Understanding the structure and properties of Pn_2Ch_3 (V_2VI_3) compounds from a bonding perspective

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ABSTRACT

A number of sesqui-chalcogenides show remarkable properties which make them attractive for applications like phase change materials. Atom probe tomography studies and DFT calculations reveal that Bi_2Te_3, Bi_2Se_3, and Sb_2Te_3, and β-As_2Te_3 show an unconventional bond breaking mechanism. And in the four metavalently bonded chalcogenides, the weak electronic coupling crossing the van der Waals like gaps is rather strong. This finding indicates that these chalcogenides are not 2D solids. These results are indicative for an unconventional bonding mechanism – metavalent bonding in these compounds, which is distinctively different from other conventional chemical bonds. Finally, combining with the electron transfer and sharing between adjacent atoms, the property-based 3D maps reveal discernible property trends and enable material design.

Key words: metavalent bonding, atom probe tomography, sesqui-chalcogenides, materials design.

1. INTRODUCTION

Chalcogenides enable a wide range of applications including phase change materials due to their unconventional property portfolio[1]. For IV-VI compounds such as GeTe, this property portfolio has been attributed to a novel bonding mechanism – metavalent bonding[1] which is accompanied by an unusual bond breaking process[2]. However, the bonding mechanism in sesqui-chalcogenides such as Sb_2Se_3 or Sb_2Te_3 compounds has attracted much less attention. In this work, multiple techniques including Atom Probe Tomography (APT) and DFT are utilized to understand the bonding mechanisms in V_2VI_3 compounds.

2. EXPERIMENTS

A standard lift-out process is applied to prepare needle-shaped specimens. During a laser-assisted APT measurement, a DC voltage is applied to a specimen, which is exposed to laser pulses employing

a fixed pulse length of 10 ps. DFT approach is applied to assess electrons transfer and electrons shared between neighboring atoms.

3. RESULTS & DISCUSSION

Generally, in APT, a successful laser pulse dislodges a single ion from the tip called single event, while only a small fraction of laser pulses leads to multiple ions called 'multiple events'. As shown in Fig. 1a, for Sb_2Se_3 and GaSe, we mainly observe single events whose probabilities are 95% and 81%, respectively. On the contrary, both the proportion and 'size' of multiple events is much larger in Bi_2Se_3. Only Bi_2Te_3, Bi_2Se_3, Sb_2Te_3 and β-As_2Te_3 show a high probability to form multiple events, while others are characterized by an ordinary bond rupture, i.e. low probability of multiple events as observed in other conventionally bonded compounds.

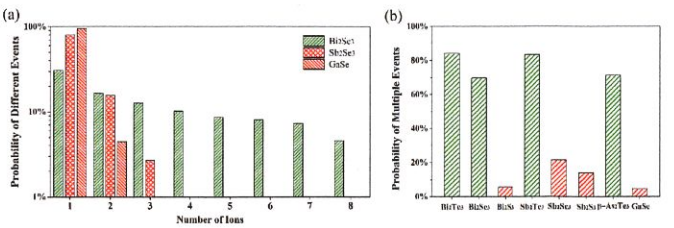

Figure 1. (a) Distribution of the size of multiple events; (b) Probabilities of multiple events.

From the property-based 3D maps in Fig. 2, metavalent bonding is located in a region where about one electron is shared between two nearest neighbors, while the electron transfer is rather modest. Together with the unique bond breaking process, anomalously high physical properties observed for these sesqui-chalcogenides is indicative for metavalent bonding in this material class.

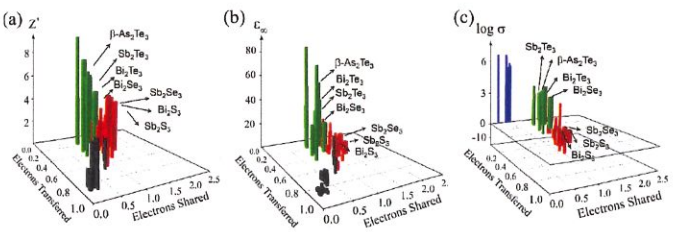

Figure 2: 3D electronic maps using three independent properties, i.e. the Born effective charge Z^*, epsilon infinity ε_∞ and the electrical conductivity log σ.

4. CONCLUSION

In summary, a unique bonding mechanism has been identified in Bi2Te3, Bi2Se3, Sb2Te3 and □-As2Te3 using both APT and DFT calculation. Three property-based maps can be utilized to design material properties, in particular for materials with metavalent bonding.

REFERENCES

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Biographies

Yudong Cheng is currently a Ph.D. student in the I. Institute of Physics at RWTH Aachen. His scientific interests include APT and the chemical bonding mechanism of PCMs.