by NPL. The relative VUV excitation intensities of the samples were corrected by dividing the measured excitation spectra of the samples with the excitation spectrum of sodium salicylate ($o\text{-}C_6H_4OHCOONa$) under the same excitation conditions.

All measurements were performed at room temperature and ambient pressure. Decay measurements were carried out at the Debye Institute for Nanomaterials Science using an Excistar ArF VUV laser for excitation at 193 nm (10 ns pulses) and a Tektronix 2440 digital oscilloscope (1 GHz) for time resolved detection of the emission.

3. Results and discussion

The crystal structures of β-$NaLaF_4$ and of β-$NaPrF_4$ are isomorph. Therefore, the solid solution has no miscibility gap. A concentration series, wherein lanthanum was continuously substituted by praseodymium, was prepared according to the general formula $Na(La_{1-x}Pr_x)F_4$ (with $x=0.01$, 0.02, 0.05, 0.1, 0.2, 0.4, 0.6, 0.8, 1.0). Our solid state synthesis approach yielded single phase powders (see Fig. 1) comprising agglomerated particles with an average particle size (d_{50}) of about 20–30 μm.

Reflection spectra of the $Na(La_{1-x}Pr_x)F_4$ concentration series clearly demonstrate that with increasing Pr^{3+} concentration the absorption strength of the $[Xe]4f^2-[Xe]4f^2$ intraconfigurational transitions increases too (see Fig. 2). Absorption takes place in the visible region between 430 and 490 nm due to the $^3H_4-{}^3P_J$ transitions and around 590 nm due to the $^3H_4-{}^1D_2$ transition. These two absorption multiplets result in a greenish body colour of all samples.

Excitation spectra of the emission from Pr^{3+} in these ternary fluorides show a broad band absorption with a maximum around 190 nm due to a transition from the ground state term $^3H_4$ to the excited state levels of the $[Xe]4f^15d^1$ configuration (see Fig. 3). Furthermore, the absorption of the $^3H_4-{}^1S_0$ transition is clearly visible at 215 nm. All excitation spectra were recorded for the most intense emission line at 406 nm which originates from the $^1S_0-{}^1I_6$ transition. The broadening of the $[Xe]4f^15d^1$ excitation band with increasing Pr^{3+} concentration can be explained by the reduction of the average Pr^{3+}–Pr^{3+} distances and thus by an increase of interaction between 5d orbitals of neighbouring Pr^{3+} ions which may lead to d-band formation. Alternatively, the broadening may

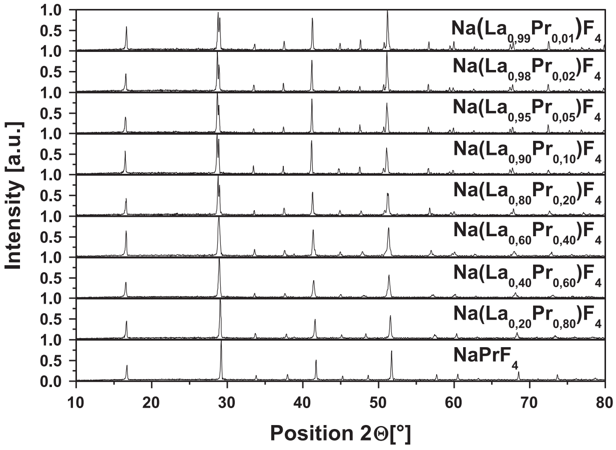

Fig. 1. Powder diffraction pattern of the μ-scale $Na(La_{1-x}Pr_x)F_4$ samples.

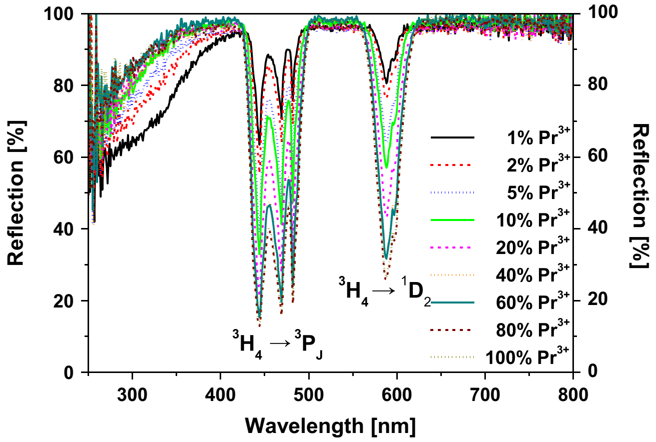

Fig. 2. Reflection spectra of the $Na(La_{1-x}Pr_x)F_4$ samples ($BaSO_4$ was used as white standard).

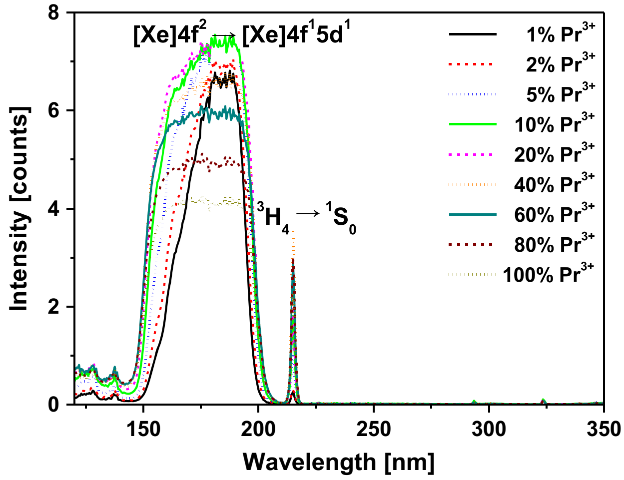

Fig. 3. Excitation spectra of the $Na(La_{1-x}Pr_x)F_4$ samples monitored for 406 nm emission.