Contribution of symmetrized projections in HREM analysis for the characterization of $Ca_{1-x}Cd_xWO_4$ crystal microstructures

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1. INTRODUCTION

The electron diffraction (ED) is a powerfull tool for the structure analyzes at a nanometric scale. Among the ED techniques, microdiffraction [1] can contain many data in only one pattern, like unit-cell parameters, crystal system, Bravais lattice and the presence of translation symmetries. Recently, the invention of the electron precession diffraction (PED) [2] brought new hope to the field of quantitative electron diffraction for structure refinement. We show here an additional method in crystallographic image processing (CIP) based on the analysis of the symmetrized experimental HREM maps [3]. The method was already used for different ordered and disordered complex tungstate structures [4, 5] also characterized in X-ray diffraction (XRD).

To understand the role of crystal structures and local ordering states in the photonic properties of a system $(1-x)CaWO_4$ - $xCdWO_4$ with $0 < x < 1$, two phases with specific compositions x=0.5 (scheelite) and 0.8 (wolframite) were studied. ED and CIP analyzes allowed confirming the lattices and space groups $I4_1/a$ and P2/c at the local scale. Quantitative HREM associated with XRD data were consistent with a statistical distribution of Ca or Cd atoms on $Ca_{1-x}Cd_x$ sites in each lattice.

2. RESULTS

2.1 Samples and experimental details

Metal tungstates AWO_4 are classified into two main structural classes: tetragonal scheelite ($I4_1/a$) and monoclinic wolframite (P2/c) depending on the size of A^{2+} divalent cationic radii. Then, the structures are based on tetrahedral $(WO_4)^{2-}$ or octahedral units $(WO_6)^{6-}$ forming specific $[WO_4\text{-}AO_8]$ or $[WO_6\text{-}AO_6]$ bounds. Two calcium-cadmium tungstate crystal phases $Ca_{0.5}Cd_{0.5}WO_4$ and $Ca_{0.2}Cd_{0.8}WO_4$ were obtained using a co-precipitation method at room temperature and thermal treatment at 1000°C under air for three hours. The powder samples were at first analyzed and refined by XRD then by electron microscopy.

The TEM studies were achieved with a LaB6 Tecnai G20 (super-twin objective lens) with 0.25 nm point-to-point resolution at 200kV. The main objective of these experiments was to confirm the space group, the ordering state of crystal phases at the local scale and the distribution of calcium and cadmium atoms on their site. Quantitative EDS analyzes performed on nanometric areas in individual single crystal particles were found in agreement with the two compositions. The percentage change in atomic concentration has never exceeded 2%, revealing no local variation in composition. No evidence of stacking fault or amorphous areas was noticed.
The data processing required three main steps :

- We first performed a series of microdiffraction (beam size of 20 nm) and SAED (illuminated areas of 250 nm) experiments to measure the lattice parameters and identify the possible space groups.
- We compared CIP to simulated images calculated from X-ray diffraction data.
- Average atoms $Ca_{1-x}Cd_x$ were introduced in simulations, taking into account the statistical occupancy factors. Then, additional tests with single Ca or Cd atoms were performed to test the influence of atomic scattering factors on simulated images.

2.2 Main results

For the monoclinic crystal, the microdiffraction (Fig. 1) and SAED results converged to three possible space groups: Pc, P2/c and $P2_1/c$. A way to find the right one consisted in identifying the symmetry projections of HREM images in the main zone axes. Thus, from an experimental map recorded in [001] zone axis, three images were processed by imposing the relative symmetry projections p11m (Pc), p2mm (P2/c) and p2gm ($P2_1/c$) to the amplitudes and phases of diffracted waves in the FFT (Fig. 2). The projection p2mm clearly showed the best agreement with the experimental data. Consequently, the only space group consistent with these results was P2/c. A simulated HREM map calculated with the atomic positions found from our XRD data, for

defocus and sample thickness values of d_f = 67.2 nm and t = 4,4 nm respectively, was found in good agreement with the processed map.

HREM simulations calculated in the main projections showed no difference between disordered ($Ca_{0.5}Cd_{0.5}WO_4$ ($I4_1/a$) and $Cd_{0.8}Ca_{0.2}WO_4$ (P2/c)) and ordered models ($CaWO_4$ and $CdWO_4$ respectively). An example was illustrated in Fig. 3 concerning the [110] zone axis of the tetragonal structure, where four profile lines were drawn and averaged along stacking of atoms in the [1-1-2] direction of the experimental HREM map. A feature with a strengthening of intensity every two atoms could be observed for each model in some calculated maps, here for t = 19,89 nm and df = 67,2 nm.

3. CONCLUSION

HREM images were compatible with the existence of average atoms Ca_{1-x}/Cd_x and argue in favor of total disorder of these sites, as suggested by XRD data. No extra-reflection was observed in our TEM analyzes and both compounds can be considered as crystallized disordered solid solutions.

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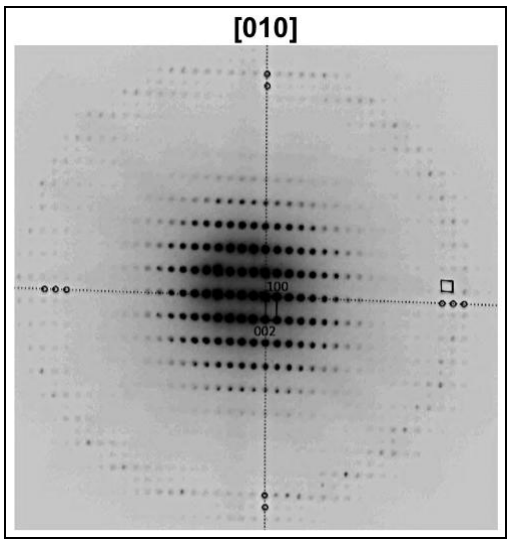

Figure 1. Microdiffraction pattern in [010] zone axis for the monoclinic crystal system.

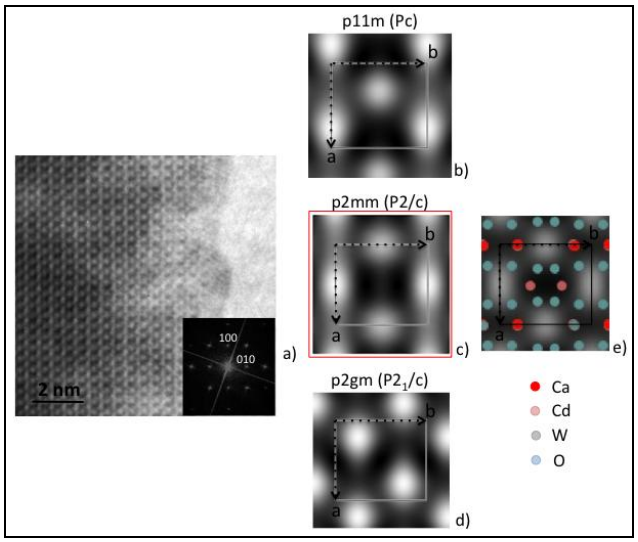

Figure 2. Experimental HREM map recorded in [001] zone axis a); Processed images from a) by imposing the symmetry projections p11m b), p2mm c) and p2gm d); simulated HREM map e) calculated for defocus and sample thickness values of d_f = 65 nm and t = 1.5 nm respectively.

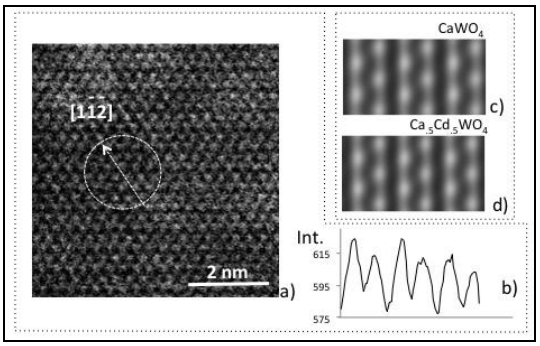

Figure 3. Profile line along stacking of atoms in the [1-1-2] direction in the experimental HREM map of the tetragonal phase in [110] zone axis (a, b). The profile feature was observed for each ordered c) and disordered d) model in the simulated maps for a thickness t = 19,89 nm and a defocus value df = 67,2nm.