# NIR- and upconverted luminescence from rare earth sodalites

© M.M. Lezhnina[*,**], Ulrich H. Kynast[*]

[*] University of Applied Sciences Muenster,
48565 Steinfurt, Germany
[**] Mari State Technical University, Institute of Physics,
424000 Yoshkar-Ola, Russia

E-mail: marina@fh-muenster.de,
uk@fh-muenster.de

In the recent past, numerous attemps have been untertaken to utilize nano-meso- and microporous materials as hosts for luminescent guest species. The accessible spectral range now spreads from the vacuum ultraviolet to the near infrared (NIR), if sodalites are included in this scope. Although borderline materials in this context with respect to pore sizes, examples of the sodalites' versatility in accomodating small but efficient luminescent entitites are discussed. In particular, optical materials, whose spectral range of operation is allocated in the NIR, have recently attracted our attention and will form the focus of this report.

We would like to express our gratitude to the German BMB+F (Grant 03N8019F) for financial support of part of this research (M.L.).

## 1. Introduction

Zeolites are crystalline alumosilicates, in which tetrahedral $SiO_2^-$ and $AlO_2^-$ are arranged such as to yield a microporous framework. Each negative charge of the lattice brought about by an $AlO_2^-$ building unit is compensated by a cationic species in the voids of the structure (see, e. g., Fig. 1), additionally, most zeolites also readily occlude remarkable amounts of water. One of the most prominent zeolitic materials is synthetic zeolite $X$ exhibiting rather large „supercages“ with a diameter of 1200 pm. These are capable to contain not only a high number of ions but also complexes of these. The second representative in this context are the sodalites and their derivatives which assume a bottom position with respect to the accessible cavity size of approximately 900 pm (distance from the center of opposite six ring windows, see Fig. 2). Zeolites in general are interesting as matrixes for luminescence centers owing to their stability, transparency in UV and visible spectral areas, relative simplicity and, therefore, cheapness of synthesis and, last but not least, the ease of accommodation of luminescent components. The simplest way of optical activation is by means of an aqueous ion exchange in the case of rare earth ions or via gas phase loading in the case of volatile organic substances.

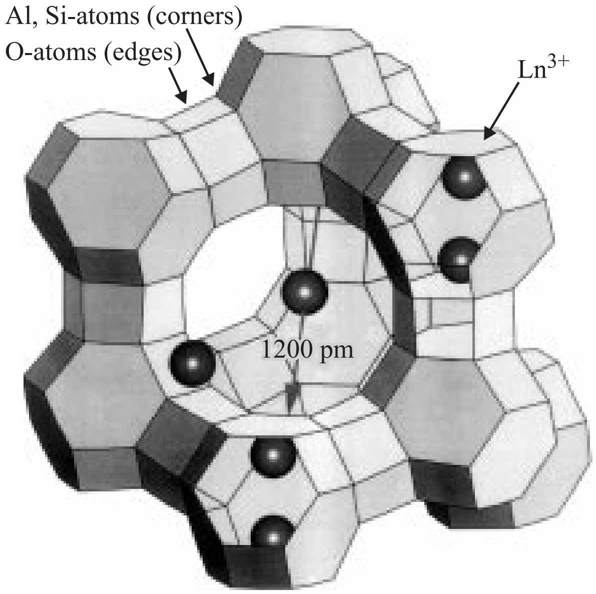

**Figure 1.** Sketch of the Faujasite structure (zeolite $X$). Cation sites are indicated by spheres. Positions outside of the cuboctahedral sodalite cages are not occupied in the zeolites $X$ discussed in this report.

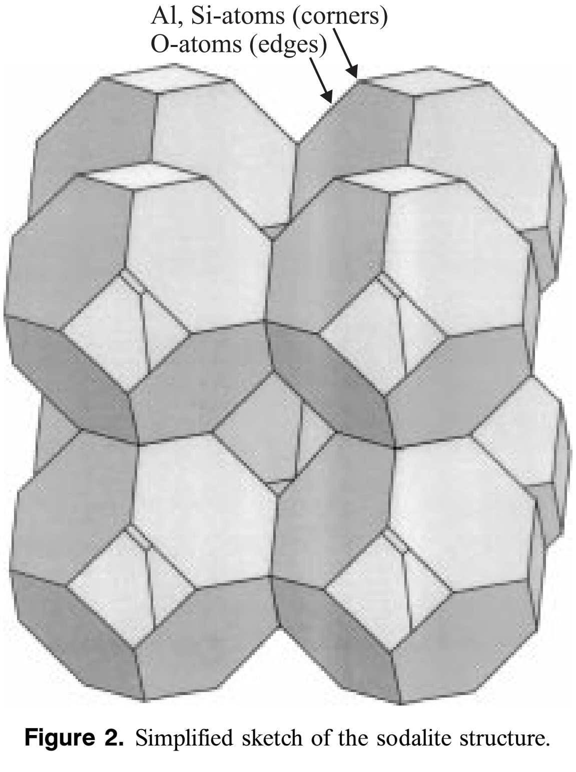

**Figure 2.** Simplified sketch of the sodalite structure.

While the luminescence properties of some lanthanide ions in the zeolite $X$ matrix ([Ln–X]) have extensively been investigated only little is known about the potential of rare earth functionalised sodalites.

With regard to luminescence effeciency, it has been shown that the quantum output of zeolite occluded rare earth ions decreases in the series [Ce–X] (100% [1]), [Tb$-X$] (18% [2]), [Eu–X] ($<$ 5% [3]), [Nd–X] (ca.0%, own results) with decreasing energy of the emission. This tendency is connected to the increase of probability of radiationless processes, vibration relaxation in particular [4]. In the present work we investigate luminescence processes involving electronic transitions of rare earth ions in the spectral energy range between 800–1200 nm near infrared (NIR), for which the probability of vibrational relaxation will be particularly high.

## 2. Results and discussion

In the zeolite $X$ matrix, at room temperature, no emission is observed in case of neodymium or coupled holmium-ytterbium ions. Within the zeolite, the coordination sphere of rare earth ions is completed by coordination of lattice oxygen atoms, and, depending on the state of (re-)hydration, occluded water. In order to decrease the probability of radiationless processes it is necessary to introduce ligands with low vibrational energies. Recently, Hasegawa and coworkers observed emission of neodymium ions in the zeolite $X$ matrix on complexation of $Nd^{3+}$ with bis- (perfluormethanesulfonimide), $H[(F_3C–SO_2)_2N]$ [5], a ligand without protons and thus devoid of high frequency C–H or N–H vibrations. Analogously, the approach chosen in our work is a modification of the rare earth environment in crystal alumosilicate matrices in such a way as to allow luminescence processes including electron transitions within low energy states.

2.1. Fluoride complexes in zeolite $X$. According to the literature, such processes have good intensity in fluorides, or more generally halides, and tungstates [6,7]. We have thus carried out a fluoridation of the couple $Ho^{3+}/Yb^{3+}$ in doped zeolite $X$. This couple is of interest due to upconversion processes, the emission of a high energy photon on excitation with two or three low energy photons; particularly desirable are upconversion materials enabling visible emission on excitation with NIR laser diodes.

The excitation of this system is based on a (spin allowed) electronic transition of the $Yb^{3+}$ ion ($^2F_{7/2} \to {}^2F_{5/2}$), followed by an energy transfer to a nearby electronic level of the $Ho^{3+}$ ion ($^5I_6$). At sufficiently high excitation densities, i. e. sufficient population of the $^5I_6$ state, consecutive transition on the same ion can occur ($^5I_6 \to {}^5F_4$ or $^5S_2$), followed by an emissive return to the ground state under yielding a visible 541 nm photon. Alternatively, the $Ho^{3+}$ can undergo an intermediate relaxation to the $^5F_5$ state, which emits a 650 nm photon. Similar processes may also be observed for the pair $Er^{3+}/Yb^{3+}$. Encaged, pure fluoro-complexes were obtained from excess $NH_4F$ and rare earth doped zeolite $X$, for a composition of $[Y_8Ho_8-X]$ loaded with $10\,NH_4F$ (at 250°C, sealed under vacuum in glass ampoule, $X$ denoting the unit cell of zeolite $X$ with composition $Na_{87}Al_{87}Si_{105}O_{384}$; for the preparation of [Ln–$X$] refer to e. g. [2]). Partically independent of the rare earth content, analytically ratios of 5 to 6 $F^-$ per rare earth ion are obtained, while the crystal structure of the zeolite is mostly conserved (XRD). For the example given, this corresponds to an overall composition of the zeolite of $[(NH_4)_{48}(Eu_4Gd_{12})F_{96}-X]$. Assuming an even distribution of the fluoride species throughout the zeolite, this would yield aggregates of $(NH_4)_6Eu_{0.5}Gd_{1.5}F_{12}$ within each of the eight supercages of the unit cell. Fig. 3 depicts the upconverted emission obtained from exciting $Yb^{3+}$ with a 50 mW/980 nm diode laser, focussed on an area of ca. 2.5 mm$^2$ (Acton Monochromator SP 150 with focal length 150 mm and 1200 g/mm grating Acton Photomultiplier tube P2). This green upconverted emission could alsoclearly be seen in bright daylight, storage under ambient atmosphere did not alter the emission intensities.

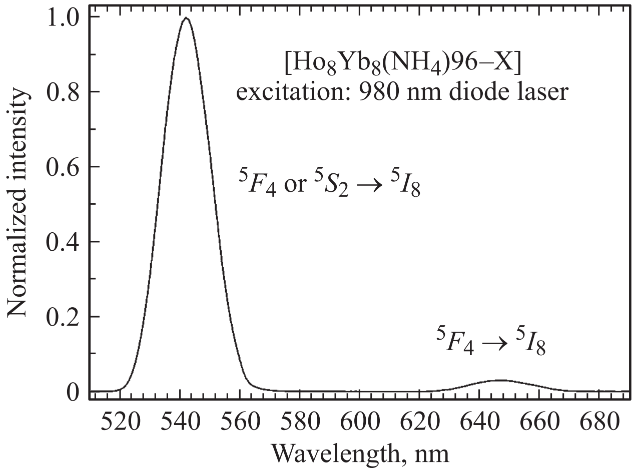

**Figure 3.** Upconversion spectra of $Yb^{3+}/Ho^{3+}$ fluoro complexes obtained in zeolite $X$.

A problem of the material is that the ammonium complexes are unstable thermally and is thus not suitable for further application. Unfortunately, attempts to decompose the complexes to zeolite encaged fluoride proceed under partial destruction of the zeolite matrix and formation of rare earth oxifluoride nanoparticles, which no longer exhibit the upconversion phenomenon.

2.2. Upconversion in sodalites. Recently, we detected an unexpected access to tungstate loaded zeolite $X$ [8]. In attempts to find low vibrational frequency partners for upconverting and NIR emitting rare earth ions, we used the method described in [3] to synthesize correspondingly modified zeolites $X$ $[Ln(WO_3)-X]$ (Ln = Yb/Ho; Yb/Er; Nd). However, neither of the materials obtained could be activated to yield the desired upconversion or $Nd^{3+}$ emission. Instead, we were rewarded with upconversion and

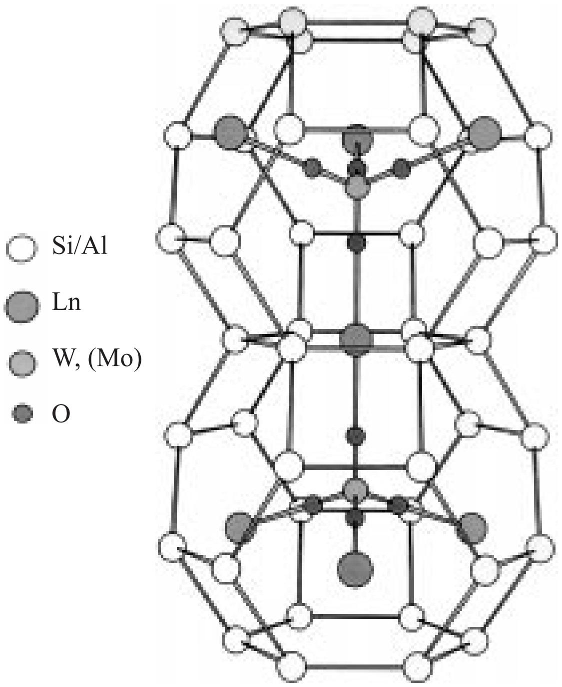

**Figure 4.** Structure of sodalite with included rare earth tungstates $[Ln_4(Al_8Si_4O_{24})(WO_4)_2]$.

NIR emission, respectively, after the solid state conversion to sodalite derivatives (Hauyne $[Ln_4(Al_8Si_4O_{24})(WO_4)_2]$ and Noseane $[Ln_3(Al_7Si_5O_{24})WO_4]$) [7]. This synthesis may be performed by heating a solid mixture of rare earth doped zeolite *X* and $WO_3$ to 650°C to allow for the penetration of tungsten oxide into the zeolite matrix. Followed by an annealing step at 1000°C, the sodalites crystallise. Rare earth ions located in hexagonal windows of the sodalite cage, thus being coordinated by six framework oxygens. Additionally, two oxygen atoms of $WO_4$-ions in neighbouring cages complete the coordination sphere to eight as visualised in Fig. 4. The composition of zeolite *X* slightly differs from the composition required for the sodalite, which leads to small amounts of undesired foreign phases [8] and mediocre crystal qualuty at best. However, upconversion and effecient neodymium emission can for the first time be observed; for corresponding upconverted spectra we would like to refer to [7]. As opposed to that, the direct synthesis of tungstate sodalites in analogy to [3] yields crystalline powders of good quality (crystal sizes of ca. 20 $\mu$m) and purity. The corresponding $Nd^{3+}$ excitation and emission spectra are reproduced in Fig. 5 (emission excited with a pulsed diode laser at the wavelength of 803 nm, detection with a CCD-camera, excitation spectra with the 450 W Xe lamp, Acton 300 Monochromators of 300 mm focal length, gratings 1200 g/mm (250–700 nm), 600 g/mm (700–1200 nm), detection with the Acton Silicon detector SI-440-UV. Labsphere white standards and an optical grade $BaSO_4$ were used as references). The comparison with a commercial $Nd^{3+}$ glass suggests that the novel material already in this non-optimised state (see also the remarks below) is an interesting candidate for optical applications in the NIR.

In attempts to optimize the efficiency of the sodalites, problems arose with the dilution/substitution of the active ions with $La^{3+}$ or $Y^{3+}$ within the sodalite, correspondingly, pure $[La_4\ (Al_8Si_4O_{24})(WO_4)_2]$ or $[Y_4(Al_8Si_4O_{24})(WO_4)_2]$ could not be obtained either; in case of $La^{3+}$, the maximum content was restricted to 2.5 ions per unit cell, and $Y^{3+}$ notoriously gave undefined by-products. We had thus to fall back on the use of $Gd^{3+}$ as a dilutant which gave phase pure materials, however to a high cost in crystallinity. Bearing this problem in mind, the concentration dependence of the $Nd^{3+}$ emission intensity as a function of dilution with ($Gd^{3+}/La^{3+}$), as given in Fig. 6, suggests that dramatic improvements might be possible, if pure and well crystallised $[La_{3.8}Nd_{0.2}(Al_8Si_{14}O_{24})(WO_4)_2]$ were available.

Only recently we discovered that readily accessible nitrite-sodalites [9] can also serve as starting materials for the

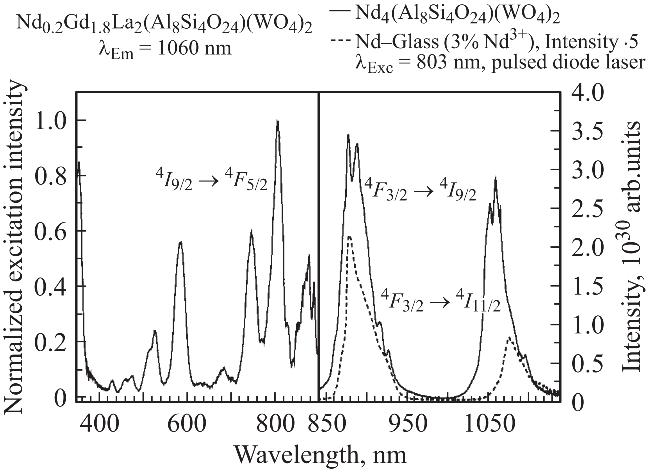

**Figure 5.** Excitation (left) and emission (right) spectra of $Nd^{3+}$ activated sodalites $[Ln_4(Al_8Si_4O_{24})(WO_4)_2]$; dotted line: comparison with a commercial Nd-glass (details see text).

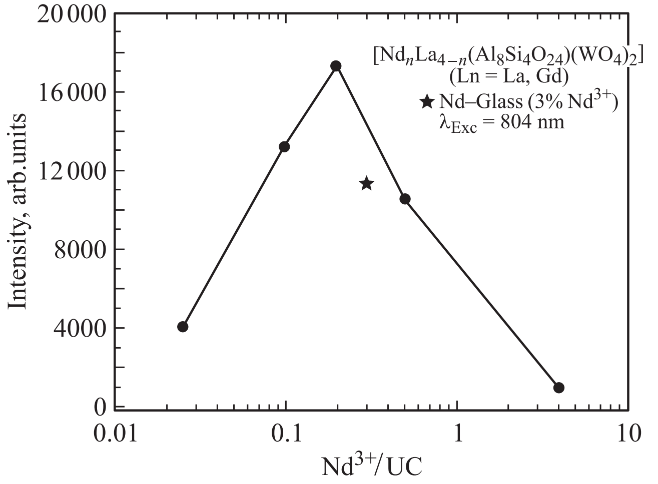

**Figure 6.** $Nd^{3+}(^4F_{3/2} \rightarrow {}^4I_{11/2})$ emission intensity as the function of the $Nd^{3+}$ content.

preparation of $[Ln_4(Al_8Si_4O_{24})(WO_4)_2]$, in that at 800°C the thermally labile $NO^{2-}$ can be raplaced by $WO_4^{2-}$. We expect this to be a feasible route to optimize, e. g., the $Nd^{3+}$ content in the sodalite system, and thus develop an efficient NIR emitting material, which we hope to use eventually in the manufacture of a NIR microlaser in analogy to the zeolite microlasers described in combination with organic dyes [10].

## 3. Summary and conclusion

Fluoride complexes of rare earths have been synthesized in zeolite $X$ for the first time. $Yb^{3+}/Ho^{3+}$ and $Yb^{3+}/Er^{3+}$ fluorides exhibit comparably efficient upconversion, but are unfortunately too labile thermally. Instead, tungstate loaded faujasites, which can subsequently be converted into the sodalite system and also showed the upconvertersion effect, albeit at lower efficiency, and proved to be efficient NIR emitters, despite phase impurities. Phase pure materials were subsequently synthesized directly from individual precursors using a high temperature route. However, several and morphological restrictions have to be overcome and stoichiometric parameters remain to be optimised in striding for the ultimite goal of a sodalite laser. In view of the efficient fluoride complexes in zeolite $X$, the scope of future experiments will include the synthesis of sodalite encaged rare earth fluorides as well.

We owe special thanks to F. Laeri and L. Benmohammadi of the Technical University Darmstadt, Germany, for the intense cooperation on the Nd-sodalites.

## References

[1] U. Kynast, V. Weiler. Adv. Mater. **6**, 937 (1994).

[2] T. Jüstel, D.U. Wiechert, C. Lau, D. Sendor, U. Kynast. Adv. Funct. Mater. **11**, 105 (2001).

[3] C. Borgmann, J. Sauer, T. Jüstel, U. Kynast, F. Schüth. Adv. Mater. **11**, 45 (1999).

[4] G. Blasse, B.C. Grabmeier. Luminescent Materials. Springer, Berlin (1994). P. 72.

[5] M. Ryo, Y. Wada, T. Okubo, T. Nakazawa, Y. Hasegawa, S. Yanagida. J. Mater. Chem. **12**, 1748 (2002).

[6] C. Fouassier. In: Advanced Inorganic Fluorides / Eds. T. Nakajima, B. Zemva, A. Tressaud. Elsevier, Amsterdam (2000). P. 315.

[7] M. Lezhnina, U. Kynast. J. Alloys Comp. **380**, 55 (2004).

[8] C. Lau, H.-J. Mai, U. Kynast. Micropor. Mesopor. Mater. **47**, 339 (2001).

[9] F. Hund. Z. Anorg. Allg. Chem **511**, 225 (1984).

[10] G. Ihlein, F. Schüth, O. Krauss, U. Vietze, F. Laeri. Adv. Mater. **10**, 1117 (1998).