

## MS26-05 The incommensurately modulated phase in (2-methylimidazolium) tetraiodobismuthate(III) thermochromic organic-inorganic hybrid

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(2-methylimidazolium) tetraiodobismuthate(III) (abbreviated as (2-MIm)BiI<sub>4</sub>) is a thermochromic, semiconducting hybrid. It undergoes structural first-order phase transition to incommensurately modulated phase at 308 K. The symmetry changes from  $C2/c$  to  $C2/c(0,\beta,0)_{s0}$ ; the modulation wave vector  $\mathbf{q}=0.575(2)\mathbf{b}^*$  [1]. The incommensurate phase is stable down to 100 K. The non-modulated structure consists of polymeric chains of [BiI<sub>4</sub>]<sup>-</sup> anions propagating in the  $c$  direction and stacks of 2-MIm<sup>+</sup> counter-ions that couple to the anionic substructure via weak hydrogen bond interactions. The polymeric [BiI<sub>4</sub>]<sup>-</sup> anions comprise of distorted BiI<sub>6</sub> octahedra that form zig-zag chains by sharing the *cis* edges. The cations are dynamically disordered over two equivalent positions that are related by the two-fold axis. The transformation to incommensurate phase is triggered by a collective, sinusoidal displacement of bismuth and iodide atoms from their high-temperature positions. The intra-chain bonds in modulated phase do not differ considerably from their high temperature counterparts. Much significant deviations are observed between the chains which may be shifted up to ~0.4 Å relative to each other along the  $c$  direction. Substantial variations within the inter-chain Bi...Bi distances may have an impact on the semiconducting and thermochromic properties of this material. 2-MIm<sup>+</sup> counter ions order in the incommensurate phase. In each cavity the 2-MIm<sup>+</sup> adopts one of the two positions that were equivalent in the high-temperature phase. At 220 and 150 K the reorientation movements between the sites are blocked which is confirmed by dielectric response. DOS calculations together with asymmetric local environment of bismuth ions imply the presence of the stereochemically active bismuth lone pair  $6s^2$  electrons in both phases. The change of the lone pair activity may play the foreground role in the phase transition mechanism as far as the increased contribution of bismuth states in total DOS in the incommensurate phase is noted. This interpretation is consistent with structural data that show greater deformation of the bismuth coordination geometry in the modulated structure.

[1] A. Gagor et al. CrystEngComm, 2015, DOI: 10.1039/C5CE00046G

**Acknowledgements.** Part of the research (synthesis, DSC and dielectric measurements) was supported by the National Science Centre (Poland) under grant No. 2013/11/D/ST8/03297 and by the European Union under the European Social Fund.

**Keywords:** modulated structure, organic-inorganic hybrid, phase transition

## MS27. Electron crystallography methods

Chairs: Alex Eggeman, Lukáš Palatinus

## MS27-01 Deformation mapping in the TEM by dark holography, nanobeam diffraction, geometrical phase analysis and precession electron diffraction. A comparison of the different techniques

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In the last few years there has been an explosion in the number of transmission electron microscopy based (TEM) techniques that can be used for strain mapping with nm-scale resolution. These include dark field electron holography, the geometrical phase analysis of high-resolution images, nanobeam diffraction and more recently precession electron diffraction. In order to benchmark the different techniques a calibration specimen containing 10-nm-thick SiGe layers with different Ge concentrations has been grown by chemical vapour deposition. Due to the epitaxial growth, the lattice parameter of the SiGe will be expanded relative to the Si in the growth direction. Figure 1(a) shows a HAADF STEM image of the calibration specimen indicating the concentration of Ge present in each layer and deformation maps for the growth direction acquired by (b) GPA of HAADF STEM (c) dark field electron holography (d) precession electron diffraction and (e) finite element simulations are shown. The HAADF STEM deformation mapping has a spatial resolution of 1.5 nm which is imposed by the size of the mask used in Fourier space during the reconstruction and a measurement sensitivity of 0.25 % was determined by taking a standard deviation of the deformation measured in the unstrained silicon substrate. For the dark holography the spatial resolution imposed by the fringe spacing of the interference pattern is 6 nm with a measured sensitivity of 0.05 %. For precession diffraction, the spatial resolution imposed by the diameter of the electron probe is 2 nm and a sensitivity of 0.02% measured. While it is relatively straightforward to apply all of these techniques to simple calibration specimens where both large values of deformation are expected and the experiment is simplified due to the 1D nature of the strained layers. All of the techniques have been applied to a range of different specimens each with different complications, such as a 35-nm gate SiGe recessed source and drain pMOS device, a nMOS device tensily strained using a nitride film, to state of the art SOI-based semiconductors and a III/V superlattice. The advantages and disadvantages the