ELECTRON TOMOGRAPHY IN REAL AND RECIPROCAL SPACE REVEALS ATOMIC STRUCTURE AND VACANCIES IN A LUMINESCENT COPPER CHALCOGENIDE

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Summary: Copper chalcogenides are known to find applications in different fields such as photonics, photothermal therapy and photovoltaics. It is known that vacancies in the structure are a prerequisite for plasmonic activity, however an accurate understanding of the distribution of the defects and their influence on the properties is missing. We demonstrate here that the structure of $Cu_{1.5\pm x}Te$ nanocrystals can be determined using electron diffraction tomography. In addition to that real space high resolution electron tomography directly reveals the three-dimensional distribution of vacancies in the structure.

Introduction

Recently, Li et al.[1] reported a new copper telluride nanocrystalline phase, displaying a novel crystalline phase and yielding interesting plasmonic properties toward sensing applications. The structure however has remained unknown so far due to its complexity.

By applying a combination of reconstruction of the reciprocal lattice based on electron diffraction collected from the nanocrystals and a tomographic reconstruction based A high angle annular dark field scanning transmission electron microscopy (HAADF-STEM) images both the structure and the distribution of Cu vacancies within the material was revealed in 3 dimensions.

1. RESULTS

To investigate the atomic structure in detail, a tilt series of selected area electron diffraction (SAED) patterns was acquired from a CuTe nanocrystal over a tilt range of -62.9°/+64.2° with an increment of 0.1°. This tilt series was combined into a 3D reconstruction of the reciprocal lattice, as shown in Fig. 1a. The reflections can be indexed in a cubic unit cell with an average cell parameter of 7.51 Å. Based on the intensities extracted from the reconstructed reflections an *ab initio* structure determination resulted in a basic structure yielding 8 Te atoms and 24 possible sites for Cu in one unit cell. Based on the composition it we know that half of the Cu sites must be absent.

In order to retrieve more details regarding the complex distribution of vacancies require the use of imaging methods and high resolution electron tomography. We carried out a tomographic reconstruction based on five high resolution HAADF-STEM images acquired with the rotation axis oriented along the short dimension of the cuboid shaped nanocrystal. Orthoslices through the reconstruction, perpendicular to the [100] and [010] directions, presented in Fig. 1b enable the visualization of the distribution of vacancies in 3D. In this figure the low intensity regions (blue) in between the Te atoms show the distribution of the Cu deficiencies. At this local scale the order of the vacancies has a preference for a modulation of four average unit cells along one dimension of the nanocrystal.

References

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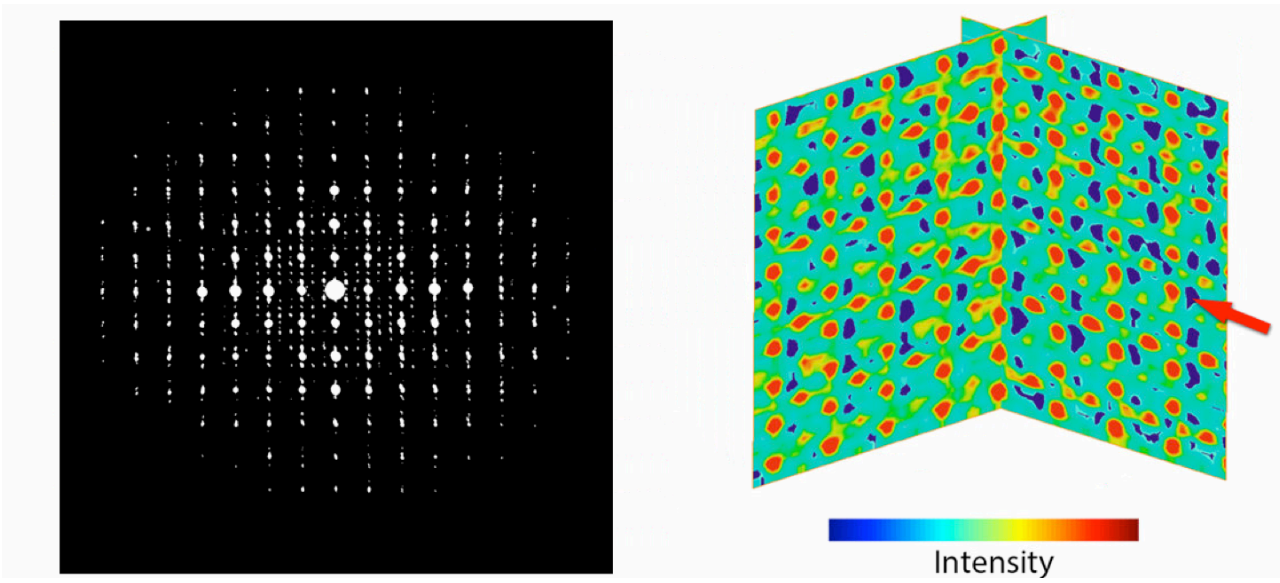

(a) (b)

Figure 1: (a) The 3D reconstruction of the reciprocal lattice of a CuTe nanocrystal. (b) Two perpendicular orthoslices through a subvolume of the reconstruction of a CuTe nanocrystal. The high intensity (red) domains corresponds to the Te atoms and the lowest intensity domains (blue) shows Cu deficient regions corresponding to Cu vacancies in the structure.