

Identification of Structure and Chemical Occupancy of Emerging Complex Compounds via Analytical Electron Microscopy

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Anion-deficient fluorite is a family of complex compounds that exhibits a variety of interesting properties that derives from the specific arrangement of anion vacancies in combination with possible cation disorder in the fluorite parent structure [1]. Given this structural complexity, many more permutations are possible opening the need for more detailed investigations. Analytical microscopy plays an important role on probing atomic structure and local chemical occupancy. Here, we present a detailed structural study on a recently reported member of anion-deficient fluorite family $(\text{Cu}_x\text{Zn}_{1-x})_{0.456}\text{In}_{1.084}\text{Ge}_{0.46}\text{O}_3$ (CZIGO), ($0 \leq x \leq 1$) by using convergent beam electron diffraction (CBED) and high-resolution scanning transmission electron microscopy (HRSTEM). $\text{Zn}_{0.456}\text{In}_{1.084}\text{Ge}_{0.46}\text{O}_3$ (ZIGO) structure is the only known example with its particular complex structure in which cation coordination span one 4-coordinate (4b), two 6-coordinate (8e and 16f), and one 8-coordinate (4a) site, as shown in the left of Figure 1 [2]. A new, complete, solid solution has been discovered via the isovalent substitution of Cu^{2+} for Zn^{2+} , significantly expanding the known phase space of this structure [3].

One of the challenges of structure determination is the difficulty in obtaining single-crystal samples which are large enough to do single-crystal X-ray diffraction. CBED is a very well-established technique that can uniquely determine space-group symmetries at the scale of few nanometers enabling probing defect-free areas within the crystal and has been applied to many different materials over the past few decades [4-6]. Space group symmetry elements such as screw axes, glide planes, and non-centrosymmetric axes can be identified by observing the presence or absence of dynamical extinction lines due to dynamical scattering effects [7]. Furthermore, higher-order Laue zone (HOLZ) reflections in CBED are sensitive to the subtle displacements of atoms along the projected beam direction and can be used to depict whole-crystal symmetry and identify the symmetry departures from its ideal structural phase.

To obtain the whole crystal symmetry, Figure 2(a) shows a CBED pattern of CZIGO with $x=0.25$, along [221] zone axis. The mirror and rotation symmetries are marked and depict a whole crystal symmetry $I4_1/amd$. Magnified CBED from the boxed areas in orange, purple and green are shown in (b-d), showing more details of the structure. In Figure 2(b) symmetry elements can be identified in the zero-order Laue zone (ZOLZ), such as mirrors. The dynamic absence line was observed on the +g and -g disc shown in Figure 2(c) which possibly comes from a d-glide plane. In Figure 2(d) we can have information from the ZOLZ, first-order (FOLZ) and second-order Laue zone (SOLZ) at the same time which gives the lattice parameter along the beam direction. The radius of the FOLZ ring and SOLZ ring are 14.9 1/nm and 21.2 1/nm respectively, therefore the average distance between the plane of the reciprocal lattice is 0.279 1/nm which is consistent with the [221] direction.

As previously shown in Figure 1, there are four cations with unusual site-specific mixing in the compound. Based on the structure of ZIGO, we hypothesized that Cu replacement of Zn at the 16f site is favored over the 4a, 4b, and 8e sites. This hypothesis is strongly supported by bond valence (BV) analysis and the literature on related phases [3]. In order to directly determine the elements in the cation position, we use the contrast on the HAADF image that sensitively depends on the atomic number. No obvious contrast variation between individual columns means there is no ordering of those cations on the 16f site. Also, no

more symmetry breaking or superstructure were observed, because no extra spots, spot splitting, or streaking were observed in the selected area diffraction pattern of [001] zone axes (inset in Figure 2(e)). The presentation will cover similar examples of usage of analytical electron microscopy to elucidate structures and site occupancies in complex compounds [8].

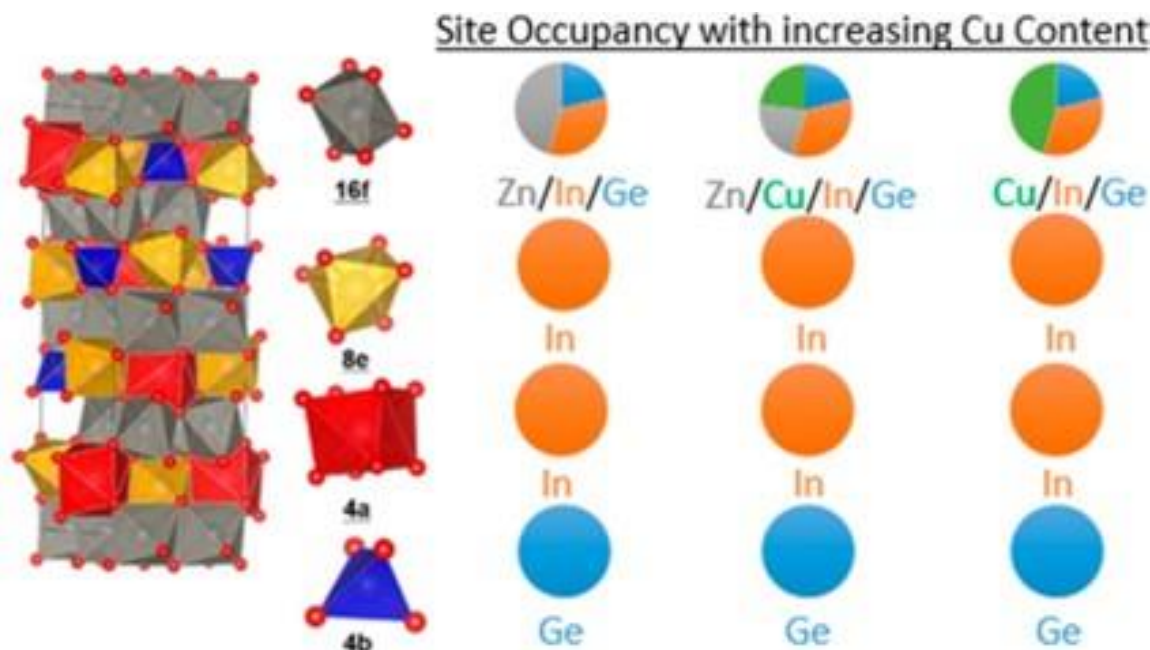


Figure 1. (Left) Crystal structure of ZIGO. (Right) Four distinct cation sites and their occupancies in CZIGO. Modified from [2].

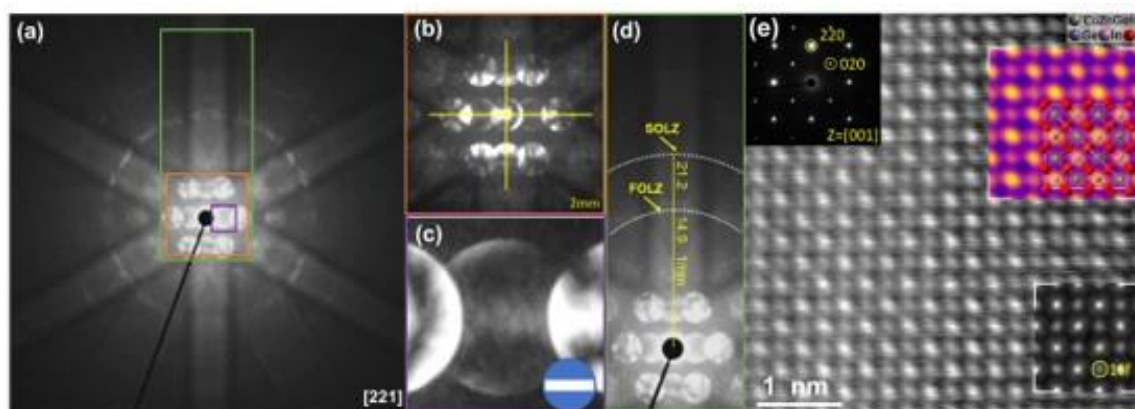


Figure 2. (a) CBED pattern of CZIGO along [221] zone axis and higher magnification images of the areas of orange, purple and green boxes were shown in (b-d) respectively. (b) CBED pattern of ZOLZ, which shows some symmetry elements. (c) The magnified image of the discs which show the dynamic absent line. (d) Shows ZOLZ, FOLZ and SOLZ, the distances from the FOLZ and SOLZ to the center were marked in the image. (e) High-resolution HAADF and SAED along [001] zone axis. The average unit cell was calculated from the image (upper right) overlaid with the structure schematic. The simulated HADDF image was also shown in the lower inset in (e).

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