E-MRS 2011 Spring Meeting

Ce^{3+} Sensitized Emission of Nd^{3+} in Garnet Structures

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Introduction

This work is part of the BMBF project CoMaMed – Converter Materials for Laser Diodes in Medical Applications. The main objective is the development of novel optical materials which main emission is peaking within the optical window of (human) tissue. From 700 to 1300 nm tissue components like water, melanin, oxygenated and deoxygenated hemoglobine have only low absorption coefficients (Fig. 1). Fig. 2 demonstrates, that human tissue – here the hand – is transparent for the light of a red laser pointer to a certain extent. Upon using laser diodes as excitation source converter materials with an absorption band are preferred to such with narrow lines and due to the recent advantages it should be located in the blue spectral range. Taken all this requirements into account the main focus in the project will be on activators emitting in the NIR and their sensitization by suitable co-dopants with a large absorption cross-section in the blue spectral range as well as appropriate energy levels for an efficient energy transfer to the activators.

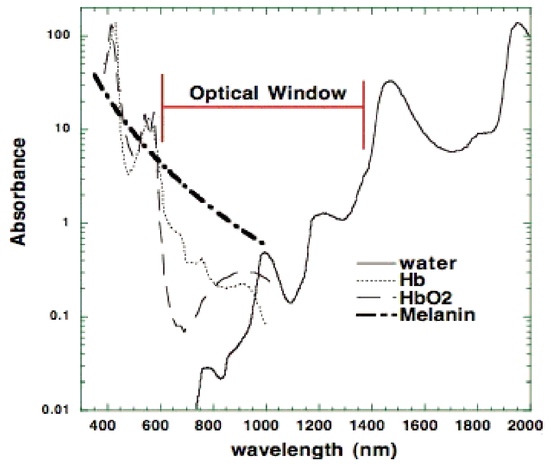

Fig. 1: Absorbance over wavelength in the visible and near infrared for components of human tissue. (www.photobiology.info/Hamblin.html (March 12th, 2009))

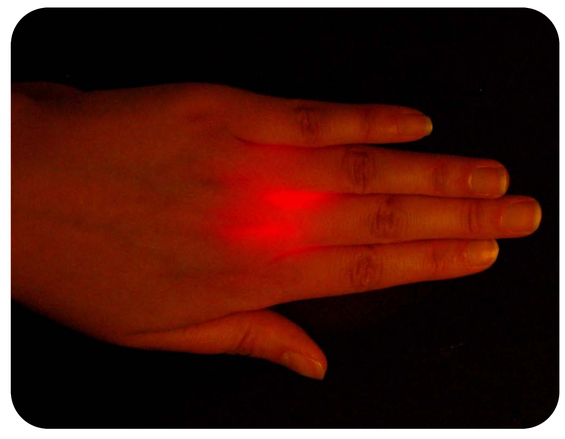

Fig. 2: Example for the weak absorbance of human tissue: Deep red light of a laser pointer is partly transmitted through a human hand

Synthesis

All samples of the system $(Ln_{1-x-y}Ce_xNd_y)_3Al_5O_{12}$ have been prepared by a combustion route employing tris(hydroxymethyl)aminomethane (TRIS). After combusting the nitrates with TRIS and sintering at elevated temperature in air or reducing atmosphere phase analysis done by x-ray powder diffraction is showing a single phase garnet type structure for all discussed samples (Fig. 3).

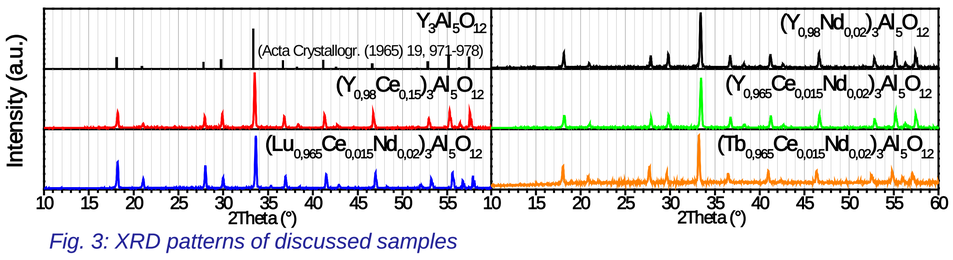

Fig. 3: XRD patterns of discussed samples

Results and Discussion

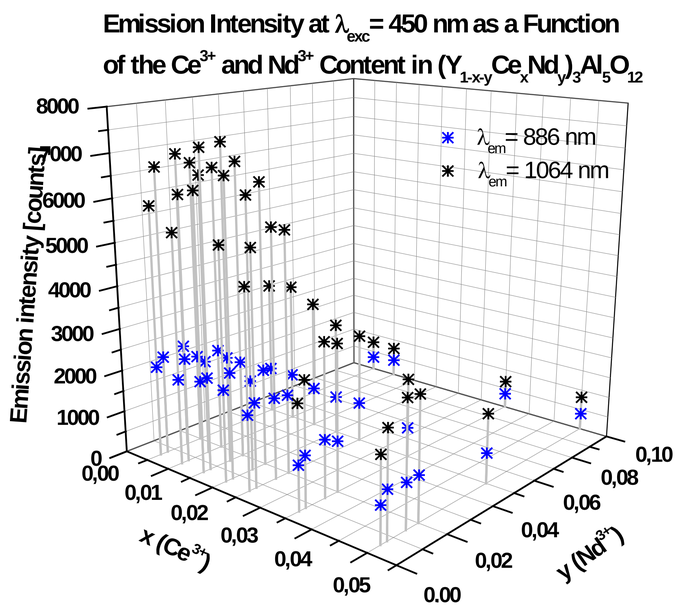

Fig. 4 The most intensive emission at 1064 nm for excitation at 450 nm has been observed for $(Y_{0,965}Nd_{0,02}Ce_{0,015})_3Al_5O_{12}$.

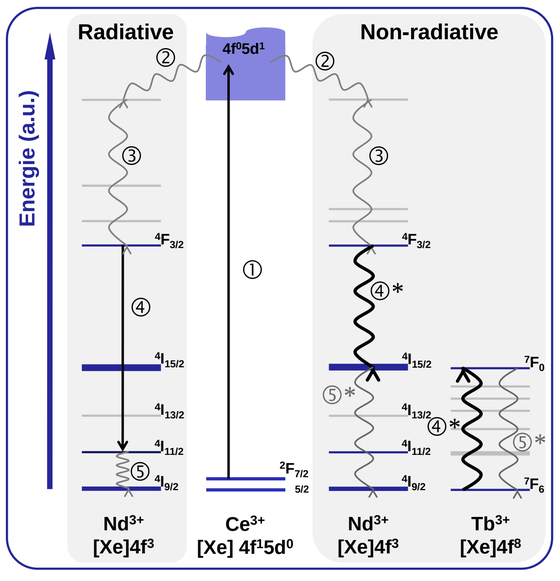

Fig. 5: Schematic representation of the energy transfer processes for radiative and non-radiative relaxation in Ce^{3+}-co-doped YAG:Nd^{3+}

Ce^{3+} is a suitable sensitizer for Nd^{3+} in garnet type hosts. Fig. 6 depicts the strong band absorption at 450 nm, which is characteristic for YAG:Ce, in both excitation spectra for the NIR emission of YAG:Ce,Nd. Excitation of YAG:Ce,Nd at 450 nm can be even more efficient than direct excitation of the activator itself in the deep red (Fig. 7). After the absorption of a blue photon by a sensitizing Ce^{3+} ion an energy transfer to the activator Nd^{3+} takes place and yields in an intense emission in the NIR (Fig. 5). Samples with varying concentrations of Ce^{3+} and Nd^{3+} have been characterised to find the optimal concentration ratio of activator to sensitizer. Fig. 4 shows that the highest emission intensities for excitation at 450 nm arise from samples with approx. 2 atom-% Ce^{3+} and 2 atom-% Nd^{3+}. The absolute emission intensity at 1064 nm has been selected as first assessment criterion until a method for the determination of the quantum efficiencies of phosphors emitting in the NIR will be found. Research on the effects of modifications of the host lattice, e.g. by substituting Y^{3+} by Gd^{3+}, Tb^{3+}, or Lu^{3+} as well as by replacing Al^{3+} by Ga^{3+}, or Sc^{3+} has just started. Fig. 7 shows emission spectra and integrals of modified garnets all comprising the same concentration of the sensitizer and the activator. Whereas Y and Lu garnets exhibit promising emission properties the Tb garnet does not show any NIR emission due to cross relaxation processes. As depicted in Fig. 5 the energy differences of the $^4F_{3/2}$-$^4I_{15/2}$ transition of Nd^{3+} and the $^7F_0$-$^7F_6$ transition of Tb^{3+} are equal and therefore a pathway for non-radiative relaxation is paved. The normalised emission spectra in Fig. 8 reveal that differences in the crystal field of the Lu garnet compared to the Y garnet result in a narrowing of the Nd^{3+} multiplet at 1064 nm.

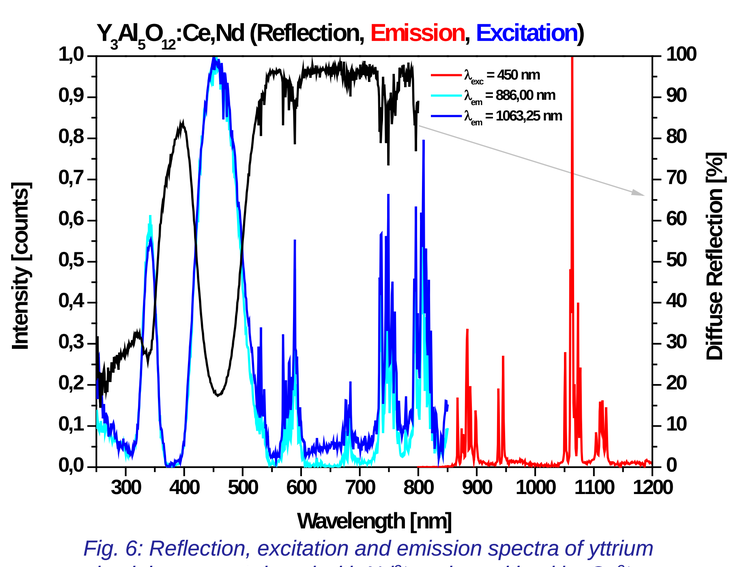

Fig. 6: Reflection, excitation and emission spectra of yttrium aluminium garnet doped with Nd^{3+} and sensitised by Ce^{3+}.

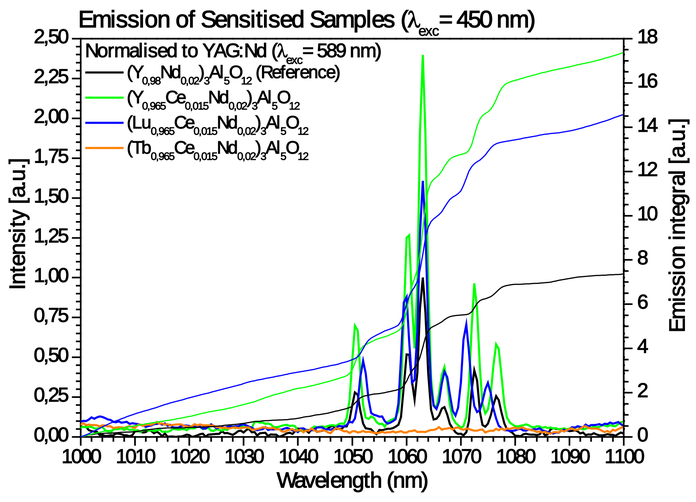

Fig. 7: Excitation of $(Y_{0,965}Nd_{0,02}Ce_{0,015})_3Al_5O_{12}$ at 450 nm yields a higher NIR intensity than excitation of $(Y_{0,98}Nd_{0,02})_3Al_5O_{12}$ at 589 nm.

Fig. 8: Normalised emission spectra reveal a slight shift within the multiplet of the $^4F_{3/2} - {}^4I_{11/2}$ transition for the lutetium garnet.

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