Characterization of the solid solution series $NaYb_{1-x}Lu_xS_2$ in the α-$NaFeO_2$-type

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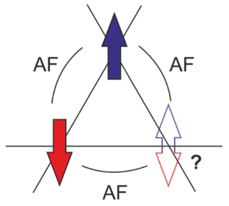
Motivation

Yb-based magnets, with a perfect triangular lattice of pseudospin-1/2 Yb^{3+} ions, have emerged as candidates for realizing a quantum spin-liquid (QSL) state, with $NaYbS_2$ being a prominent example.
To get further insight into the electron spin interactions we substituted Lu^{3+} into $NaYbS_2$, resulting in the solid solution series $NaYb_{1-x}Lu_xS_2$ with well-defined single crystals over the entire substitution range $0 \le x \le 1$.



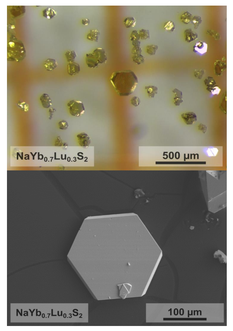
Antiferromagnetically interacting electron spins on a triangular lattice

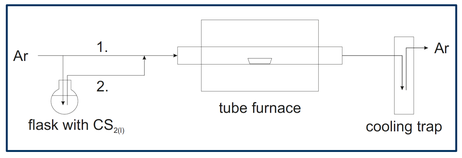
Synthesis

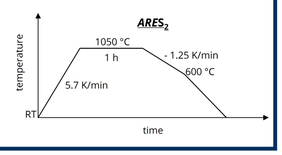
Crystals were grown from the melt using a modified procedure adopted from Masuda *et al.* [1] Stoichiometric amounts of the RE_2O_3 + excess of Na_2S (as reagent and flux) were ground together and filled into a glassy carbon boat, which was put in a tubular furnace. While dwelling at 1050 °C for 1h, $CS_{2(g)}$ as additional sulfur source was transported to the reaction zone (see sketch.)

Idealized reaction equation:

$$2\ Na_2S + 2\ RE_2O_3 + 3\ CS_2 \rightarrow 4\ NaRES_2 + 3\ CO_2$$

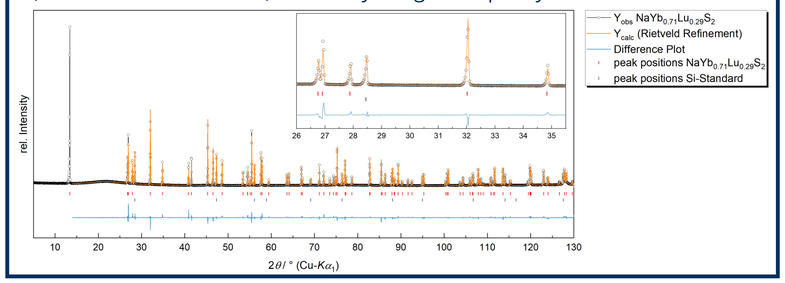


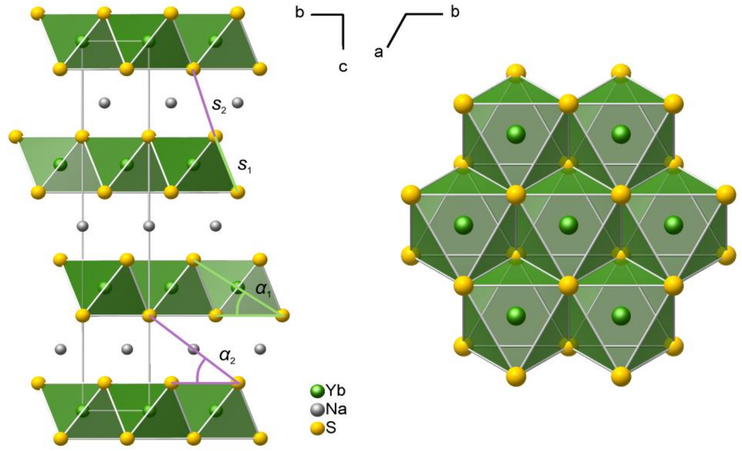




Rietveld refinements

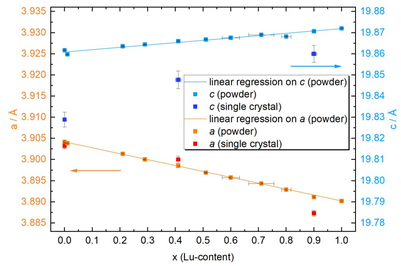
The lattice parameters were refined in the course of the Rietveld fits using the fundamental parameter approach in Topas academic [2]. The atomic positions of $NaYbS_2$ [3] were taken as starting model and a mixed occupancy of the Wyckoff site 2*a* with Yb and Lu was considered. The background was modelled manually to take care of the enhanced background at low angles (between 14° and 30° 2θ) caused by the glass capillary.

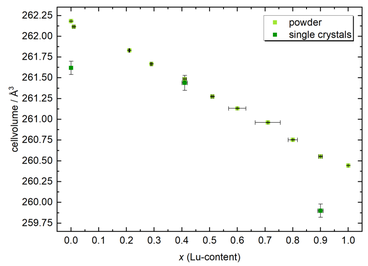


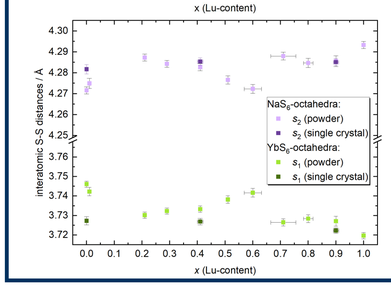


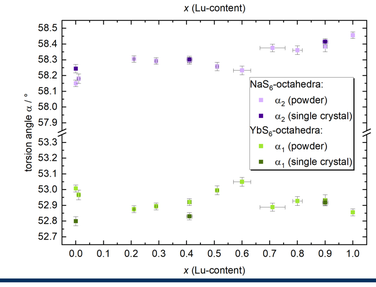
Structural characterization

Powder and single crystal diffraction data of all samples of the of the solid solution series $NaYb_{1-x}Lu_xS_2$ could be refined in space group $R\bar{3}m$ (SG. 166) of the α-$NaFeO_2$ structure type. In this structure type *A* and *B* cations are both found in octahedral coordination surrounded by sulfur forming separated layers of equilateral triangular lattices (see above).
In the analyses of powder and single crystal diffraction data we found no evidence for a phase separation or inhomogeneous distribution of the *RE* ions within the structure. The lattice parameters ideally follow Vegard's rule. Whereas the lattice parameter *a* decreases linearly with increasing Lu content, *c* gets elongated. As the change in *a* is seven times larger than the change in *c*, the unit cell volume decreases slightly as well. As the only free coordinate in the structure is the z coordinate of the sulfur atom, the interlayer distances and torsion angles show a slight scattering but follow the same trends as the lattice parameters.





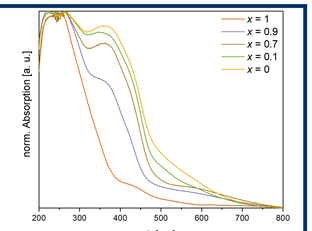


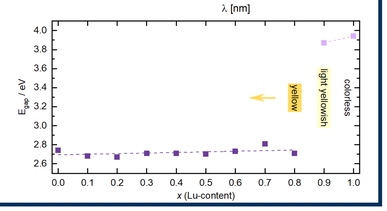


Optical properties

UV-vis absorption spectra were measured in reflectance mode with $BaSO_4$ as white standard. An additional broad band (at 360 nm) in the Yb-compounds is attributed to a sulfur to rare earth ion charge transfer (CT) transition.

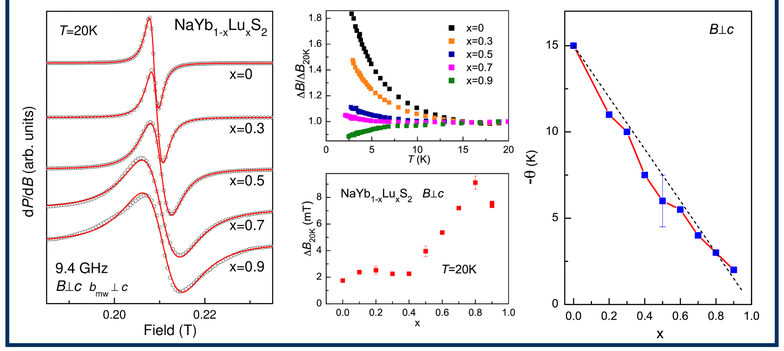
The band gaps calculated from Tauc plots remain constant at around 2.73 eV until $x \le 0.8$, but jump to 3.87 eV for $x = 0.9$. This jump can be attributed to the suppressed CT transition in Lu-rich samples.





Magnetic properties

Electron spin resonance (ESR) experiments were performed at X-band frequencies (ν = 9.4 GHz) using a continuous wave ESR spectrometer. The ESR experiments were performed on single crystalline platelets with a typical size of 0.4 x 0.4 x 0.05 mm^3. The sample temperature was set with a helium-flow cryostat allowing for temperatures between 2.7 and 300 K [4].



Summary and Outlook

The structural characterization shows that the established solid solution series $NaYb_{1-x}Lu_xS_2$ is well suited in terms of linear evolution of its structural properties to study magnetic dilution without interference of inter site cation disorder or structural defects.
As magnetization measurements show no magnetic ordering down to 2 K further measurements, such as heat capacity, AC susceptibility or μSR spectroscopy, in the sub-Kelvin regime are necessary and scheduled to examine if the QSL state is preserved upon Lu doping up to the percolation threshold, as suggested by the results from the ESR spectroscopy.

Member in the network of: DRESDEN concept

Founded by: DFG Deutsche Forschungsgemeinschaft

References:
[1] H. Masuda, T. Fujino, N. Sato, K. Yamada, *Materials Research Bulletin* **1999**, *34*, 1291–1300.
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[3] A. W. Verheijen, W. J. P. V. Enckevort, J. Bloem, L. J. Giling, *J. Phys. Colloques* **1975**, 36, 39–45.
[4] S. J. Campbell, I. R. Herbert, C. B. Warwick, J. M. Woodgate, *J Phys E* **1976**, 9, 443–446.
[5] E. Häußler, J. Sichelschmidt, M. Baenitz, E. C. Andrade, M. Vojta, T. Doert, arXiv:2203:02199.

Acknowledgements:
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