Imaging antisite defects in Ag-substituted $Cu_2ZnSnSe_4$

Cherns, D.[1], Griffiths, I.[2] and Jones, L.[3,4]

[1] University of Bristol, United Kingdom, [2] Oxford University, United Kingdom, [3] Advanced Microscopy Laboratory (CRANN), Ireland, [4] School of Physics, Trinity College Dublin, Ireland

There is great interest in $Cu_2ZnSn(SSe)_4$ (CZTS) as an earth abundant replacement for CdTe and $CuInGaSe_2$ (CIGS) in thin film solar cells. However, the efficiency of CZTS cells has reached only 12% compared to over 20% for CdTe and CIGS. It is widely believed that the limited efficiency is due to antisite defects, particularly Cu_{Zn} and Zn_{Cu}, detected at high densities by (e.g.) neutron diffraction studies, but whether these are due to local disorder or long range clustering remains uncertain. In TEM, observation of this material, which has a kesterite structure, down the [010] axis (Figure 1) provides a method of studying antisite defects directly. In this orientation, end-on atom columns are composed of a single element in the perfectly ordered structure. High angle annular dark field (HAADF) images of Cu_2ZnSnS_4 show the Sn columns as the brightest spots, forming a near hexagonal array. Displacements in this array reveal antisite domain boundaries (ADBs) as illustrated in Figure 2

Figure 3 examines $Ag_2ZnSnSe_4$, where Ag substitution of Cu has been proposed as a method of reducing antisite defect densities. This shows the result of combined HAADF and EDX mapping in an aberration-corrected JEOL ARM200F (S)TEM. To achieve sufficient X-ray counts, 230 separate scans over closely adjacent 11x11nm areas have been superimposed, with Figure 3 showing the result of further superimposing data from 112 identical motifs, representing an equivalent total electron dose of $8.9x10^{11}$ $e^{-}nm^{-2}$. Despite extensive superimposition, the spatial resolution in the HAADF image remains sub 0.1nm. The results suggest, contrary to expectation, that there is complete intermixing of Ag and Zn on the Wyckoff 2c and 2d sites, and about 15% substitution of Zn for Ag on the 2a sites. In contrast, however, individual HAADF images show a contrast asymmetry between the 2c and 2d sites in nanometer-sized regions, suggesting that domains exist with more ordering of Ag and Zn on the 2c and 2d sites. Overall the TEM shows that the role of antisite defects in limiting the efficiency of CZTS solar cells has been misinterpreted. The paper will present the TEM results and explain their significance.

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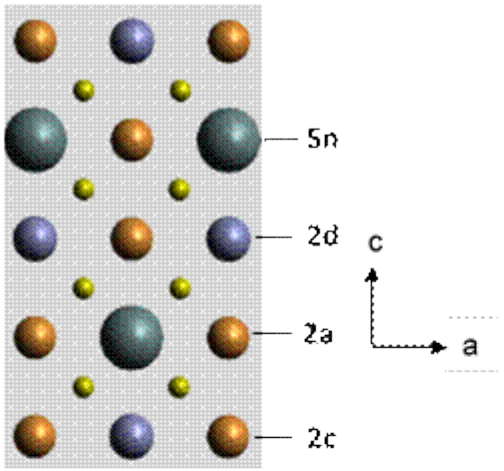

Figure 1: [010] projection of ordered CZTS kesterite structure. 2a and 2c: Cu or Ag, 2d: Zn

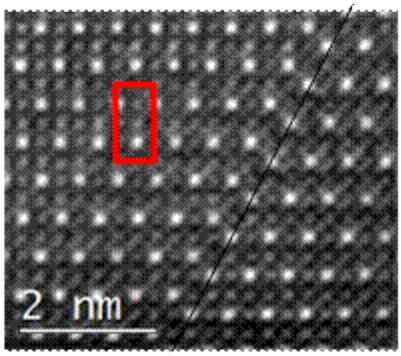

Figure 2: Cu_2ZnSnS_4 showing an ADB and unit cell in red

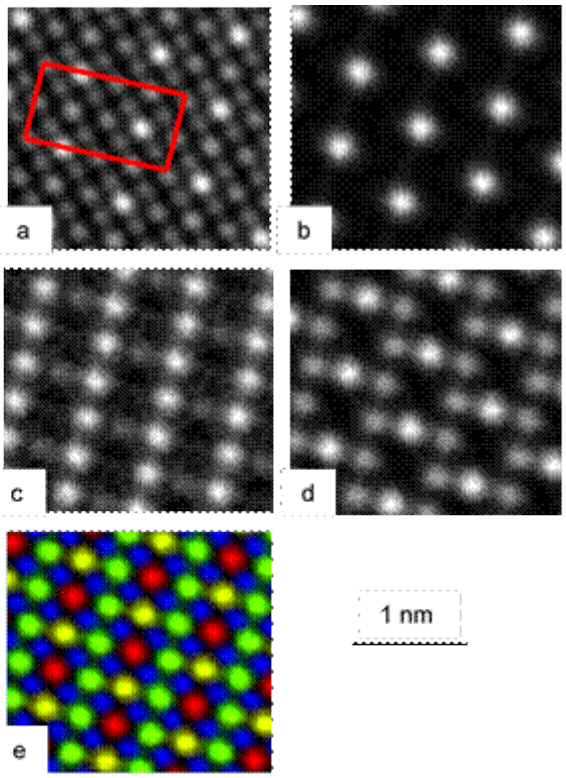

Figure 3: HAADF and EDX maps of $Ag_2ZnSnSe_4$. a: HAADF, b: Sn, c: Ag, d: Zn, e: combined EDX map with Sn(red), Ag(2a,yellow), Ag/Zn(2c/2d,green), Se(blue). Unit cell in red