The Elusive $LiBi_3S_5$: Synthesis, Characterization, and Topological Analysis

Dennis Wiedemann[1], Suliman Nakhal[2], Bernhard Stanje[2], Oleksandr Dolotko[3], Martin Wilkening[2], Martin Lerch[1]

[1] *Institut für Chemie, Technische Universität Berlin, Straße des 17. Juni 135, 10623 Berlin, Germany;* [2] *Institute for Chemistry and Technology of Materials, Christian Doppler Laboratory for Lithium Batteries, Graz University of Technology, Stremayrgasse 9, 8010 Graz, Austria;* [3] *Heinz Maier-Leibnitz Zentrum, Technische Universität München, Lichtenbergstr. 1, 85747 Garching, Germany*

E-Mail: dennis.wiedemann@chem.tu-berlin.de

Semiconducting chalcogenides are sought-after materials for thermoelectric refrigeration and portable power generation. Because of their favorable properties, ternary and quaternary alkali-metal bismuth sulfides (*e.g.*, $RbBi_3S_5$, KBi_3S_5, and $Na_{0.66}K_{0.33}Bi_3S_5$) have been a focus of research. The lightest member of this class, $LiBi_3S_5$, has hitherto eluded directed synthesis and proper characterization, in spite of having been announced as early as in 1977 [1].

Inspired by this, we have synthesized $LiBi_3S_5$, characterized it structurally, and analyzed its topology with respect to possible pathways for lithium-ion migration. Two solid-state routes starting from $LiBiS_2$ and Bi_2S_3 led to success in synthesis. The crystal structure was then determined using powder neutron diffraction and NMR experiments, followed by inspection of the probable conduction pattern using void-surface analysis and Voronoi-Dirichlet partitioning (VDP).

$LiBi_3S_5$ was found to be of the $AgBi_3S_5$ type with a strongly disordered cation lattice (three/two positions mainly occupied by bismuth/lithium, respectively). The topological analyses of genuine and derived structural models showed generation of Frenkel defects by displacement of lithium ions into tetrahedral voids to be possible. Subsequent 1D migration may only occur in channels along b (see Fig. 1). In reality, these will be blocked by bismuth ions, thus making the disordered material a poor long-range lithium-ion conductor [2].

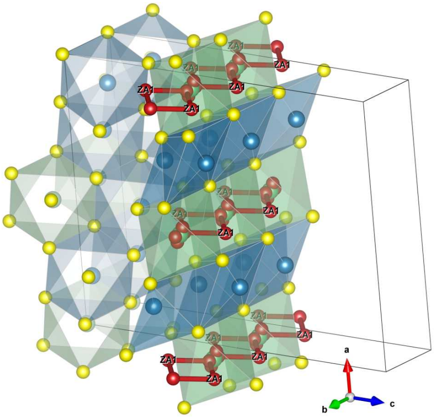

Figure 1: Detail of ordered model of $LiBi_3S_5$ with migration channel (blue: bismuth, green: lithium, yellow: sulfide ions, red: migration pathway; unit cell in black).

[1] Equilibrium Diagram of the Bi_2S_3–Li_2S System, V. B. Lazarev, S. I. Berul', A. F. Trippel', Russ. J. Inorg. Chem. 22 (1977) 1218.

[2] $LiBi_3S_5$ – A Lithium Bismuth Sulfide with Strong Cation Disorder, S. Nakhal, D. Wiedemann, B. Stanje, O. Dolotko, M. Wilkening, M. Lerch, J. Solid State Chem. 238 (2016) 60.