Metavalent Bonding : Characterisation and Implications for Applications in Phase Change Materials, Thermoelectric and Photovoltaic compounds.

Jean-Yves Raty
Condensed Matter Simulation Group
University of Liège & FRS-FNRS

In the last two decades, Phase Change Materials have emerged as active components of non-volatile memories thanks to their ability to switch extremely rapidly from a conducting crystal to a semiconducting glass. Ab Initio simulations helped understanding the structure and some properties of the glassy phase, like aging, but also led us to reinvestigate the nature of chemical bonding in the crystalline phase.

Using a two electron (pair density) formalism, we develop a two-dimensional map based on a quantum-topological description of electron sharing and electron transfer in binary solids. This map intuitively identifies the fundamental nature of ionic, metallic, and covalent bonding in a range of elements and binary materials. More interestingly, it highlights a distinct region where phase change materials are found and for which bonding has been qualified as ‘metavalent’. Extending this map into the third dimension by including physical properties interesting for applications, we show that bonding in metavalent compounds differs from the usual views of bonding. This map could then be used to help designing new materials: by searching for desired properties in a 3D space and then mapping this back onto the 2D plane of bonding. Indeed, the metavalent region of the map encompasses compounds with other enhanced properties, such as high thermoelectric performance or photovoltaic efficiency. We illustrate metavalent bonding for lead chalcogenides and V-VI compounds, and the transition between covalent and metavalent regions of the map is described.

Remarkable, metavalent bonding in crystal does not survive upon disordering, which makes their glassy phase exceptions to the Zachariasen’s rule.