Pressure-induced polymerization and electrical conductivity in polyiodides

T. Poreba[1,2]*, N. Casati[1], M. Ernst[2] and P. Macchi[2]

[1] Laboratory for Synchrotron Radiation, Paul Scherrer Institute, 5232 Villigen – PSI, Switzerland
[2] Department of Chemistry and Biochemistry, University of Bern, Freiestrasse 3, Bern, Switzerland

Keywords: high pressure, crystalline materials, conductivity, molecular crystals

*e-mail: tomasz.poreba@psi.ch

Polyiodide compounds posses a very rich structural chemistry. They represent one of a few classes of compounds that can form extensive inorganic homoatomic polymeric networks. Moreover, polyiodides exhibit useful redox properties, as well as electrical conductivity uncommon for nonmetals (from values characteristic for insulators up to those for metals).
Hence, they have found technical applications in electronic and electrochemical devices such as batteries, fuel cells, dye-sensitized solar cells, optical devices, etc.

We investigated[1] the response of tetraethylammonium di-iodine triiodide (TEAI) to compression, using powder and single-crystal X-ray diffraction, electrical conductivity, and first principle calculations

We reported the high-pressure structural characterization of TEAI in which a progressive addition of iodine to triiodide groups occurs. Compression leads to the initial formation of discrete heptaiodide units, followed by polymerization to a 3D anionic network. Although the structural changes appear to be continuous, the insulating salt becomes a semiconducting polymer above 10 GPa. The features of the pre-reactive state and the polymerized state are revealed by analysis of the computed electron and energy densities. The unusually high elecuctivity can be explained with the formation of new bonds. These features make TEAI a tunable pressure-sensitive electric switch. Structural studies at high pressure can rationalize the synthesis and search for future organic and hybrid semiconductors based on polyiodides. This includes structures with soft I···I contacts, which are the most prone for charge transport across the crystal under increased pressure.

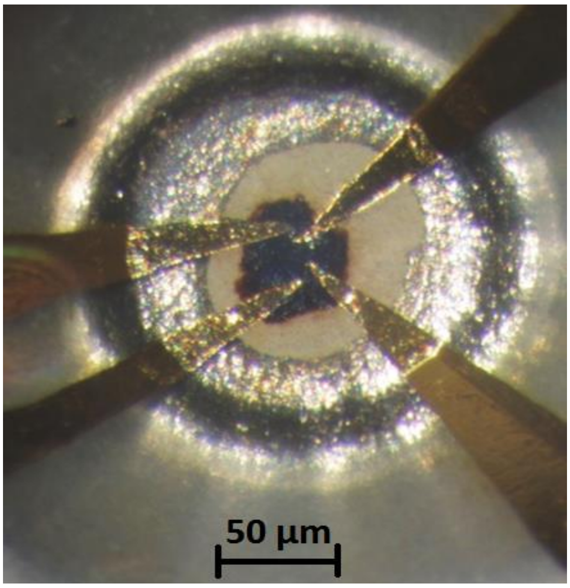

Figure 1 : Four-probe setup for resistivity measurements of TEAI under high-pressure

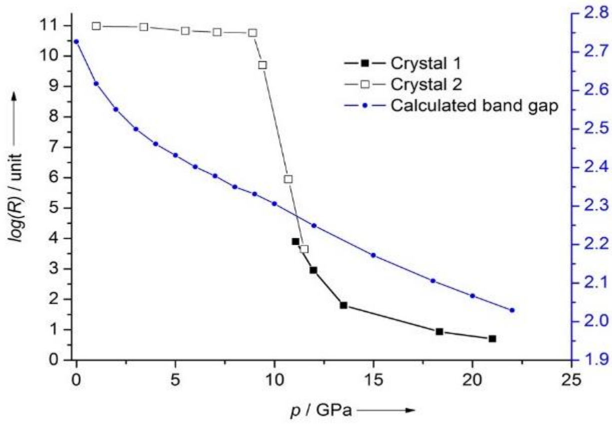

Figure 2 : Electrical resistance of TEAI crystal (measured on two different samples) and calculated band gap.

Acknowledgments: This work was supported by the Swiss National Science Foundation (Project Nr. 162861 and NCCR Marvel).

[1] T. Poreba et al., *Angew.Chem. Int. Ed.* 2019