

TEM Characterization of Ball Milled Synthesized CIGS, CIS and CGS Nanoparticles for Energy Applications

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Solar light can be captured by semiconducting particles and transformed into a fuel by inducing CO₂ reduction and water decomposition. Thus appropriate semiconducting particles need to be identified and synthesized with appropriate and inexpensive processing. Ball milling is used in this investigation to synthesize CuIn_xGa_(1-x)Se₂ (CIGS) nanoparticles to capture solar light. Different intermediate stoichiometries are synthesized in order to completely determine the processing variables and conditions to achieve the main goal. CIGS is a family of semiconductors with a chalcopyrite crystalline structure and a variable bandgap that relates to the Ga-In relative contents from 1 for CuInSe₂, (CIS) to about 1.7 eV for CuGaSe₂, (CGS). Usually these materials are synthesized in thin films for solar cells and the corresponding composition must be kept within rather strict limits to avoid charge recombination. Nevertheless the use of nanoparticles in nanostructured devices can render sufficiently small distances to be traveled by the charges as to relax such a restriction. In the present investigation nanoparticles are produced with combinations of components of the CIGS materials by mechanical milling and starting from the corresponding chlorides in a dispersing excess of NaCl. X ray diffraction and electron microscopy are combined to characterize the resulting nanoparticles as a function of processing time (1 to 10 h) and chemical composition. Milling is done in a high energy device (Spex mill ®).

Figure 1 shows X ray diffraction results as a function of milling time. Short milling times (1-3h) already produce nanoparticles of the expected phases. However, as the milling time increases the corresponding peaks become sharper indicating that the chemical composition reaches stoichiometry. Figure 2 shows phase images with atomic resolution of CIS, CGS and CIGS nanoparticles at different milling times. The structural evolution of the nanoparticles can be followed as a function of the milling time. Especially short milling times produce nanoparticles with intermediate to large sizes (> 10 nm) and with the expected structural characteristics. Nevertheless for times as short as 3 h, the typical tetragonal structure of the CIGS compound can be readily identified together with an atomic distribution that satisfies the expected stoichiometry. This is shown in Fig 2. by means of the simulated atomic distributions that have been overlapped. Electron microscopy is performed in the aberration corrected TEAM 05 electron microscope. Invariably, an exit wave reconstruction (EWR) procedure is performed with 40 different images taken at different focus, in low dose rate and 80 kV. The software MacTempass ® is used to perform the EWR procedure from which phase and amplitude images are recovered [1]. The phase images show in detail both accurate lattice spacings and intensity maxima that depend on the nature of the chemical elements in the sample atomic column. Thus Figure 2 shows the atomic distribution of the elements conforming the sample that agrees rather well to the corresponding structural simulations. Electron diffraction patterns can also be obtained from the reconstructed waves, they are nevertheless localized in nature. Such diffraction results agree rather closely to the X ray diffraction results [2].

References:

[1] C. Kisielowski *et al*, Physical Review B **88** (2013), p. 024305.

[2] HAC acknowledges support from IPN (SIP, COFAA) for a sabbatical stay at the Molecular Foundry-LBNL. Work at the Molecular Foundry was supported by the Office of Science, Office of Basic Energy Sciences, of the U.S. Department of Energy under Contract No. DE-AC02-05CH11231.

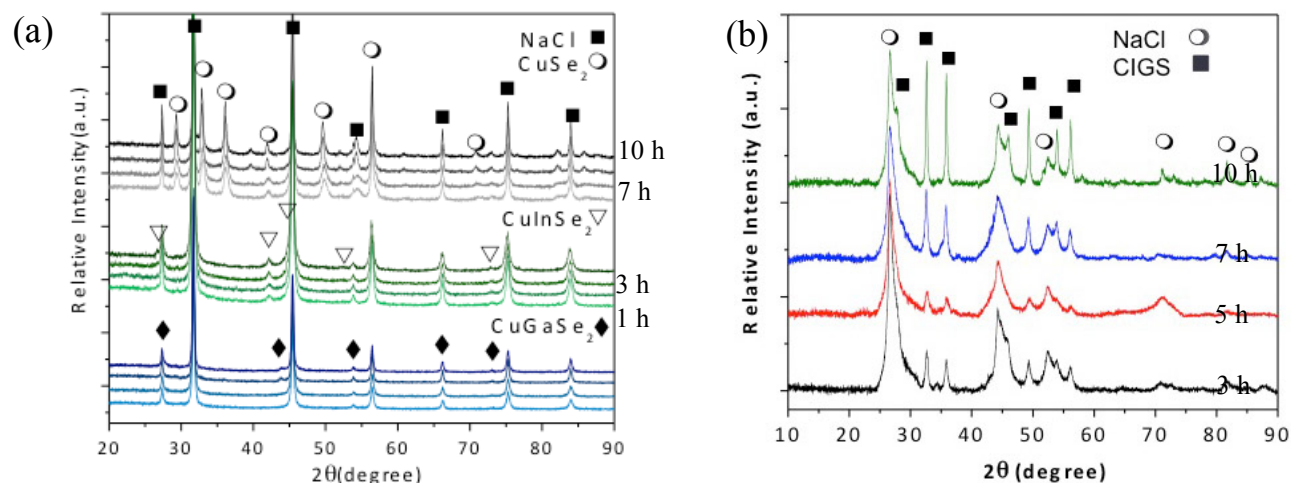


Figure 1. X ray diffraction patterns as a function of milling time. (a) CuSe₂, CuInSe₂ and CuGaSe₂ nanoparticles dispersed in NaCl. (b) CuIn_{0.7}Ga_{0.3}Se₂ in NaCl after partial cleaning.

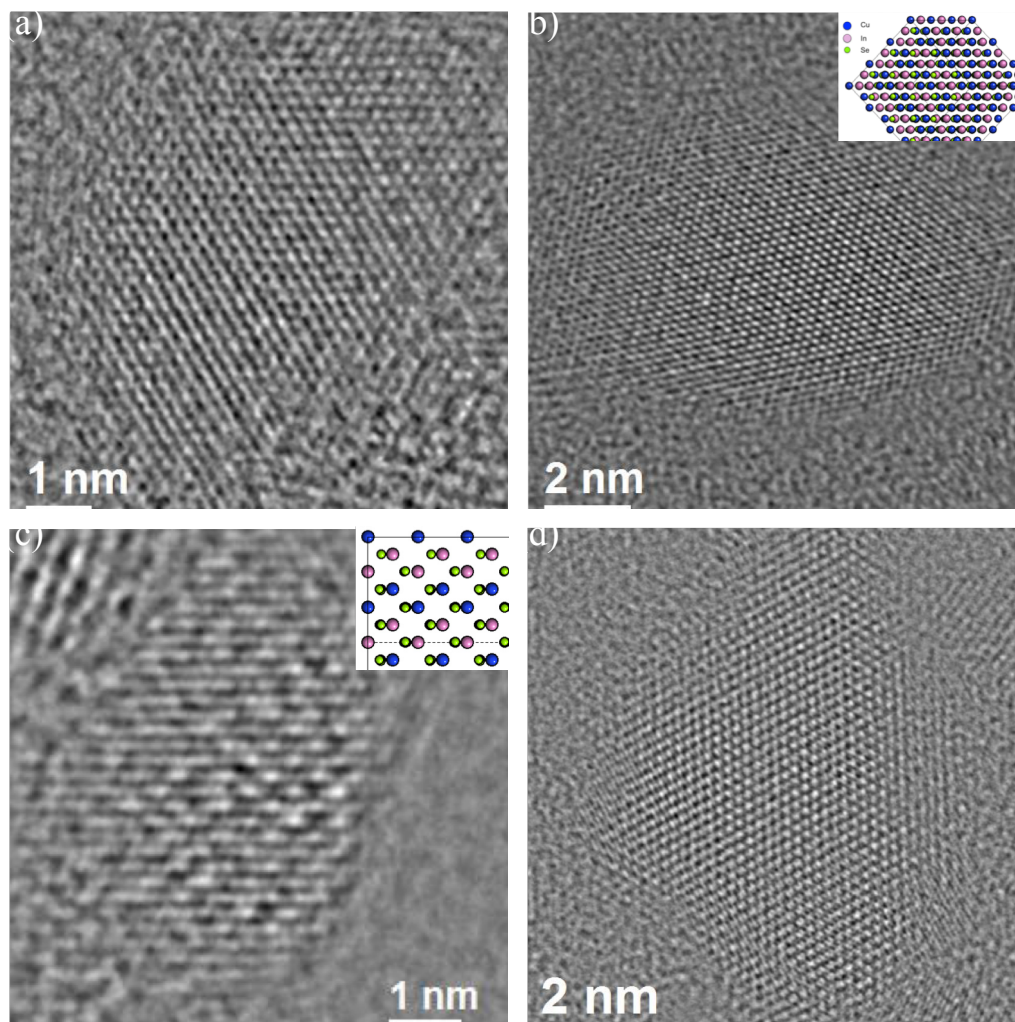


Figure 2. Phase images of nanoparticles as prepared by mechanical milling. (a) CGS 7 h milling, (b) CIS 10 h of milling near a [112] zone axis, (c-d) CIGS, 10 h milling. In (c) the zone axis is near [021]. A low dose rate is used in all cases to avoid a strong beam sample interaction.