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Report:

Besides being studied and developed as the absorber material in photovoltaic cells, $CuInSe_2$ is of fundamental interest because it is a semionic semiconductor, i.e., at least one type of the electrically active defects can be mobile under conditions of extrinsic semiconductivity. Thus, subjecting $CuInSe_2$ crystals to a strong electric (E)-field can type-convert the material and yield transistor formation. Radioactive tracer experiments confirmed this to be due to thermally assisted Cu electromigration. Cu electromigration was invoked also to explain the remarkable stability of solar cells made with the material. However, the mechanism of electromigration is not at all clear. Using short wavelength (0.24 Å) synchrotron XRD, to minimize absorption (μ=3.7mm^{-1}), we could perform high resolution crystallographic structure determinations to elucidate this mechanism..

We prepared all $CuInSe_2$ single crystals by the traveling heater method (THM). This gives the best quality of crystals and prevents twinning along the (112) plane. Three

types of samples were prepared from one large crystal: -n-type as-grown; p-type converted samples (by annealing in Se); samples subjected to an E-field.

For each sample nearly 22,000 reflexions were collected. The structure was refined using the SHELX-97 and JANA98 programs in space group I-42d. Corrections for anisotropic thermal displacements, extinction and twinning were introduced one after the other. R(free) and R parameter decreased with each step. Because of the proximity of the wavelength to the In absorption edge, we had to correct for anomalous dispersion. SHELX refinement with anisotropy and extinction correction gave an R factor of 2.66% for as-grown, 2.69% for p-type, and 3.63 % for the E-field treated sample. A considerable increase of the thermal parameters for Cu, Se and In was found in E-field treated samples relative to the as-grown and p-type samples. A small decrease in the Cu site occupancy after E-field treatment is suggested by the refinement results.

We calculated 3 types of electron density (ED) maps using SHELX and JANA98 programs: 1) using F_{obs}; 2) deformation ED (DED) maps (F_{obs}-F_{calc}); 3) valence electron density maps (VED) (F_{obs}-$F_{calc\ ions\ Cu1^+,\ In3^+}$). Use of VED yielded smaller R factors and smaller values of maximums and minimum on the maps. We compared the actual and difference ED maps of as-grown, E-field treated and Se-annealed crystals.

Because the as-grown (n-type) samples were In-rich and Cu- and Se-poor, with respect to the 1:1:2 stoichiometry, we can expect a significant number of selenium vacancies, V_{Se}, of copper vacancies V_{Cu} and of In_{Cu}. The occurrence of In_{Cu} makes the Cu SOF factor less sensitive to Cu deficiency than expected. However the map of the as-grown sample shows ED *in between* the Cu ions. This indicates the presence of V_{Se}, (in analogy to F centers in ionic solids). We also see evidence for Cu displacement from its lattice sites and its migration to interstitial sites, as a result of E-field application. In addition the maps show Se anneal to minimize interstitial ED.

These results represent a first step towards correlation of electrical activity and features of electron density distribution, i.e., in terms lattice and interstitial site occupancy for this important optoelectronic material.