Ceramics, Oxides, Geomaterials

MS.2.P026
HAADF-STEM Imaging and Simulation of $(Sb_{1/3}Zn_{2/3})GaO_3(ZnO)_3$

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Keywords: zinc oxides, HAADF-STEM, simulation

A high temperature (1350 °C) processing route in sealed Pt tubes was used for the synthesis of $(Sb_{1/3}Zn_{2/3})GaO_3(ZnO)_3$ from appropriate powder mixtures of pure binary oxides as starting materials. $(Sb_{1/3}Zn_{2/3})GaO_3(ZnO)_3$ consists of an alternate stacking of octahedral layers $[(Sb_{1/3}Zn_{2/3})O_2]^-$ and $[(GaZn_3)O_4]^+$ units corresponding to CdI_2 and wurtzite structure type motifs, respectively. Inversions of the ZnO_4 tetrahedra occur (i) at the octahedral layers and (ii) halfway in the wurtzite type domains where trigonal bipyramidal coordinated cations constitute the boundary.

Crystal structure determination by single-crystal X-ray diffraction revealed the space group $R\bar{3}m$ with lattice parameters a_0 = 3.2366(3) Å; c_0 = 41.793(8) Å, and the structural characteristics as known from other members with general formula $ABO_3(ZnO)_m$ [1]. The composition of the octahedral layer can be refined without constraint to a ratio of Sb/Zn = 1/2. Electron diffraction and HRTEM clearly indicate ordering of these cation positions by presence of superstructure reflexions and contrast modulations of the cation columns in relevant orientations [2]. This indicates a real structure of $(Sb_{1/3}Zn_{2/3})GaO_3(ZnO)_3$ present on a local scale that is averaged by stacking disorder of the octahedral layers $[(Sb_{1/3}Zn_{2/3})O_2]^-$ as indicated by streaks parallel to 000*l* (Figure 2.). The cation ordering within the octahedral layers can be described by a model deduced earlier for single defect layers in ZnO doped with antimony [3]. The observed ED patterns, neglecting diffuse intensities by non-periodicity, can be described with corundum-like, well ordered octahedral layers $[(Sb_{1/3}Zn_{2/3})O_2]^-$ periodically translated by a 3_1 screw axis. This leads to a structure model with discrete positions for all ions in $P3_112$ with a = 5.6 Å and c = 41.8 Å (Figure 1.), where the Sb ions along the c-axis are stacked in ABC sequence.

To confirm the deduced structure model of $(Sb_{1/3}Zn_{2/3})GaO_3(ZnO)_3$ HAADF-STEM imaging was carried out in an advanced analytical TEM/STEM system (JEOL JEM-ARM 200CF) equipped with cold field-emission gun (C-FEG), probe Cs-corrector, X-ray (JED 2300) and electron spectrometer (GATAN GIF Quantum ER) attachments. The present setup provides sub-Å resolution capability in high-angle annular dark-field (HAADF) STEM imaging, whereas bright-field (BF) and particularly annular bright-field (ABF) with increased sensitivity for light elements enable the elucidation of true atomic structures by imaging both cation and anion sites [4]. The QSTEM software package [5] was used for simulation of HAADF images (Figure 3.).

HAADF imaging reveals the periodic order of antimony and zinc in the octahedral layers with columns of the heavier Sb atoms giving rise to bright Z-contrasts. The intensity ratio of the Zn and Sb columns can be measured to 0.42. This corresponds to an exponent of 1.7 ($Int_{(Zn)}/Int_{(Sb)}=30^{1.7}/51^{1.7}$= 0.41), which is in excellent agreement with theoretical predictions [6,7]. In some areas the stacking of the octahedral layers corresponds well with the structure model in $P3_112$. However, the stacking of larger regions does not correlate to the ABC stacking, i.e. stacking disorder occurs. This leads to an averaging of the Sb cation positions and in turn to streaks in SAED patterns at $\{h\bar{h}0l\}$, $h \neq 3n$, $n \in \mathbb{Z}$ (Figure 2.).

Currently, compounds of this structure type draw much attention and are considered promising materials systems for various technological applications such as transparent conducting materials, field emission applications, and as color pigments.

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8. We thank E. Arzt for continuous support through INM

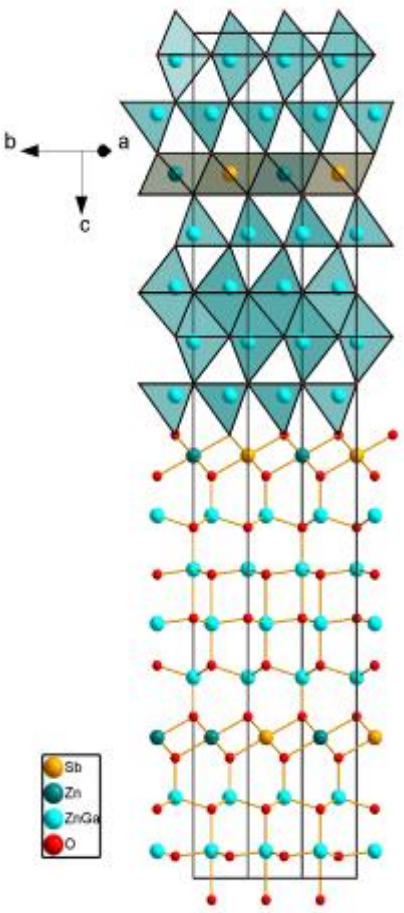

Figure 1. Crystal structure of $(Sb_{⅓}Zn_{⅔})GaO_3(ZnO)_3$ in $P3_112$ in $\langle 1\bar{1}00 \rangle$ zone axis, drawn as ball and stick model and as polyhedron representation, respectively.

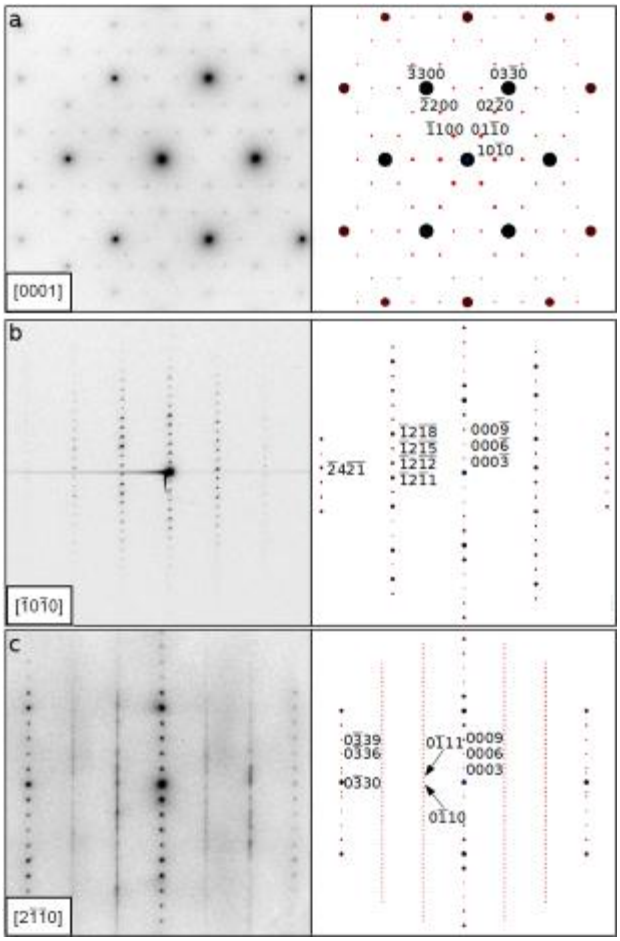

Figure 2. Electron diffraction patterns of $(Sb_{⅓}Zn_{⅔})GaO_3(ZnO)_3$ in principal orientations using the structure model in $P3_112$ and calculated patterns. Diffuse scattering in (c) is caused by stacking disorder of the octahedral planes.

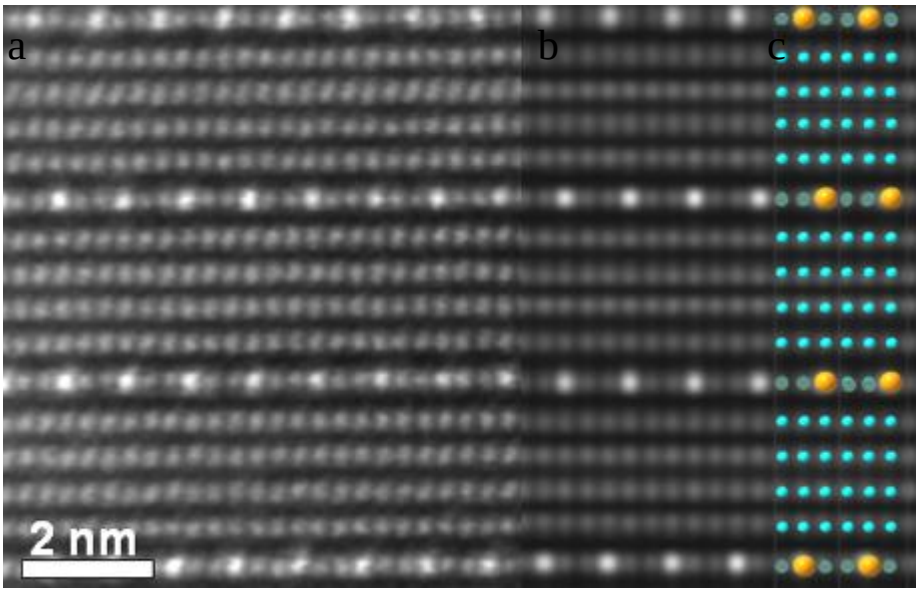

Figure 3. HAADF image (a), simulated HAADF image (b) and structure model (c) of $(Sb_{⅓}Zn_{⅔})GaO_3(ZnO)_3$ in *a*-axis orientation.