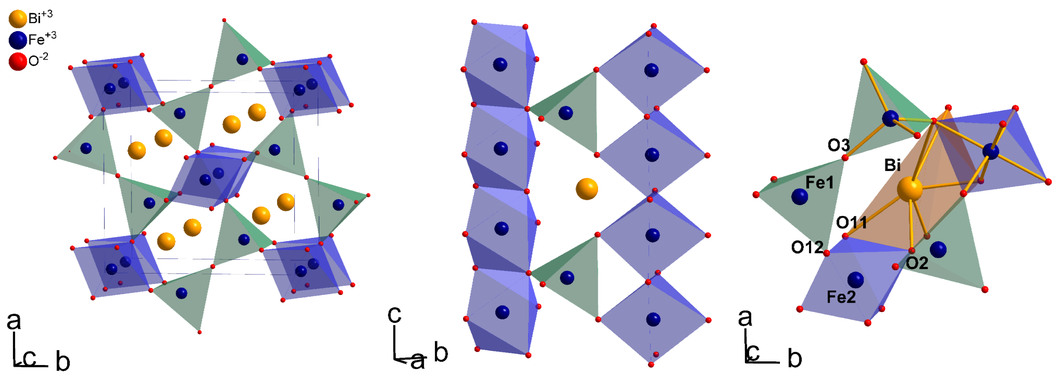
Size-dependent structural, spectroscopic and thermoanalytic properties of nano- to poly-crystalline $Bi_2Fe_4O_9$

Andrea Kirsch[1,2], M. Mangir Murshed[1,2], F. Jochen Litterst[3], Thorsten M. Gesing[1,2]

[1]Universität Bremen, Chemische Kristallographie fester Stoffe, Bremen, Germany,
[2]Universität Bremen, MAPEX Center for Materials and Processes, Bremen, Germany
[3]Technische Universität Braunschweig, Institute for Condensed Matter Physics, Braunschweig, Germany

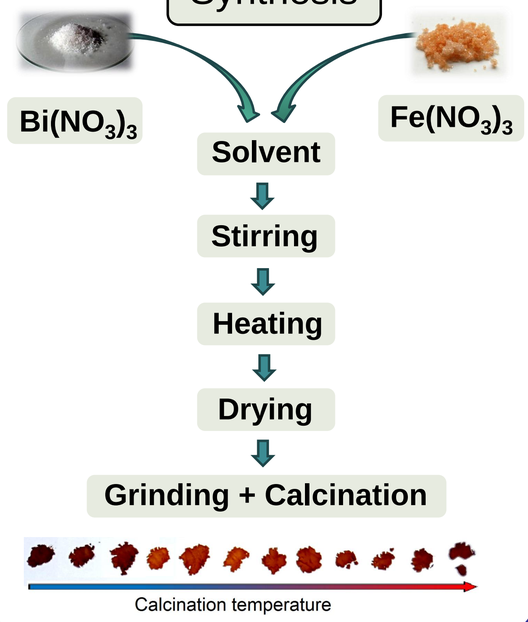
Materials in the nano-size regime often show interesting size-dependent physical properties. Mullite-type $Bi_2Fe_4O_9$ has been investigated as a suitable photocatalyst due to its high chemical stability and small band gap (1.9 - 2.1 eV)[1]. It is also the first analogue of a Cairo pentagonal magnetic lattice[2].

Crystal structure of $Bi_2Fe_4O_9$

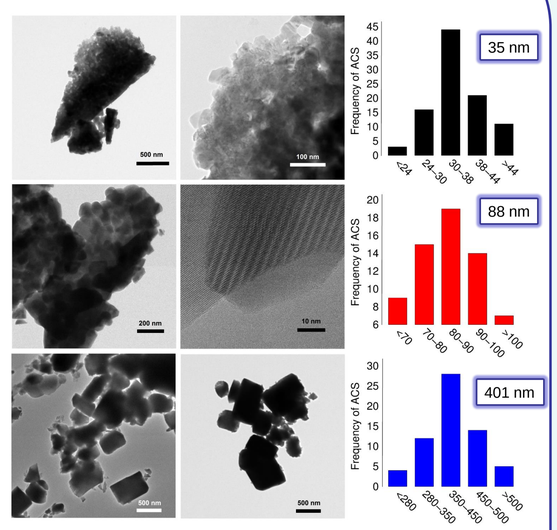


$Bi_2Fe_4O_9$ crystallizes in the space group *Pbam* with $Z = 2$. It has a mullite-type structure with typical chains of edge-sharing FeO_6 octahedra parallel to the **c**-axis. The chains are cross-linked by corner-sharing FeO_4 double-tetrahedral units.

Synthesis



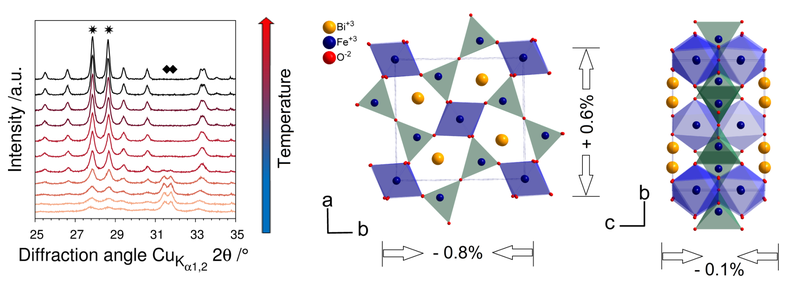
TEM

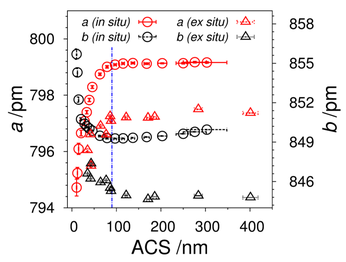


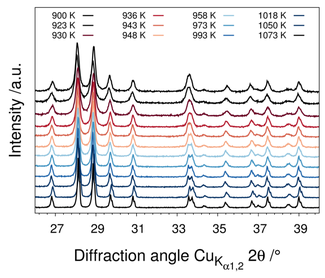
TEM micrographs of three samples.

X-ray powder diffraction

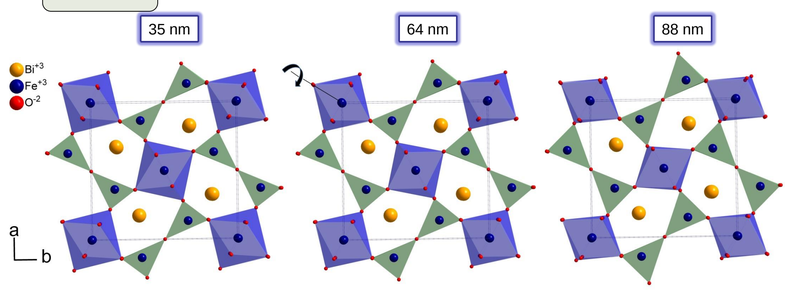
In situ

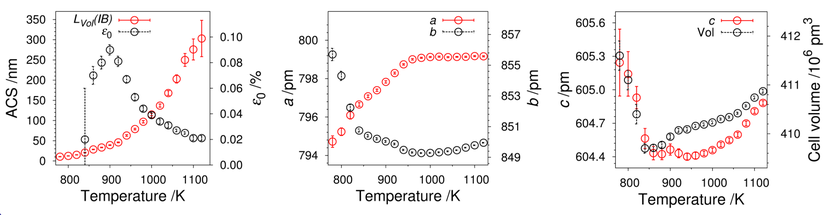




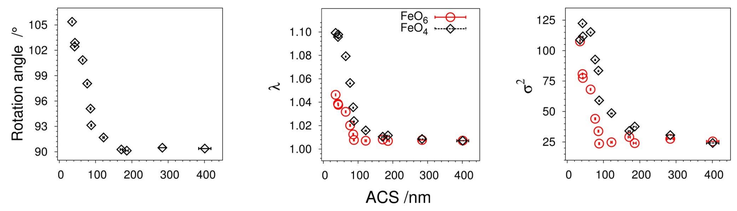


Ex situ

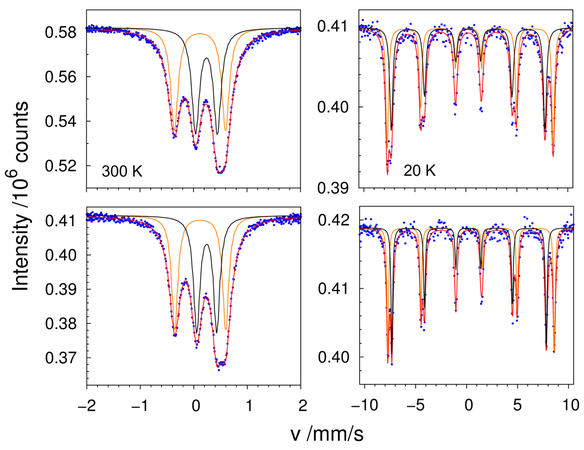




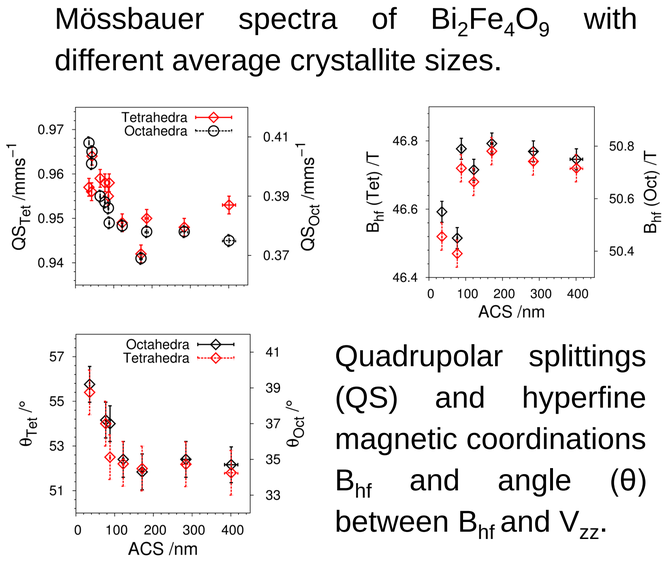
Heating of the precursor lead to the formation of $BiFeO_3$ followed by a transformation into $Bi_2Fe_4O_9$. Samples with different average crystallite sizes were produced by heating the precursor for 2 h at temperatures 900 K – 1073 K.



^{57}Fe Mössbauer spectroscopy

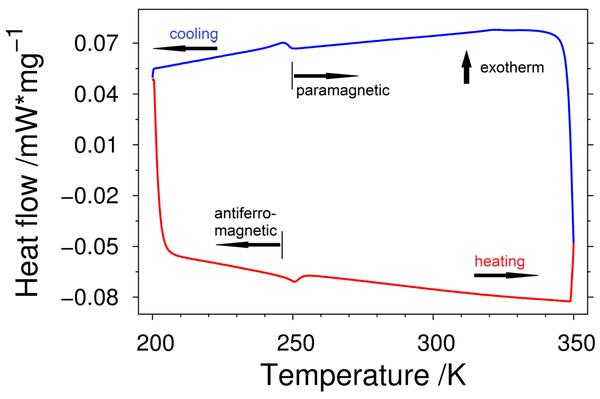


Mössbauer spectra of $Bi_2Fe_4O_9$ with different average crystallite sizes.

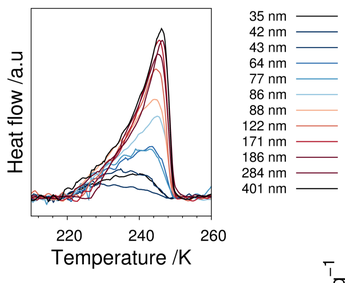


Quadrupolar splittings (QS) and hyperfine magnetic coordinations B_{hf} and angle (θ) between B_{hf} and V_{zz}.

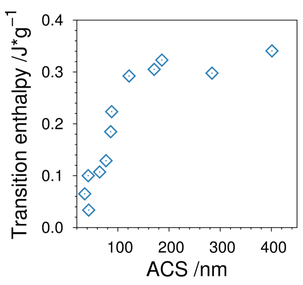
DSC



DSC curves of $Bi_2Fe_4O_9$ with an average crystallite size of 284(9) nm.

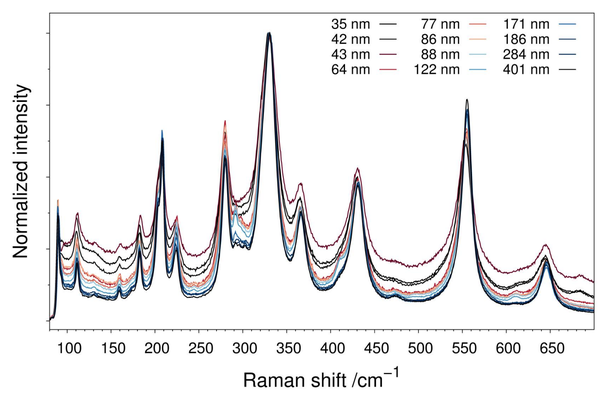


Exothermic peak for samples with average crystallite sizes from 35.3(4) – 401(17) nm.

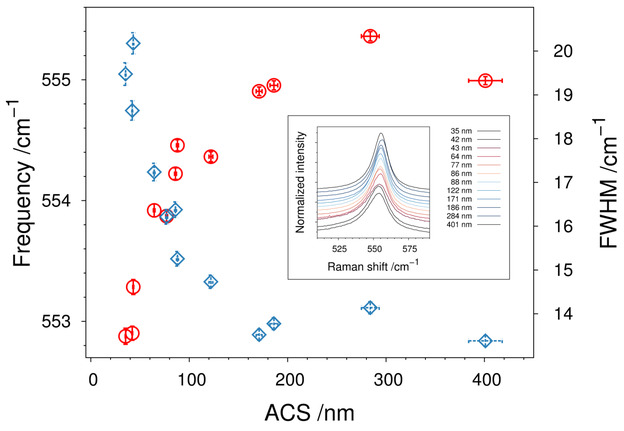


Transition enthalpy as a function of average crystallite size (ACS).

Raman spectroscopy



Normalized Raman spectra of samples with different average crystallite sizes.



Changes of frequency and FWHM as function of average crystallite size (ACS).

Conclusion: Strong polyhedral distortions below a critical average crystallite size of 122(2) nm change the local spin orientations in $Bi_2Fe_4O_9$ as evidenced by the combination of X-ray diffraction, Raman and Mössbauer spectroscopy as well as differential scanning calorimetry (DSC)[3].

Universität Bremen

Dr. Andrea Kirsch
Chemische Kristallographie fester Stoffe
Anorganische Chemie und Kristallographie Universität Bremen
Leobener Strasse /NW2, D-28359 Bremen
Tel.: +49 421 218 63146, Email: a.kirsch@uni-bremen.de

References: [1] Q. Zhang et al., *J. Phys. Chem. C* 115 (2011) 25241.
[2] E. Ressouche et al., *Phys. Rev. Lett*. 103 (2009) 267204.
[3] A. Kirsch et al., *J. Phys. Chem. C* 123 (2019) 3161.