X-Ray Diffraction Guided Optimisation of Mechanochemical Synthesis for Energy Storage Materials

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Bismuth-based compounds have been widely explored as electrode materials for supercapacitors and lithium-ion batteries because of their high theoretical capacity and low toxicity. Meanwhile, mechanochemical synthesis has emerged as a green, clean, and efficient approach for materials preparation.

In this study, a novel bismuth-based material, $[C_4H_7N_6S_2][BiI_4]$ was synthesised by a simple mechanochemical grinding method using $C_2H_3H_3S$ and BiI_3 as the starting materials. Grinding with different reagent ratios was performed, producing a series of materials with similar powder X-ray diffraction (PXRD) patterns. Single crystals obtained from a similar solution reaction were successfully grown, and the crystal structure $[C_4H_7N_6S_2][BiI_4]$ was solved by single crystal X-ray diffraction (SCXRD) and determined to be monoclinic, in space group $P2_1/c$, with the unit cell parameters a = 12.6618(15) Å, b = 18.899(2) Å, c = 7.5485(9) Å, β = 103.795(4) °. Comparison between the theoretical and observed PXRD patterns confirmed the formation of this phase, although several additional, unassigned peaks were observed. PXRD data on selected samples are under analysis using a multiphase Pawley fitting routine, in order to identify residual starting reagents along with the targeted $[C_4H_7N_6S_2][BiI_4]$ material and obtain refined unit cell parameters. The synthesis conditions are also under optimisation to target phase pure $[C_4H_7N_6S_2][BiI_4]$.

Both the initial multi-phase product and the optimised material were tested as electrode materials using three-electrode electrochemical measurements to investigate their capacitive behaviour. The material shows a pseudocapacitive charge-discharge process, associated with Bi^{3+} redox centre, and has a capacitance of 123.4 F g^{-1}. Furthermore, in-situ PXRD measurements during electrochemical cycling will be conducted to monitor structural changes in the electrode materials.

Overall, this work provides new insights into the development of novel materials prepared by green mechanochemical synthesis methods for energy storage devices, and demonstrates the importance of X-ray diffraction analysis in guiding the optimisation of mechanochemical synthesis and understanding electrochemical behaviour for energy storage materials.

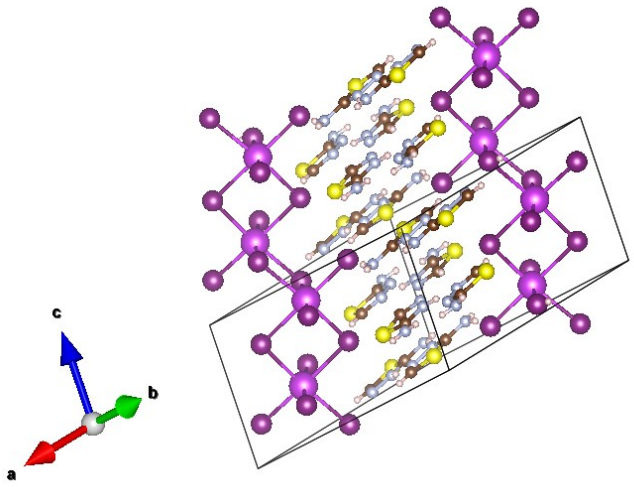


Figure 1. *Perspective view of the crystal structure of monoclinic $[C_4H_7N_6S_2][BiI_4]$*