Solvothermal Synthesis of Nanocrystalline Copper Nitride From an Energetically Unstable Copper Azide Precursor

Jonglak Choi and Edward G. Gillan*
Department of Chemistry and the Optical Science and Technology Center
University of Iowa, Iowa City, Iowa 52242-1294

Abstract
Non-aqueous solvothermal chemical reactions have found extensive utility in the growth of inorganic non-oxide materials. This report describes the successful use of organic solvothermal environments to synthesize energetically unstable copper azide precursors that are then decomposed in situ to crystalline metastable copper nitride at temperatures below 200 °C. A comparison of Cu$_3$N products formed from non-polar (toluene) and coordinating (THF) solvents is described. The cubic Cu$_3$N products are nanocrystalline with aggregated particle-like extended structures and were characterized by X-ray diffraction, electron microscopy, IR spectroscopy, and mass spectrometry. The thermal stability and composition of Cu$_3$N was examined by thermogravimetric analysis and bulk elemental analysis. The particle surfaces contain bound residual solvent species that can be removed by heating. The poorly coordinating solvent, toluene, lead to a more crystalline product containing less residual organic content. Bench top reactions were performed to follow the temporal formation and decomposition of metal azide intermediates. These studies provided more detailed information on the progression of metal azide to metal nitride materials in a solvothermal environment.