

## Title: Local structure of dopants in bismuth chalcogenides probed with EXAFS

Krzysztof Maćkosz (*AGH University of Science and Technology, Academic Centre for Materials and Nanotechnology, Kraków, Poland and AGH University of Science and Technology, Faculty of Physics and Applied Computer Science, Kraków, Poland*)

Joanna Stępień (*AGH University of Science and Technology, Academic Centre for Materials and Nanotechnology, Kraków, Poland*)

Marta Waśniowska (*Universität zu Kiel, Institut für Experimentelle und Angewandte Physik, Kiel, Germany*)

Kai Rosnagel (*Universität zu Kiel, Institut für Experimentelle und Angewandte Physik, Kiel, Germany*)

Ireneusz Miotkowski (*Purdue University, West Lafayette, United States*)

Virginia Monteseuro-Padron (*European Synchrotron Radiation Facility, Grenoble, France*)

Olivier Mathon (*European Synchrotron Radiation Facility, Grenoble, France*)

Olga Safonova (*Swiss Light Source, Paul Scherrer Institute, Villigen, Switzerland*)

Maarten Nachtegaal (*Swiss Light Source, Paul Scherrer Institute, Villigen, Switzerland*)

Andrzej Kozłowski (*AGH University of Science and Technology, Faculty of Physics and Applied Computer Science, Kraków, Poland*)

Zbigniew Kąkol (*AGH University of Science and Technology, Faculty of Physics and Applied Computer Science, Kraków, Poland*)

Marcin Sikora (*AGH University of Science and Technology, Academic Centre for Materials and Nanotechnology, Kraków, Poland*)

[mackosz@agh.edu.pl](mailto:mackosz@agh.edu.pl)

### **Background:**

Thermoelectrics are very promising materials from the point of view of potential applications in the conversion of thermal energy into electricity. Even the smallest portions of heat generated by the devices can be recovered and reuse. But those materials should be characterize by three important features: high electrical conductivity, high Seebeck coefficient and low thermal conductivity. The best ratio of these values is found in the bismuth telluride-based alloys with the tetradimite structure. However, their use was extremely difficult due to the specific mechanical properties and difficulties in producing homogeneously doped materials with predictable electrical properties.

In addition, single crystals of tetradymite also exhibit extraordinary properties resulting from their specific crystalline structure and its surface stability, which are called as topological insulators. Topological insulators show excellent electrical conductivity on the surface layer with a thickness of only a few nanometers, while their interior is an insulator. Similar properties are found in some semiconductors, but in topological insulators, the flow of electrons on the surface layer is not affected by impurities and foreign dopants (except magnetic), which makes them particularly promising for use in magnetoelectrics and spintronics. Recent discoveries have shown that quantum anomalous Hall effect has been observed in thin films of V and Cr doped topological insulators, i.e. magnetic topological insulators, where robust bulk ferromagnetic ordering is spontaneously developed.

**Methods:**

Systematic investigation of local structure of Mn, Fe, Co, Ga, Sb and S dopants into bismuth chalcogenides single crystals by means of Extended X-ray Absorption Fine Structure (EXAFS) spectroscopy are presented. The spectra were collected at absorption edges of host crystal atoms and dopants at SuperXAS (SLS) and BM23 (ESRF) beamlines. Using partial fluorescence yield the spectra of Bi  $L_3$ -edge as well as of Se, Te, Ga, Sb and transition metals  $K$  edges were detected. EXAFS analysis was performed using ATHENA & ARTEMIS software – a part of DEMETER package. Fitting was performed simultaneously on Bi and Se edges using hexagonal lattice constants ( $a$ ,  $c$ ) and crystallographic coordinates as free parameters. Spectra of dopants were fitted using multiple site analysis in order to estimate the amount of dopants per site.

**Results:**

Due to the complex crystal structure of  $\text{Bi}_2\text{X}_3$  ( $\text{X}=\text{Se,Te}$ ) with its layered hexagonal unit cell consisting of three X–Bi–X–Bi–X quintuple layers (QL) bonded together across a van der Waals (vdW) gap, several different possible lattice sites exist for the incorporation of dopants. We assume, that doping atoms may substitute Bi or X sites as well as to enter the crystal structure in a tetrahedral ( $T_d$  vdW) or octahedral ( $O_h$  vdW) interstitial sites within van der Waals gap, and octahedral sites within QL layers ( $O_h$  QL).

Preliminary results show that S and Sb ions substitute predominantly into chalcogenide sites and Bi sites. A complex distribution of transition metals is observed. They dope also interstitial sites both within quintuple layers as well as van der Waals gap. The distribution of interstitials varies significantly among dopant and host crystal kinds. The highest amount of substitutional doping is observed for  $\text{Bi}_2\text{Te}_3:\text{Mn}$  crystals. Mn doping into  $\text{Bi}_2\text{Se}_3$  crystals results in equal distribution between Bi substitutional sites and  $O_h$  interstitials within vdW gap and small amount of other kind of interstitials. On the other hand Fe doping into  $\text{Bi}_2\text{Se}_3$  results in predominant intercalation into  $O_h$  vdW sites.

**Conclusion:**

XAFS measurements occur to be sensitive for local structure of dopants in bismuth chalcogenides single crystals. We observed that chalcogenide atoms clearly indicate substitutional character of dopants leading to a slight modification (local distortion) of the unit cell parameters, while transition metals occupy predominantly interstitial position within QL and vdW layers.

**Acknowledgements:**

We acknowledge ESRF and SLS for provision of beamtime, M. Rams (Jagiellonian University, Kraków) for low temperature magnetic characterization, and AGH fellows (M. Chrobak, M. Gajewska, M. Jurczyszyn, M. Przybylski, A. Szkudlarek, Z. Tarnawski, W. Tokarz and A. Żywczak) for structural, microscopic and electronic characterizations as well as many fruitful discussions. Supported by National Science Centre, Poland (grant number: 2015/17/B/ST3/00128). The access to ESRF was financed by the Polish Ministry of Science and High Education - decision number: DIR/WK/2016/19.