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Background

Research efforts for novel materials as converter or gain media in optical applications as e.g. solid state lasers are currently growing world-wide. For this application single crystals are presently state of the art. Nevertheless, transparent ceramics are getting more and more in the focus of interest due to the potential of cheaper production and higher yield over time compared to single crystal manufacturing. Moreover, an arbitrary design of the converter and a more homogeneous distribution of the dopants can be easily realized. A material class of wide interest as a host for laser activator ions are ternary fluorides. Their low phonon frequency, low melting point, wide band gap amongst other properties distinguishes fluorides from other host materials. Most relevant activator ions for solid state laser gain media are Praseodymium, Neodymium, Terbium, Holmium, Erbium, Thulium, and Ytterbium.

Host lattice	NaYF ₄
Crystal system	hexagonal
Space group	P-6 (174)
Coordination number	2 Ln sites both CN 9
Ln – F distance [nm]	0.2328- 0.2405
Phonon frequency [cm ⁻¹]	441

Table 1 Crystallographic data of NaYF₄

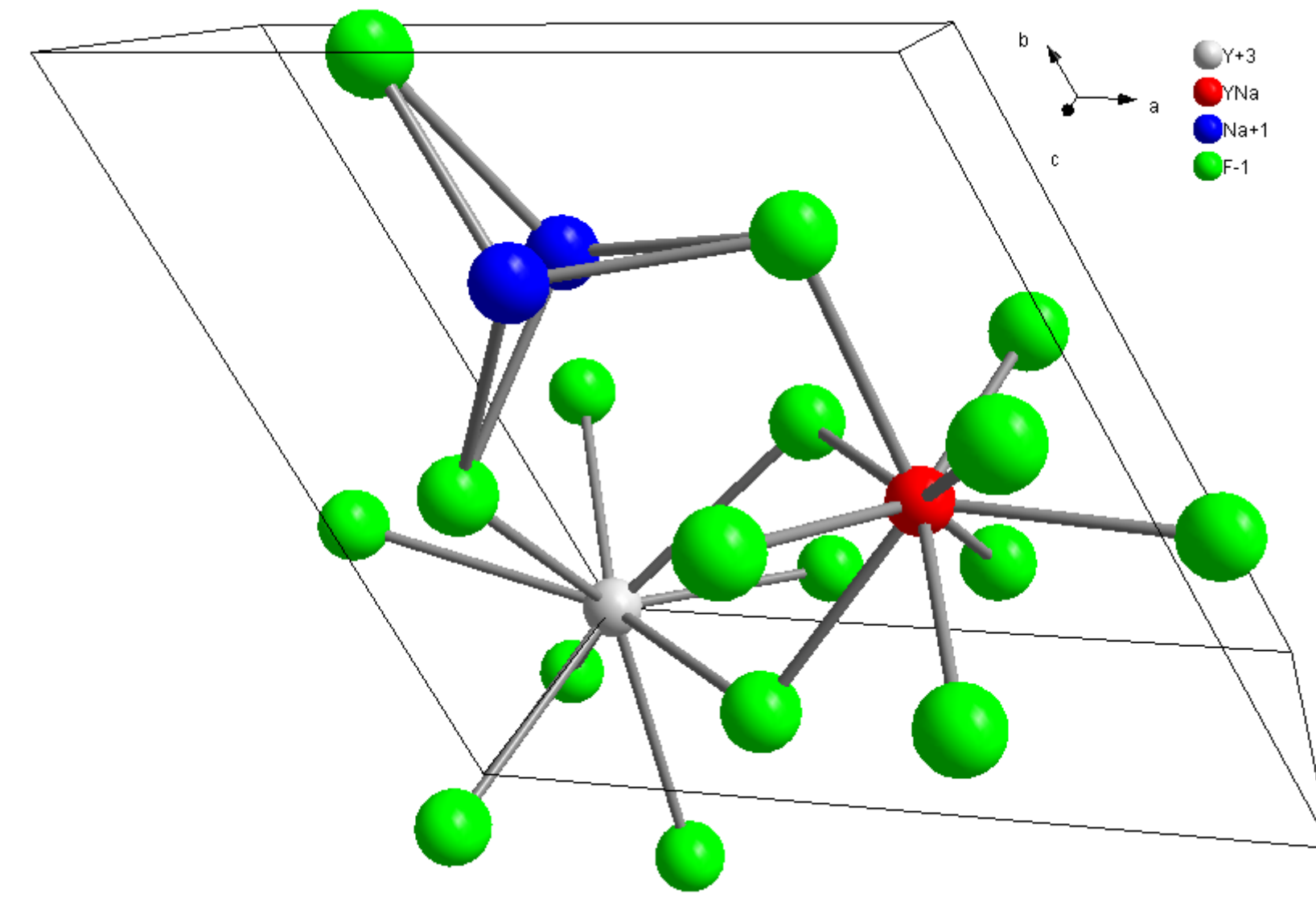


Fig. 1 Unit cell of NaYF₄

In this study, the host lattice NaYF₄ was investigated, which was doped by a trivalent rare earth element, viz. Pr³⁺, Nd³⁺, Tb³⁺, or Er³⁺. Two different structure types, a cubic one and a hexagonal one, have been confirmed, whereby the presence of the one or the other depends on the synthesis method. The hexagonal phase, which was chosen for this investigation, exhibits three different cation sites, whereby the first site is fully occupied by Ln³⁺, the second one is randomly occupied either by Ln³⁺ or Na⁺, and the third one is fully occupied by Na⁺. Both sites, where Ln³⁺ can be located, offer a C_{3h} symmetry, i.e. a trifold capped trigonal prism.

Synthesis

Sample preparation was performed by the so called “mix and fire” technique. As starting materials high purity NaF, YF₃, PrF₃, NdF₃, TbF₃, and ErF₃, were used. Appropriate blends were sintered for 4 h at 650 °C in a Nitrogen stream. Moreover, NaBF₄ was used as a flux. 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 spectra were recorded for the most intense emission line.

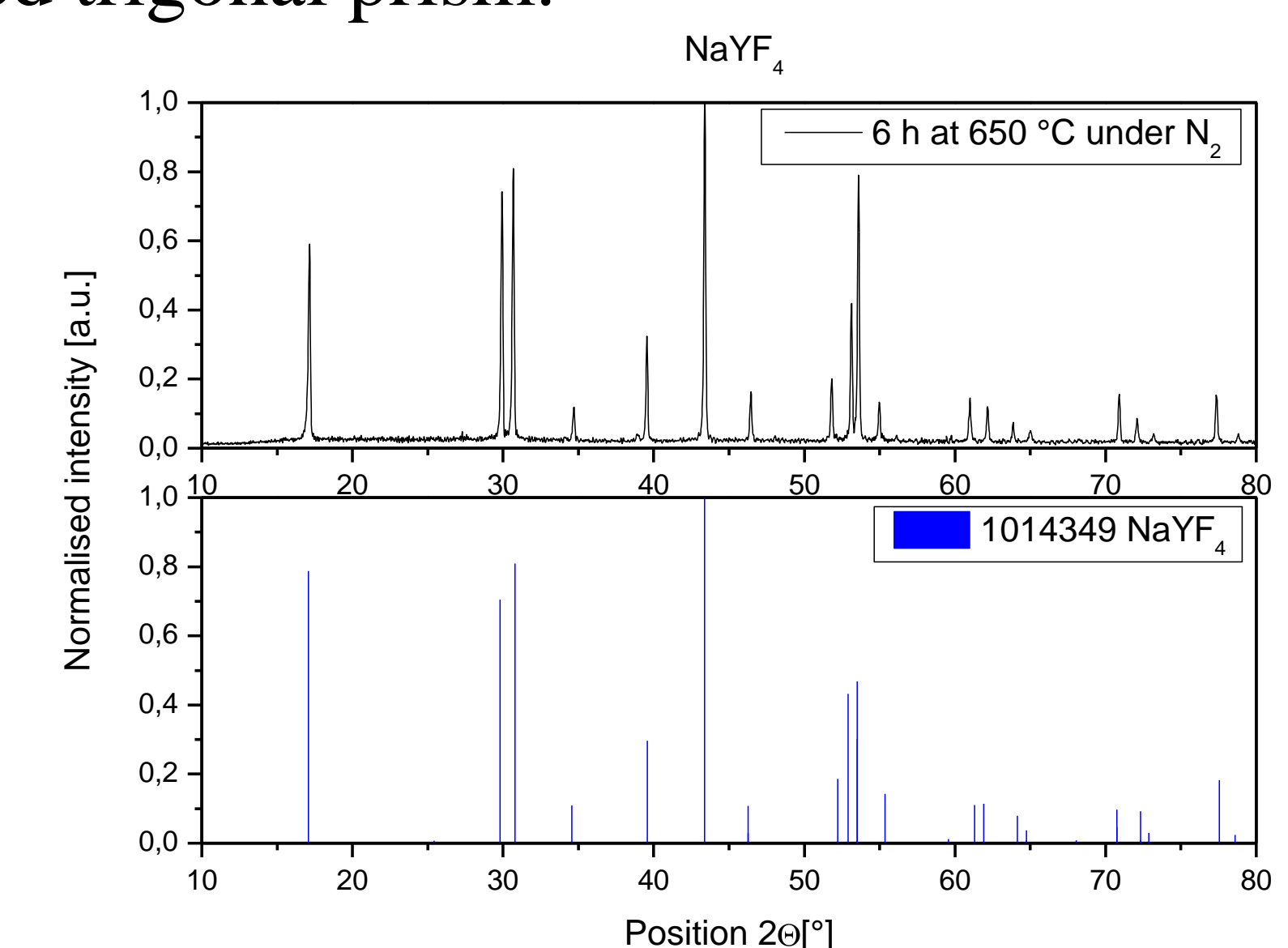


Fig. 2 Powder diffraction pattern of NaYF₄

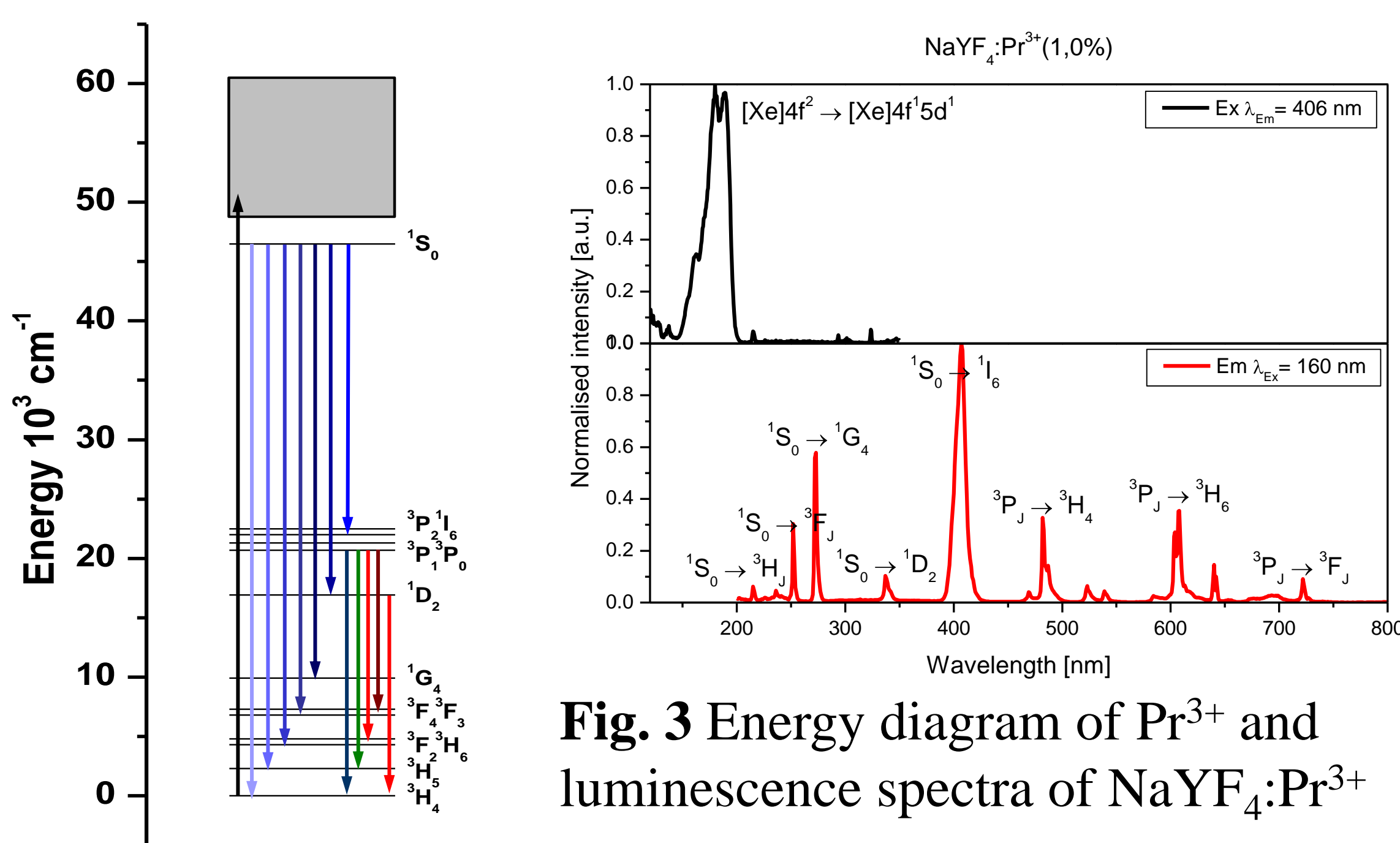


Fig. 3 Energy diagram of Pr³⁺ and luminescence spectra of NaYF₄:Pr³⁺

Host lattices based on fluorides exhibit a low covalent character due to the high electronegativity of the fluoride anion. For this reason, the position of the lowest energy level of the 5d band is mainly governed by the crystal field splitting. The crystal field splitting is related to the size, coordination geometry, and number of the crystallographic sites, whereat the trivalent Lanthanide ions are located. As a general rule, the larger the cation size is, the smaller the crystal field splitting will be. For Nd³⁺ and Er³⁺ the 5d band is higher in energy than the excitation wavelength. Therefore, excitation is solely possible into the 4f states of the ions. For Pr³⁺ and Tb³⁺ excitation takes place over the 5d band. Emission occurs in all cases exclusively from the different 4f states of the ions.

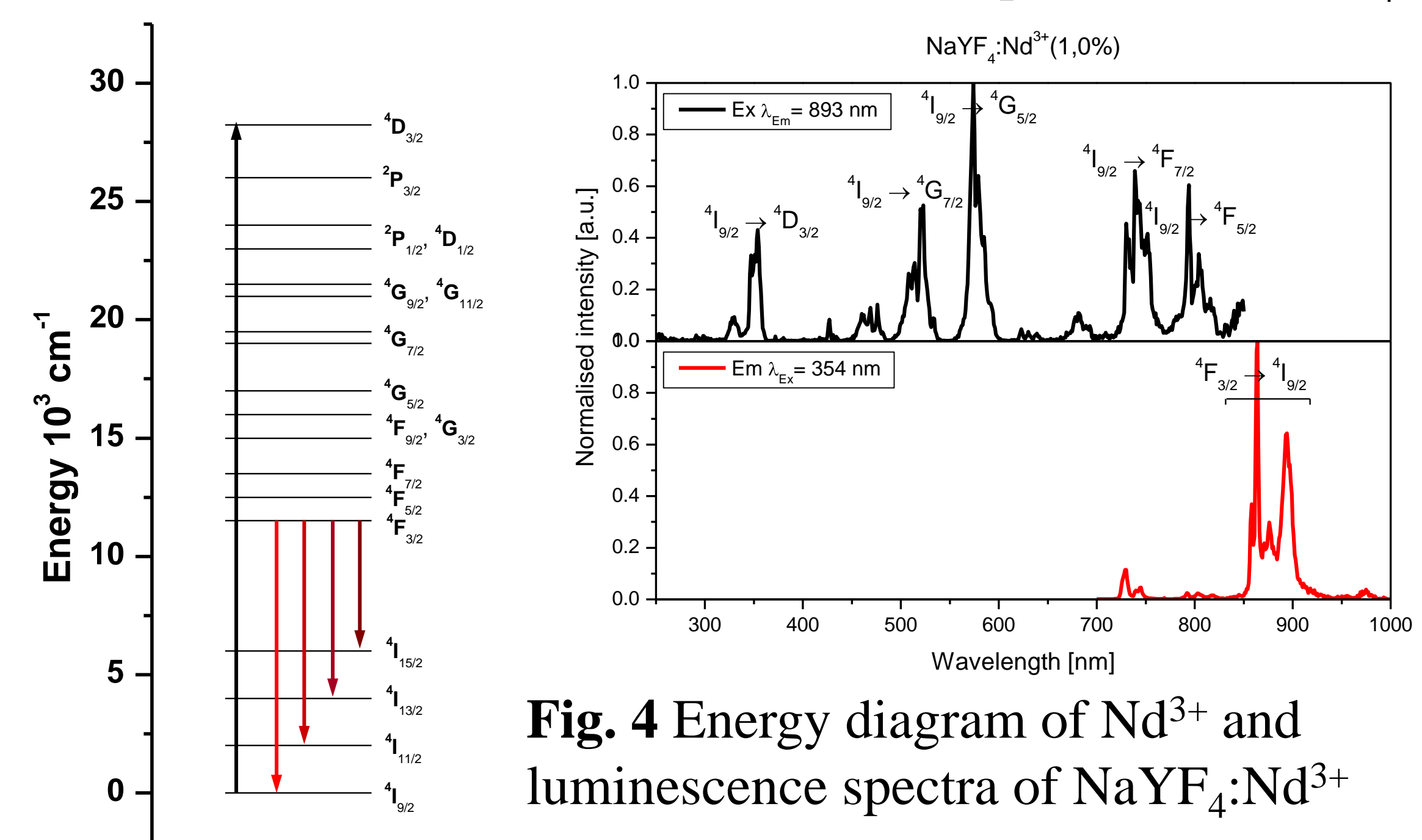


Fig. 4 Energy diagram of Nd³⁺ and luminescence spectra of NaYF₄:Nd³⁺

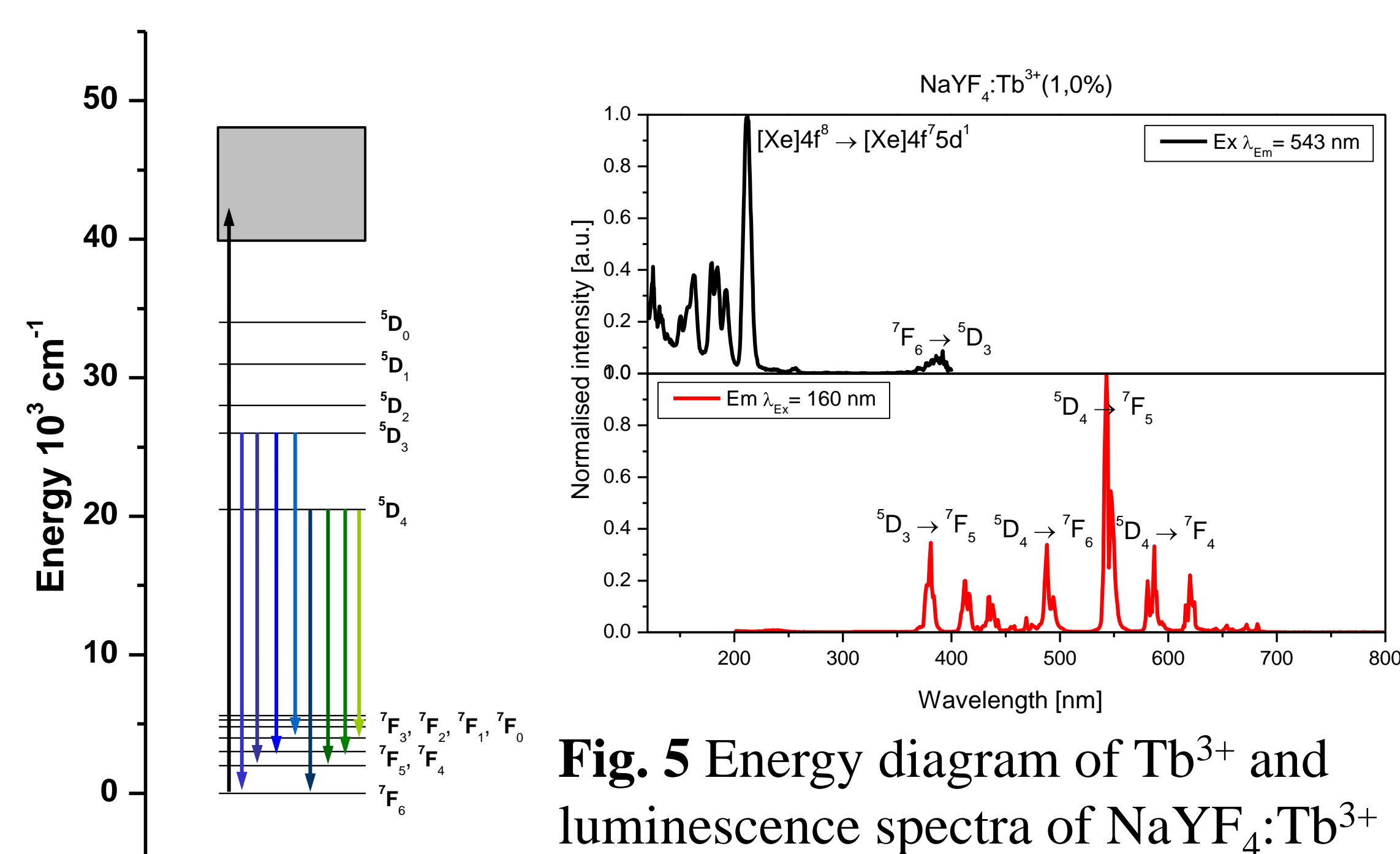


Fig. 5 Energy diagram of Tb³⁺ and luminescence spectra of NaYF₄:Tb³⁺

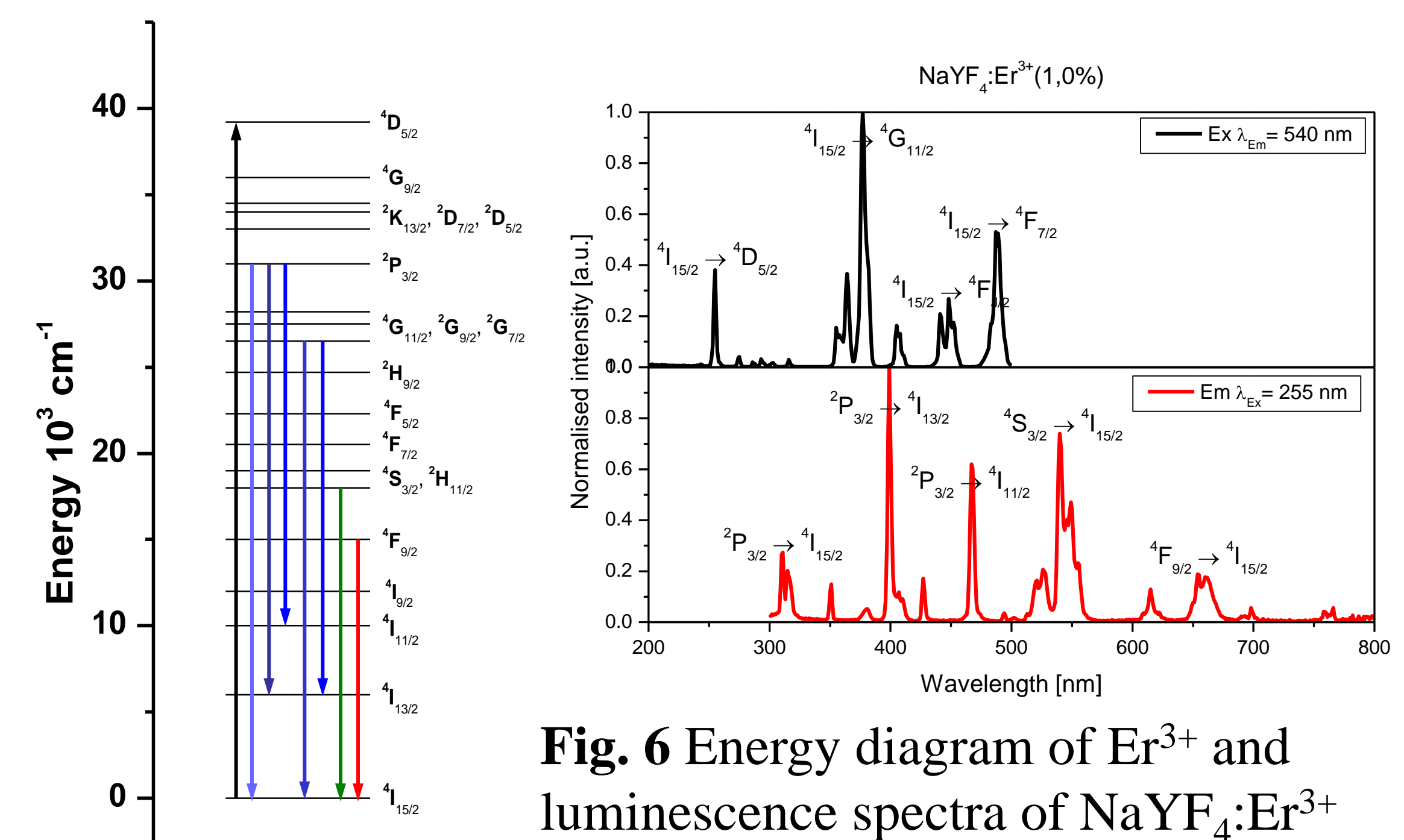


Fig. 6 Energy diagram of Er³⁺ and luminescence spectra of NaYF₄:Er³⁺

Conclusions

Single phase ternary fluorides could be prepared by sintering the respective binary fluorides in a dried Nitrogen stream. In case of Pr³⁺ and Tb³⁺ the 5d band of the ions is that low, that broad band excitation via the 5d band occurs. For Nd³⁺ and Er³⁺ excitation above 120 nm is only possible via the respective 4f states. The emission of Pr³⁺ takes place from the near UV to the near IR, whereas the most intense emission line is located at 407 nm. Tb³⁺ shows emission in the cyan and green spectral range, while the most intense emission line is observed at 543 nm. Nd³⁺ shows its typical near IR emission. The emission of Er³⁺ occurs, as for Pr³⁺, from the near UV to the near IR, whereby the most intense emission line is located at 540 nm. All samples are water stable and could be further processed to ceramics, which is part of our subsequent research activities.