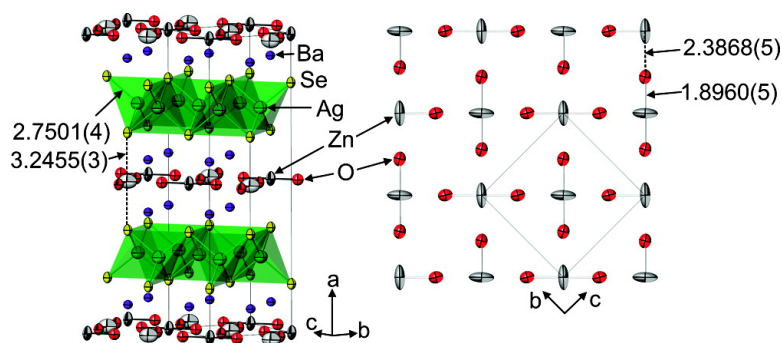


## Fragmentation of an Infinite ZnO Square Plane into Discrete [ZnO] Linear Units in the Oxyselenide BaZnOAgSe

Sebastian J. C. Herkelrath, Ian Saratovsky, Joke Hadermann, and Simon J. Clarke

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## Fragmentation of an Infinite $\text{ZnO}_2$ Square Plane into Discrete $[\text{ZnO}_2]^{2-}$ Linear Units in the Oxyarsenide $\text{Ba}_2\text{ZnO}_2\text{Ag}_2\text{Se}_2$

Sebastian J. C. Herkelrath,<sup>†</sup> Ian Saratovsky,<sup>†</sup> Joke Hadermann,<sup>‡</sup> and Simon J. Clarke<sup>\*†</sup>

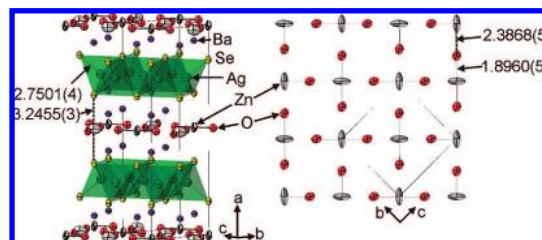
Department of Chemistry, University of Oxford, Inorganic Chemistry Laboratory, South Parks Road, Oxford, OX1 3QR, U.K., and Electron Microscopy for Materials Science (EMAT), University of Antwerp, Groenenborgerlaan 171, B-2020 Antwerp, Belgium

Received August 11, 2008; E-mail: simon.clarke@chem.ox.ac.uk

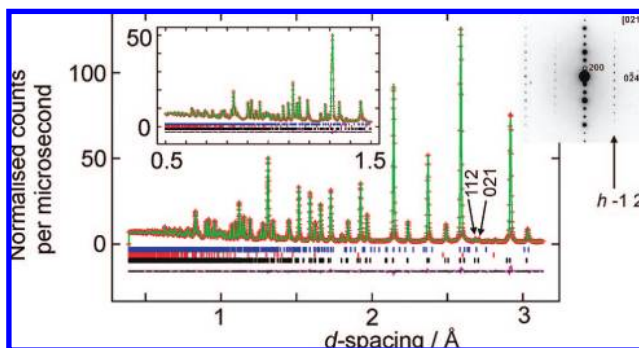
Electron diffraction, neutron powder diffraction, and EXAFS measurements show that the  $\text{ZnO}_2$  plane in the layered oxyarsenide  $\text{Ba}_2\text{ZnO}_2\text{Ag}_2\text{Se}_2$  is not continuous, but consists of discrete orientationally ordered  $[\text{ZnO}_2]^{2-}$  anions presenting a rare example of the  $\text{Zn}^{2+}$   $d^{10}$  ion in linear coordination.

Layered oxychalcogenides and oxypnictides are receiving increasing attention.  $\text{LaCuOS}$  and related materials have received particular attention as potential  $p$ -type transparent conductors.<sup>1</sup> The isostructural oxyarsenide  $\text{LaOFeAs}$  is the parent of a series of new high temperature superconductors<sup>2</sup> with critical temperatures as high as 55 K. The quinary compounds  $\text{A}_2\text{MO}_2\text{M}'_2\text{Ch}_2$ , where A is an electropositive metal ion such as  $\text{Sr}^{2+}$  or  $\text{Ba}^{2+}$ , M is a divalent first row transition metal or  $\text{Zn}^{2+}$ , M' is a chalcophilic monovalent metal ion such as  $\text{Cu}^+$  or  $\text{Ag}^+$  and Ch is a chalcogen, have a structure (Figure 1) originally described for  $\text{Sr}_2\text{Mn}_3\text{O}_2\text{Sb}_2$ <sup>3</sup> which tolerates substitution of all the nonoxide species.  $\text{Sr}_2\text{ZnO}_2\text{Cu}_2\text{S}_2$ ,<sup>4</sup> which has been investigated as a possible  $p$ -type transparent conductor when hole-doped,<sup>5</sup> contains infinite  $\text{ZnO}_2$  sheets with  $\text{Zn}^{2+}$  ions in square planar coordination by four oxide ions 2.0 Å distant, and is weakly coordinated by two apical sulfide ions.  $\text{Cu}^+$  ions are coordinated tetrahedrally by sulfide, forming antiferrotype  $\text{Cu}_2\text{S}_2$  layers, and the two anionic layers are separated by  $\text{Sr}^{2+}$  ions. The space group of this and related compounds is  $I4/mmm$  with two formula units in the unit cell. Here we describe the crystal structure of the analogous compound  $\text{Ba}_2\text{ZnO}_2\text{Ag}_2\text{Se}_2$  and show that when the  $\text{ZnO}_2$  plane is placed under tension in order to accommodate the large  $\text{Ba}^{2+}$ ,  $\text{Ag}^+$ , and  $\text{Se}^{2-}$  ions, the square planar coordination of zinc by oxide is unsustainable, but the structure is essentially retained and the plane fragments in an ordered fashion forming what appear to be the first examples of discrete  $[\text{ZnO}_2]^{2-}$  linear anionic units.

$\text{Ba}_2\text{ZnO}_2\text{Ag}_2\text{Se}_2$  was targeted by stoichiometric reaction between  $\text{BaO}$  and elemental Zn, Ag, and Se at 825 °C for 2 days in an alumina crucible sealed inside a predried silica tube. Preliminary single crystal X-ray diffraction (SXRD) measurements on single crystals extracted from the orange-red polycrystalline product produced a structure solution<sup>6</sup> in space group  $I4/mmm$  (i.e., like  $\text{Sr}_2\text{ZnO}_2\text{Cu}_2\text{S}_2$ ) in which the displacement ellipsoid for the oxide ion was extremely elongated in the direction of the Zn–O bonds ( $U_{11}:U_{22}:U_{33} \sim 8:1:1$ ) suggesting that the oxide ion is displaced from its ideal position. The refined lattice parameters were  $a = 4.2849(4)$  Å and  $c = 19.879(2)$  Å for the tetragonal cell (150 K) and the Zn–O distance is equal to  $a/2$  in the ideal structure. With four Zn–O contacts of 2.142(1) Å and two Zn–Se contacts of 3.24 Å,  $\text{Zn}^{2+}$  is extremely underbonded (bond valence sum (BVS) of 1.35 using standard parameters<sup>7</sup>), suggesting that the ideal structural



**Figure 1.** Crystal structure of  $\text{Ba}_2\text{ZnO}_2\text{Ag}_2\text{Se}_2$  obtained from refinement against NPD data. Interatomic distances are shown in Å. Displacement ellipsoids are shown at the 99% level. The right-hand diagram shows the linear  $[\text{ZnO}_2]^{2-}$  units.



**Figure 2.** Result of Rietveld refinement against powder neutron diffraction data. The data (red points), fit (green line), and difference (purple lower line) are shown with tick marks indicating reflection positions for  $\text{Ba}_2\text{ZnO}_2\text{Ag}_2\text{Se}_2$  (97 mol %; lower),  $\text{ZnO}$  (1.8 mol %; middle) and  $\text{BaCO}_3$  (1.2 mol %; upper). The reflections observed by NPD and electron diffraction ( $[021]$  zone inset) but forbidden in the  $I4/mmm$  model are indicated.

model is unsatisfactory. For comparison, in  $\text{Sr}_2\text{ZnO}_2\text{Cu}_2\text{S}_2$ <sup>4</sup> the four Zn–O contacts of 2.005 Å and two Zn–S contacts of 3.05 Å produce a satisfactory BVS for Zn of 1.91. In cases where Zn is coordinated tetrahedrally by four oxide ions in the presence of large electropositive ions, mean bond lengths do not exceed 2 Å: 2.00 Å in  $\text{Ba}_2\text{ZnO}_3$ ,<sup>8</sup> (BVS = 1.80) and 1.98 Å in  $\text{BaZnO}_2$ <sup>9</sup> (BVS = 1.90).

A 5% Zn deficiency was indicated from the SXRD refinement consistent with the observation of a ZnO impurity in material made with the stoichiometry  $\text{Ba}_2\text{ZnO}_2\text{Ag}_2\text{Se}_2$ . Subsequently material that appeared phase pure according to powder X-ray diffraction measurements was synthesized on the 5 g scale for neutron powder diffraction (NPD) measurements by introducing a 5% Zn deficiency in the reaction mixture. Rietveld refinement<sup>10</sup> against NPD data (Figure 2) which are more sensitive than X-ray diffraction data to the scattering of the oxide and selenide ions revealed clear deficiencies at the Zn and O sites and suggested a very small deficiency on the Se site producing a refined composition of

<sup>†</sup> University of Oxford.

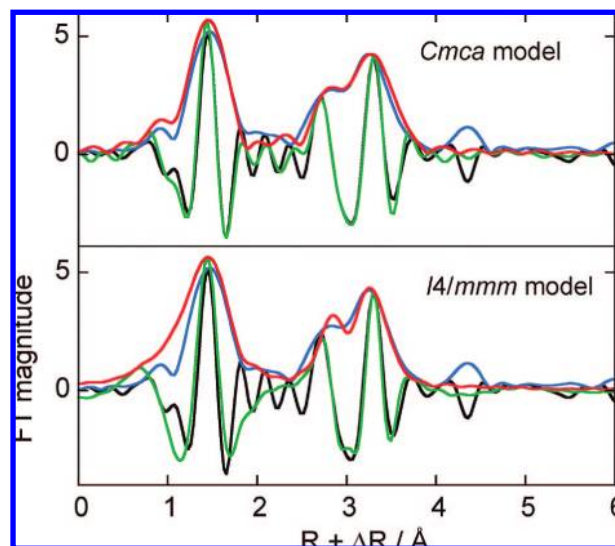
<sup>‡</sup> University of Antwerp.

$\text{Ba}_2\text{Zn}_{0.91(1)}\text{O}_{1.94(1)}\text{Ag}_2\text{Se}_{1.98(1)}$  which is charge balanced, consistent with the orange-red color and insulating properties.

Furthermore the NPD refinement revealed that a model with O located on its ideal position with an elongated displacement ellipsoid was inferior to models with O displaced from its ideal site toward Zn and suggested negligible scattering density on the ideal oxide position. Disordered displacement of the oxide ions from their ideal sites may still be modeled in  $I4/mmm$  with oxide ions half-occupying two sites related by a mirror plane perpendicular to the Zn–O bonds and located at the ideal oxide site. However electron diffraction (ED) measurements at room temperature (Figure 2) clearly showed the presence of additional sharp reflections disallowed for the  $I4/mmm$  cell, but consistent with an orthorhombic cell with  $Cmca$  symmetry which is a  $c \times \sqrt{2}a \times \sqrt{2}a$  expansion of the tetragonal cell ( $a = 19.9076(8)$  Å,  $b = 6.0562(3)$  Å,  $c = 6.0577(3)$  Å from NPD data at 295 K). This orthorhombic symmetry may readily be derived by inspection of a structural model in which displacement of the oxide ions from their ideal positions along the Zn–O bonds occurs in a completely ordered fashion resulting in orientationally ordered linear  $[\text{ZnO}_2]^{2-}$  units (Zn–O = 1.8956(5) Å from the refinement against NPD data) (Figure 1). This distortion from tetragonal symmetry is analogous to the cooperative distortion of the  $\text{CrCl}_2$  plane in  $\text{Rb}_2\text{CrCl}_4$  driven by the Jahn–Teller distortion of the  $\text{Cr}^{2+}$  ion.<sup>11</sup> The model of ordered displacements in  $Cmca$  indicated by the ED results also accounts for weak reflections in the NPD pattern (Figure 2) which are forbidden in the  $I4/mmm$  model. These weak reflections were apparent in SXRD data on close inspection, but refinement in  $Cmca$  in this case resulted in poorer residuals than the  $I4/mmm$  refinement; the inability of SXRD to readily distinguish the two models is presumably a consequence of the unit cell remaining metrically tetragonal within the resolution of the SXRD diffractometer and the symmetry breaking being almost solely due to displacement of the poorly scattering oxide ions. Bond valence calculations using the atomic coordinates obtained from the refinement against NPD data, but neglecting the site deficiencies, resulted in a BVS for Zn of 1.63 which still suggests underbonding, but is much more reasonable than the value of 1.35 obtained for the tetragonal model. The observed Zn deficiency (Zn:O ratio of 1: 2.13(3)) is likely a consequence of the underbonding of Zn.

Zn  $K$ -edge EXAFS measurements were performed on station BM29 at the ESRF as a further probe of the Zn coordination environment. With  $I4/mmm$  ( $D_{4h}$ ) symmetry enforced around Zn (i.e., four equal Zn–O distances) the best fit to the EXAFS (Figure 3) produced four equal distances of 1.89(2) Å, which is much less than  $a/2$  and only allows half of the Zn ions to be satisfied. Lowering the symmetry at Zn to approximately  $D_{2h}$  (actually  $2/m = C_{2h}$ ) to reflect the symmetry of the  $Cmca$  model resulted in a far superior fit to the EXAFS (Figure 3). In particular the real component of the Fourier transform in  $R$ -space between  $1.8 \leq R + \Delta R$  (Å)  $\leq 2.8$  is far better reproduced in the  $Cmca$  model than in the  $I4/mmm$  model. In the  $Cmca$  model the refined Zn–O distances of  $2 \times 1.88(1)$  Å and  $2 \times 2.40(1)$  Å match very closely those obtained in the refinement against NPD data.

Linear coordination is commonly found for  $d^{10}$  ions such as  $\text{Hg}^{2+}$  and results from mixing between the Hg-6s and an O-2p/Hg-5d<sub>z<sup>2</sup></sub>-derived state of the same symmetry. This is promoted by the stabilization of the Hg-6s through relativistic effects and because of the lanthanide contraction. Although isoelectronic with  $\text{Hg}^{2+}$ , the higher energy of the Zn-4s levels in  $\text{Zn}^{2+}$  mean that the driving force for linear coordination is much less strong than in  $\text{Hg}^{2+}$ .  $\text{Zn}^{2+}$  normally occurs in tetrahedral coordination by oxide, and we have



**Figure 3.** Fits to the Fourier transform (FT) of the EXAFS spectrum for the  $I4/mmm$  and  $Cmca$  models. Two fits are shown: to the real part of the FT (data, black; fit, green) and to its magnitude (data, blue; fit, red).

been unable to find other examples of compounds containing discrete  $[\text{ZnO}_2]^{2-}$  units, although isoelectronic  $[\text{ZnN}_2]^{4-}$  linear anionic units are found in  $\text{A}_2\text{ZnN}_2$  (A = Sr, Ba)<sup>12</sup> and  $\text{Ba}_3\text{ZnN}_2\text{O}$ .<sup>13</sup> The adoption of linear coordination for  $\text{Zn}^{2+}$  in  $\text{Ba}_2\text{ZnO}_2\text{Ag}_2\text{Se}_2$  is consistent with observations on other  $d^{10}$  ions species such as  $\text{Cd}^{2+}$ ,  $\text{Hg}^{2+}$ ,  $\text{Cu}^+$ , and  $\text{Ag}^+$ , but it seems to require the rather unusual circumstances of a  $\text{ZnO}_2$  square plane placed under tension, and presumably a lack of alternative products of lower energy to be realized in practice. Electronic structure calculations will shed light on the behavior of this and related systems.

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**Supporting Information Available:** Further experimental details, CIF files, tables of bond lengths and angles, fit results to EXAFS analysis. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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