

MS44- Operando and in-situ crystallographic studies using powder diffraction

Chairs: Prof. Simona Galli, Dr. Gavi Vaughan

MS44-P01

Structural and spectroscopic investigation on the crystallization behavior of $\text{Bi}_2\text{Fe}_4\text{O}_9$

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Materials in the nano-sized regime often show unique and size-dependent properties. Despite intense studies on nano-materials a systematic structural and spectroscopic study on a given system and the associated size-dependent physical properties is rarely studied, in particular from nano-crystalline into poly-crystalline (bulk) material through a critical size-regime. We carefully investigate the crystallite size-dependent structural features of $\text{Bi}_2\text{Fe}_4\text{O}_9$, *ex-situ* as well as *in-situ*. Temperature-dependent X-ray powder diffraction (XRPD) on an X-ray amorphous precursor of $\text{Bi}_2\text{Fe}_4\text{O}_9$, stoichiometry revealed that both $(\text{Bi}_{1-x}\text{Fe}_x)\text{FeO}_3$ and $\text{Bi}_2\text{Fe}_4\text{O}_9$ simultaneously crystallize from 780 K on, and the perovskite phase transformed into $\text{Bi}_2\text{Fe}_4\text{O}_9$, above 860 K. Thus, heating the precursor above this point for 2 h at a subsequent higher temperature produces pure $\text{Bi}_2\text{Fe}_4\text{O}_9$ samples with greater average crystallite sizes. As such, twelve samples with different crystallite sizes from 35.3(4) nm to 401(17) nm were produced using the temperatures between 900 K and 1073 K. Rietveld refinements on X-ray powder data collected at ambient condition *ex situ* showed that the lattice parameters depend on the crystallite size; similar to the trend observed for the evaluated data of the *in-situ* XRD measurements. Significant changes of the lattice parameters are caused by strong distortions of the FeO_4 tetrahedra and cooperative rotation of the FeO_6 octahedra. Analyses of the widths and frequencies of the Raman modes support these structural features. The electronic bandgap and the 2nd absorption edge observed at around 700 nm are found to be a function of the crystallite size. Why the Urbach energy steeply drops down from 0.33 eV to 0.19 eV at the crystallite size of 64 nm leaves an open question, which is the critical length of the magnetic cycloidal spiral of the multiferroic BiFeO_3 ¹.

References:

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Crystal Structures of Solid Fluorine and Nitrogen Trifluoride

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The crystal structures of the chemical elements belong to the fundamental knowledge of chemistry as atom distances, bond lengths and angles can be determined precisely and the data serve as benchmarks for quantum chemistry. Surprisingly, the crystal structures of α -fluorine and β -fluorine have so far only once been investigated [1,2]. Probably this is due to the fact that solid F_2 is still extremely reactive and in the case of α - F_2 the authors reported several explosions due to the highly exothermic phase change and the subsequent reaction of F_2 with the sample holder [1]. It was concluded that α - F_2 crystallizes in the monoclinic crystal system, probably in space group type $C2/m$, but space group type $C2/c$ could not be ruled out. Later the original diffraction data were reinterpreted by others and space group $C2/c$ was found to be more likely correct [3]. The precise space group of α - F_2 remained, however, uncertain, which naturally has an influence on the determined atom positions, bond lengths and displacement parameters. The crystal structure of β - F_2 was first reported in 1964 and determined by means of single crystal X-ray diffraction [2], the problem to distinguish between two cubic space group types, $P-43n$ and $Pm-3n$, was faced. The higher symmetric space group type was chosen since a disordered structure was expected. Neither the bond length of the F_2 molecules, and not the anisotropic displacement parameters of the fluorine atoms could be refined.

Therefore, we constructed a gas line attached to a sample holder inside the SPODI neutron diffractometer at the FRM-II neutron facility of the Heinz Maier-Leibnitz Zentrum in Garching, Germany. The crystal structures of α - and β -fluorine were determined using powder neutron diffraction and Rietveld refinement. We will report on the obtained models providing much more precise lattice parameters, atomic coordinates as well as bond lengths for the two polymorphs of fluorine. Using the same gas line we attempted an elucidation of the previously unknown crystal structure of solid nitrogen fluoride at various temperatures.

References:

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