Cation Reordering in $NaYF_4$:Yb^{3+},Tb^{3+} Up-Conversion Luminescence Materials: An EXAFS Study

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In photon up-conversion (UPC), low-energy radiation (NIR) is converted to higher-energy light using different combinations of a R^{3+} (rare earth) sensitizer (*e.g.* Yb, Er and Sm) and activator (*e.g.* Er, Ho, Tm and Pr). UPC luminescence has established applications in *e.g.* anti-counterfeit marking, lighting and displays [1]. Nanomaterials with efficient up-conversion are currently intensively studied for use in quantitative homogeneous whole blood immunoassays [2] and other diagnostic tools. Finally, the use of up-converting materials to enhance the harvesting of solar energy has been shown both in photosynthesis [3] and solar cells [4]. The hexagonal $NaYF_4$ ($P6_3/m$, No. 176, Z: 1.5) is considered as one of the best up-conversion luminescence hosts [5]. The structure is then close to stoichiometric and it contains two cation sites: one for Na and the other shared by Na and R. The corresponding coordination polyhedra are distorted NaF_6 and Na/RF_9 [6].

$NaYF_4$:Yb^{3+},Tb^{3+} has been reported to show UPC luminescence the intensity of which can be enhanced by 1 to 2 orders of magnitude by *not* using washing with water before annealing [7]. A structural study revealed microstrains in the R sublattice that are relaxed for the material with very high UPC intensity thus decreasing energy losses. Moreover, cation reordering was suggested by the Rietveld results [8].

In this work, the $NaYF_4$:Yb^{3+},Tb^{3+} (x_{Yb}: 0.20, x_{Tb}: 0.04) up-conversion luminescence materials were prepared with co-precipitation. The as-prepared material was washed either with or without water in addition to ethanol and thereafter annealed at 500 °C. This resulted in materials with moderate or very high UPC luminescence intensity, respectively. The local structure of Y, Yb and Tb in the $NaYF_4$:Yb^{3+},Tb^{3+} materials were studied by XAFS measurements using the beamlines A1 and C at HASYLAB (DESY, Hamburg, Germany). The measurements were carried out at 10 and 300 K in the fluorescence mode using the SDD-MI seven channel silicon drift detector. Data was collected on the Y K, Tb L_{III} and Yb L_{III} edges. The extraction of interatomic distances from the EXAFS data was performed by the EXAFSPAK program package [9].

For the material with moderate up-conversion intensity, the R-F distances (Fig., left) increase from Y-F (2.25 Å) to Tb-F (2.34) as expected based on the ionic radii [10]. The Yb-F distance (2.30) is longer than expected indicating minor local distortions around Yb^{3+}. For the material with very high up-conversion intensity (Fig., right), Y-F and Yb-F distances are very similar to each other (2.30 Å) suggesting a decrease in distortions in the R sublattice. This agrees well with the decreasing microstrains observed with the Williamson-Hall analysis previously [8]. The Tb-F distance remains the same for all materials. For the material with high up-conversion intensity, the signal for the cation-cation distances between 3.2 and 4.0 Å is increased (Fig. 6). This indicates that the R^{3+} ions have more heavy neighbors, *i.e.* Yb^{3+} and/or Tb^{3+}, in this material. Especially the Tb data shows significant intensity for distances between the Na and Na/R sites, which is more or less non-existent for the material with moderate up-conversion intensity. The results thus indicate that Yb^{3+} ions occupy the Na sites in the material with very high up-conversion intensity and that these Yb species have formed clusters with the Tb^{3+} ions occupying the regular Na/R sites. Such clustering increases the energy transfer probability between Yb^{3+} and Tb^{3+} (and the Er^{3+} impurity) thus intensifying the up-conversion emission. According to previous Rietveld refinements [8], the amount of Yb^{3+} in the Na site cannot be very high as a whole, but *ca.* 2 mole % (of the total cation amount) of Yb^{3+} can reside in this site without a deterioration in the refinement and a change the structure or chemical composition. This is already 10 % of the total Yb^{3+} content thus constituting a significant difference in the rare earth distribution. The results will be published in appropriate international journals.

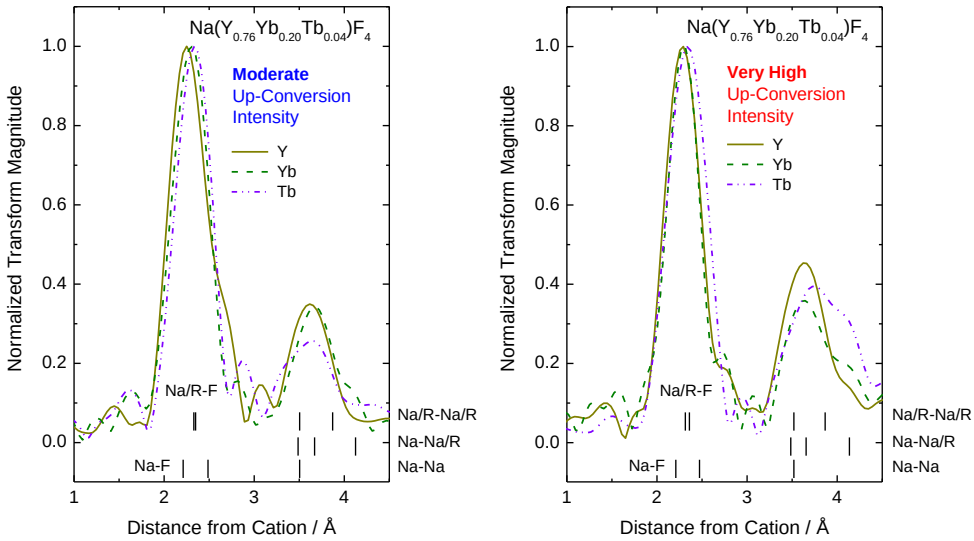

Figure: Distance distributions around Y, Yb and Tb calculated from EXAFS data for $NaYF_4$:Yb^{3+},Tb^{3+} with moderate (left) and very high (right) up-conversion intensity.

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