Density functional theory based tight binding study on theoretical prediction of low-density nanoporous phases ZnO semiconductor materials

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Abstract. Polymorphs or phases - different inorganic solids structures of the same composition usually have widely differing properties and applications, thereby synthesizing or predicting new classes of polymorphs for a certain compound is of great significance and has been gaining considerable interest. Herein, we perform a density functional theory based tight binding (DFTB) study on theoretical prediction of several new phases series of II-VI semiconductor material ZnO nanoporous phases from their bottom-up building blocks. Among these, three phases are reported for the first time, which could greatly expand the family of II-VI compound nanoporous phases. We also show that all these generally can be categorized similarly to the aluminosilicate zeolites inorganic open-framework materials. The hollow cage structure of the corresponding building block Zn_k Ok (k= 9, 12, 16) is well preserved in all of them, which leads to their low-density nanoporous and high flexibility. Additionally the electronic wide-energy gap of the individual Zn_k Ok is also retained. Our study reveals that they are all semiconductor materials with a large band gap. Further, this study is likely to be the common for II-VI semiconductor compounds and will be helpful for extending their range of properties and applications.

Keywords: Nanoporous phases, DFT, II-VI semiconductor.

1. Introduction
Zinc oxide (ZnO) is a semiconducting material with more interesting and important properties than many other materials, due to the vast number of scientific publications on ZnO, particularly since 2000 [1]. The reason for this is that ZnO can be realized very easily in many different nanostructures, its excellent luminescent properties and wide possibility of bandgap engineering, e.g. core-shell nanoheterostructures, its piezoelectric found an application as nanogenerator, its bio-compatible in chemical-sensing effects, its high transparency and room-temperature ferromagnetism in optoelectronics and spintronics [2]. To date the seek to synthesize or predict new classes of structures.

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polymorphs or phase for this compound is still of great significance and has been gaining considerable interest. Beside the extensive experiments to find new phases, purely theoretical crystal structure prediction from first principles have also been widely reported [3-6]. Since the discovery of the excellent properties and applications of aluminosilicate zeolites in the areas of ion-exchange, separations, and catalysis, the area of inorganic open-framework materials has become one of the intense research activities. One of the major goals of the research over the open-framework materials is to find materials possessing channels and other features that make them porous or nanoporous. Porous materials play an important role in many applications related to energy and sustainability, e.g. catalysis, gas separation, water purification, and batteries. Further in the current search for new and interesting nanoporous open-frameworks, the predictability of their framework design and dimensionality are essential [7]. The International Zeolite Association (IZA) database shows that the number of structural types of unique microporous frameworks has been growing rapidly, from 27 in 1970, to 38 in 1978, to 64 in 1988, to 98 in 1996 and to 174 in 2007 [8]. The properties of cages/hollow structures decide their suitability for different applications, are intimately connected with their structures. Therefore synthesize a specific architecture is important and for most cases remained challenging. Experiments are most often used a “top-down” approach involving the disassembly of a parent ‘zeolite' structure to come to the targeted topologies [9]. In the theoretical side, Bromley et al. [10] has recently proposed that it is possible to stabilize new ultralow-density phases of metal oxide materials with low-density by taking smallest nanocages as building blocks of the possible new phases, and proving that there is no barrier to stop the nanocages from coalescing to form low-density nanoporous phases, e.g. SOD, LTA, and FAU†. Subsequently, another Zn_{12}O_{12}-assembled low-density phase reported by Song et al.[11] and Zn_{12}O_{12} and Zn_{16}O_{16}-cube by Z.F. Liu [4]. On the basis of this approach “from the bottom up” that provides a viable way from free clusters to cluster-assembled solid phases, we report our results of density functional theory based prediction starting from other ZnO clusters of Zn_{9}O_{9} and Zn_{12}O_{12} of three newly found ZnO-hollow structures.

2. Bottom-up structure prediction approach

In this section we briefly describe the “bottom up” approach for theoretical crystal hollow predictions. The possibility of the formation of different low-density framework materials based on highly stable Zn_{n}O_{n} (with n=12, 16) clusters is systematically investigated [4-11]. Generally, the preferred cluster building blocks are chosen as the highest symmetries with large HOMO–LUMO gaps, that are supposed to be most energetically stable. Via the coalescence or linking scheme these cluster building blocks, many kinds of low-density framework of ZnO materials of varying porosity are thus proposed.

Fig1. The relaxed structures of the magic clusters used as the building blocks in this work from the left to right Zn_{9}O_{9} (a), Zn_{12}O_{12} (octahedron structures- SOD) (b), another Zn_{12}O_{12} high symmetry multimer (to built a GME structure) (c) and Zn_{16}O_{16}-cube-structure (d). Small (red) balls are O atoms, big (gray) ones are Zn. All graphics illustrations in this work is prepared by VESTA [10].

† these acronyms are zeolite framework type codes according to the nomenclature of the International Zeolite Association (IZA)
Starting from binary tetrahedral compounds of ZnO structures that is stable at room temperature composed of three-coordinated atoms, sets of which create the even-number of atom rings face side due to the equal role of Zn and O in tetrahedral symmetry, i.e. each Zn/O atom is connected by the three O/Zn atoms with ionic bonding. It is commonly accepted that the higher-symmetry configurations of the cluster are typically found to be more stable and have a greater stability than clusters of same and/or other sizes. Therefore for high-symmetry cluster structures are only possible for certain sizes, e.g. 9, 12, 16, 18, 24 ..., which often called the magic clusters (see Fig.1).

As is mentioned above, the magic cluster Zn_{12}O_{12} have already served as the building blocks of the constructed low-density phases, i.e., SOD, LTA, FAU [10]. The growth paths of cluster–cluster coalescence proposed by Bromley [10] and Song et al. [11] are the phases constructed by the member-ring faces linkages. For instance, the case of Sodalite cage (SOD) know as the truncated octahedron structure (see Fig. 2a first line) - the structure comes with eight six-membered rings (6-MR) and six four-membered rings (4-MR) obeying the isolated tetragon rule, with the two types of Zn–O bonds as the longer one in (4-MR) and the shorter (RSB) connecting two neighbor 4-MR ring s. The SOD linking together with 12 square (4-MR facing 4-MR ring), see details description in [4]. Where as the FAU with four hexa-links (6-MR facing 6-MR), see second line in Fig.2a, LTA with six double-square links (cubic links), see third line in Fig.2a, EMT with four double-hexa links (see the fourth line in Fig.2a).
Fig 2a. From left to right the relaxed cluster - optimized crystal lattice primitive cell – hollow-bulk structure of the investigated structures SOD, FAU, LTA by Bromley et. al. [11], EMT, Zn$_{16}$O$_{16}$-cube by Z. Liu et.al [4] and CAN, GME by Bromley et. al. [12].

As well as the Zn$_{16}$O$_{16}$-cubic, the LTA, comes with six double-square links (cubic links) (see the fifth line in Fig.2a). The other two structures CAN and GME found in [12], where CAN is resulted from Zn$_9$O$_9$ cluster and comes with two hexa-links and 12 square-links closed packed, and GME come with two double hexa-links and six square-links.

Inspired by the approach of creating assembled phases from the bottom up, we extend the search and have carried out electronic calculation for the next possible Zn$_9$O$_9$ and another type of cluster multimer Zn$_{12}$O$_{12}$ from now on denote as Zn$_{12}$O$_{12}$-GME (see fig1.c). We found the new three structure which we categorized by its symmetry according to the IZA classification as AST, SAT and SBT. Herein, we describe three new phases found by us in Fig.2b. The most specific is the AST structure (see the first
line in Fig.2b) that comes with 6 double-square (cubic) and 8 hexa-links that appear to be more packed than the previous SOD structure (see Table. 1 for comparing). Next, SAT and SBS structures, both low-density hollow structures, originated from Zn$_2$O$_4$ come with two double-hexa links (see the second and the third line in Fig.2b). The detail structure files of these newly found phases are listed in the Appendix A.

**Fig2b.** From left to right the relaxed cluster - optimized crystal lattice primitive cell – hollow-bulk structure of this work's structures AST, SAT and SBT.

### 3. Computational details

3.1. **Density-Functional-Based Tight-Binding Plus (DFTB+) method**

The spin-polarized, charge self-consistent, DFTB approach is based on a second-order expansion of the spin-dependent Kohn-Sham total energy functional with respect to a given reference charge and magnetization density. The method has been extensively discussed elsewhere [13-16] and briefly outlined here as: 1/ Expand the orbitals as a linear combination of Slater type orbitals (LCSTO):
\[ \psi_n(r) = \sum_{\text{atomic site}/\text{orbital}} \sum_{\nu} C_{\nu} \phi_{\nu}(r - R_i). \]  

The basis functions \( \phi_{\nu}(r) \) centered on the atomic nucleus \( i \), with position \( R_i \), are themselves a linear combination of single Slater orbitals \( \phi_{\nu}(r) = \left( \sum_{\alpha \nu} a_{\nu \alpha} r^{l_{\nu \alpha}} e^{-\alpha r} \right) Y_{l_{\nu \alpha} m_{\nu \alpha}} \). The angular and magnetic quantum number are indicated with \( l_{\nu} \) and \( m_{\nu} \). \( Y_{l_{\nu} m_{\nu}} \) is the corresponding real spherical harmonic.

2/ Tight-binding expansion of the wave functions (calculation of the matrix elements in the two-centers approximation).

\[ \sum_{\text{atomic site/orbital}} \sum_{\nu} |H_{\nu, j \mu} - ES_{\nu, j \mu}| C_{\nu, j \mu} = 0, \]  

with 

\[ H_{\nu, j \mu} = \left\langle \phi_{\nu} | \hat{H} | \phi_{j \mu} \right\rangle \]  

and 

\[ S_{\nu, j \mu} = \left\langle \phi_{\nu} | \phi_{j \mu} \right\rangle. \]  

3/ Second order-expansion of Kohn-Sham energy functional (self-consistency in the charge density - SCC-DFTB):

\[ E_{\text{tot}} = \sum_{\text{occ.}} n_i \langle \Psi_i | H_0 | \Psi_i \rangle + \frac{1}{2} \sum_{\mu \nu} \gamma_{\mu \nu} \Delta q_{\mu} \Delta q_{\nu} + E_{\text{rep}}, \]  

where \( \Delta q_{\mu} \) - charge fluctuation decomposed into atomic contribution (Mulliken charge), \( \gamma_{\mu \nu} \) - some integral coefficient, \( E_{\text{rep}} \) - repulsive term (see Ref. 4-6).

With all matrix elements and orbitals are derived from Density Functional calculation, the advantage of DFTB method relies on the use of small basic set of atomic orbitals (in order to reduce the matrix dimension for diagonalization speed-up) and the restriction to two center nonorthogonal Hamiltonian (allowing extensive use of look-up table). What it distinguishes from semi-empirical method is the explicit calculation of the basic wave function which allow deeper physics insight and better control of the approximation used. The method solved Kohn-Sham equation self-consistently using Mulliken charge projection. This approach have proved to have transferable and accurate interaction potential as well as numerical efficiency allowing Molecular Dynamic (MD) simulation of supercell containing several hundreds to a thousand atoms. Thus this is particular suitable to study the electronics proper and dynamics of large mesoscopic system and organic molecule such as Nano-wire, CNT's, DNA stands or absorbate on surface, semiconductor hetero-structure etc. see review in [14-15] and references there in. The advantage of DFTB parameterization is that only few, possibly well chosen systems are needed to create the parameters, i.e. in DFTB fit systems can also be purely ideal systems, if they are chemically acceptable and can be described carefully with an ab-initio approach. Next this well tested parameter, e.g. in an attention for solid state systems and for defect physics as in current case, can be used for much larger system due to its transferability. In our calculation the parameter and its transferability have been successfully applied in several DFTB works [16-18].

The electronic DFTB parameters (i.e., Hubbard parameters, \( H_{\mu \nu \gamma}^0 \) and \( S_{\mu \nu \gamma} \) matrix elements) were derived directly from DFT calculations, performed within the generalized gradient approximation (GGA) and using the Perdew, Burke, and Ernzerhof (PBE) exchange-correlation functional.
3.2. Corhersive energy, phase stability and Equation of State (EOS).
To compare the stability of these nanoporous frameworks with that of traditional ZnO phases, we have calculated total energy per ZnO-pair vs. volume for every studied structures together with well-known phases wurtzite ZnO and zincblende ZnO. The results are presented in Figure 3, in which the solid curves derive from third-order Birch−Murnaghan EOS fit.

On the basis of these fitted curves, we may draw some conclusions on their stabilities. As shown in the Figure 3 and table2, one can note that the SOD phase has the lowest equilibrium energy, indicating that it is the most energetically stable phase among the studied phases. Following next is the CAN, AST. The LTA and SAT have similar stability. Following by GME, Zn_{16}O_{16}-cub and finally FAU and SBT. Note that most of the calculated ZnO polytypes, exhibit essentially similar E(V) curve as wurtzite modification at this level of calculation and are indistinguishable on the scale of the figure.

**Fig3.** Total energy (eV/Zn-O) vs. relative volume for the considered phases of ZnO.

3.3. Electronic band structure

**Fig4.** From left to right band structure of the phases ZnO-wurtzite, ZnO-zincblende, SOD, FAU
Concerning the effects of polytypism on the electronic structure, i.e. bandstructures and gaps. Our calculations show that the band gaps among the polytypes ranging from 4.0 eV for SAT to 4.57 eV for LTA. It is noted that within our DFTB parametrization the ZnO wurtzite's bandgap is the order of 3.73eV and ZnO zincblende is equal to 4.16eV, which are close enough to the experimental values. So that all the new phases are still wide bandgap semiconducting materials.

4. Results and discussion
The stability of studied structures evident that, it is reasonable to believe that these cluster-assembled phases would be the attractive synthesis targets. In the Zn8O16-assembled phases, the coordination number for every phase is all four (except some small dangling in phase Zn16O16-cub), i.e. each Zn (O) atom has four O (Zn) neighbors forming distortional $sp^3$-type hybridization for almost all phases. Thus preserving the valuable properties of the ZnO materials, such as semiconducting, piezoelectric and optically transparent.

As is shown in characteristics Table 1, the volume per atom of ZnO hollow phases higher than the WZ and ZB phase, respectively, from 29.0% up to 85% larger than that of WZ. Naturally, it leads to higher flexibility and compressibility (lower bulk moduli) of the new hollow phases. Therefore, these new nanoporous phases if they are could be synthesized, will be one of the most promising candidates for replacing the expensive and mechanically fragile atomic or molecular selective materials.
Hereby, we also show the estimations of pore volume as well as specific surface area of the optimized primitive unit cell for these nanoporous phases (see Table 1), which does reflect the porosity of their framework to a certain extent.

The other essential structural parameters, such as the lattice contents, particle density, mass density, crystal structure together with the symmetry space group, which shows that all the phases are high symmetry, i.e. come with high stabilities, are also listed in characteristic Table 1.

Table 1. Calculated characteristics of all studied phase and most common phase of ZnO.

| Structures | WZ | ZB | SOD | LTA | FAU | Zn_{16}O_{16}cube |
|------------|----|----|-----|-----|-----|-------------------|
| Mass Density (g cm\(^{-3}\)) | 5.68 | 5.4 | 4.306 | 3.563 | 3.081 | 3.28 |
| V/at Å\(^3\) | 11.9 | 12.6 | 15.69 | 18.967 | 21.93 | 20.6 |
| Part. density \((10^{23}\text{cm}^{-3})\) | 8.8 | 4.84 | 12.64 | 48.53 | 48.46 | 32.48 |
| Coord. number | 4 | 4 | 4 | 4 | 4 | 3.75 |
| Crystall structure | Wurt (hex) | Cub | Cub | FCC | Cub | Cub |
| Symmetry groups | P63M186 | F43216 | PM3N 223 | FM3C 226 | FD-3 203 | P43-M 215 |
| Unit cell (atoms) | 8 | 4 | 12 | 48 | 48 | 32 |
| Lattice param. Å (a-c) | 3.249-5.205 | 4.63 | 5.732 | 10.89 | 16.15 | 8.704 |
| Average bond Å | 1.977 | 2.015 | 2.027 | 2.032 | 2.043 | 2.074 |
| Average angle | | | | | | |
| Zn-O-Zn | 109.5 | 109.5 | 110 | 107.3 | 109.2 | 108.18 |
| O-Zn-O | 109.5 | 109.5 | 110 | 107.6 | 108.7 | 108.88 |
| Band gap eV | 3.73 | 4.16 | 4.218 | 4.572 | 4.108 | 4.49 |
| UC specific surface area Å\(^2\) | | | | | | |
| UC Pore Volume Å\(^3\) | | | | | | |
| EMT | GME | CAN | AST | SAT | SBT |
| Mass Density (g cm\(^{-3}\)) | 3.078 | 3.702 | 4.404 | 4.089 | 4.073 | 3.242 |
| V/at Å\(^3\) | 21.953 | 18.254 | 15.35 | 16.53 | 16.592 | 20.84 |
| Part. density \((10^{23}\text{cm}^{-3})\) | 96.46 | 24.55 | 12.65 | 40.60 | 72.6 | 48.48 |
| Coordination number | 4 | 4 | 4 | 4 | 4 | 4 |
| Crystall structure | Trigonal | Trigonal | Hex | Cub | Triclinic | Hex |
| Symmetry groups | P31C 163 | P31C 163 | P63M 176 | F43M 216 | R3 148 | R3 148 |
| Unit cell (atoms) | 96 | 24 | 12 | 40 | 24 | 48 |
| Lattice param. Å (a-c) | 11.43-18.64 | 8.85-6.47 | 8.047-3.288 | 8.711 | 7.88 | 11.32-27.0 |
| Average bond Å | 2.043 | 2.037 | 2.037 | 2.031 | 2.036 | 2.043 |
| Average angle | | | | | | |
| Zn-O-Zn | 108.7 | 108.32 | 108.3 | 108.0 | 108.2 | 107.6 |
| O-Zn-O | 109.1 | 108.41 | 108.07 | 107.9 | 108.2 | 4.136 |
| Band gap eV | 4.109 | 4.327 | 4.245 | 4.054 | 4.0 | 4.136 |
| UC specific surface area Å\(^2\) | 3159 | 188.3 | 71.87 | 273 | 396.6 | 324.4 |
| UC Pore Volume Å\(^3\) | 736.7 | 608.6 | 228.9 | 188 | 120.9 | 1000.5 |
From the above table 1, the symmetry of the hollow phases also confirm that in various structures different stacking and/or linking orders, resulted from mixing the hcp- and the fcc-type stacking, would produce different polytypes.

5. Conclusions
Our theoretical prediction on the three interesting ZnO candidates for ZnO hollow phases follow by the bottom up approach from different types of ZnO magic cluster which exhibit similar stacking orders to the many investigated ZnO polytypes. Comparing with the phases found recently by others, it is clearly expected that, the hollow phases could survive in periodic systems without structural collapse, which leads to their nanoporous and low-density features. Furthermore structurally, we can relate these polytype structures to those of other II-VI semiconducting materials, such as ZnS, CdSe, CdTe where different polytypes might also be observed.

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Appendix A Structures files of the new hollow structures found by this work

1/ structure: AST

cell parameters
8.7111  8.7111  8.7111  90.0000  90.0000  90.0000

fractional coordinates
Zn1  Zn  0.75000  0.25000  0.25000
Zn2  Zn  0.25000  0.75000  0.25000
Zn3  Zn  0.25000  0.25000  0.75000
Zn4  Zn  0.75000  0.75000  0.75000
O1   O  0.25000  0.25000  0.25000
O2   O  0.75000  0.75000  0.25000
O3   O  0.75000  0.25000  0.75000
O4   O  0.25000  0.75000  0.75000
Zn5  Zn  0.11880  0.11880  0.11880
Zn6  Zn  0.11880  0.61880  0.61880
Zn7  Zn  0.61880  0.11880  0.61880
Zn8  Zn  0.61880  0.61880  0.11880
Zn9  Zn  0.88121  0.88121  0.11880
Zn10 Zn  0.88121  0.38121  0.61880
Zn11 Zn  0.38121  0.88121  0.61880
Zn12 Zn  0.38121  0.38121  0.11880
Zn13 Zn  0.88121  0.11880  0.38121
Zn14 Zn  0.88121  0.61880  0.38121
Zn15 Zn  0.38121  0.11880  0.38121
Zn16 Zn  0.38121  0.61880  0.88121
Zn17 Zn  0.11880  0.88121  0.88121
Zn18 Zn  0.11880  0.38121  0.38121
Zn19 Zn  0.61880  0.88121  0.38121
Zn20 Zn  0.61880  0.38121  0.88121
O5   O  0.88235  0.11765  0.11765
O6   O  0.88235  0.61765  0.61765
O7   O  0.38235  0.11765  0.61765
O8   O  0.38235  0.61765  0.11765
O9   O  0.11765  0.88235  0.11765
O10  O  0.11765  0.38235  0.61765
O11  O  0.61765  0.88235  0.61765
O12  O  0.61765  0.38235  0.11765
O13  O  0.11765  0.11765  0.88235
O14  O  0.11765  0.61765  0.38235
O15  O  0.61765  0.11765  0.38235
O16  O  0.61765  0.61765  0.88235
O17  O  0.88235  0.88235  0.88235
O18  O  0.88235  0.38235  0.38235
O19  O  0.38235  0.88235  0.38235
O20  O  0.38235  0.38235  0.88235
2/ structure: SAT

cell parameters
8.2486 8.2486 8.2487 60.0000 60.0000 60.0000

fractional coordinates
Zn1  Zn  0.05402  0.28158  0.54414
Zn2  Zn  0.78945  0.56183  0.30996
O1    O   0.45639  0.70881  0.95079
O2    O   0.70489  0.44874  0.19866
Zn3  Zn  0.54412  0.05404  0.28157
Zn4  Zn  0.30995  0.78943  0.56184
O3    O   0.95076  0.45643  0.70879
O4    O   0.19868  0.70488  0.44871
Zn5  Zn  0.28159  0.54410  0.05404
Zn6  Zn  0.56183  0.30989  0.78949
O5    O   0.70879  0.95080  0.45639
O6    O   0.44873  0.19869  0.70483
Zn7  Zn  0.94597  0.71843  0.45585
Zn8  Zn  0.21051  0.43818  0.69006
O7    O   0.54361  0.29118  0.04922
O8    O   0.29512  0.55128  0.80133
Zn9  Zn  0.45589  0.94596  0.71840
Zn10 Zn  0.69007  0.21056  0.43815
O9    O   0.04922  0.54358  0.29121
O10   O   0.80131  0.29513  0.55130
Zn11 Zn  0.71844  0.45586  0.94599
Zn12 Zn  0.43816  0.69011  0.21051
O11   O   0.29120  0.04920  0.54360
O12   O   0.55128  0.80133  0.29511

3/ structure: SBT

cell parameters
11.2501 11.2501 11.2501 59.7560 59.7560 59.7560

fractional coordinates
Zn1  Zn  0.36488  0.53552  0.71822
Zn2  Zn  0.20688  0.66907  0.02736
Zn3  Zn  0.84451  0.64093  0.30812
Zn4  Zn  0.51336  0.34297  0.16431
O5    O   0.64933  0.27398  0.46790
O6    O   0.79499  0.96347  0.33379
O7    O   0.16897  0.70157  0.34119
O8    O   0.48722  0.84403  0.65581
Zn9  Zn  0.71822  0.36488  0.53552
Zn10 Zn  0.02736  0.20688  0.66907
Zn11 Zn  0.30812  0.84451  0.64093
Zn12 Zn  0.16431  0.51336  0.34297
O13   O   0.46790  0.64933  0.27398
| Element | Type | X-coordinate | Y-coordinate | Z-coordinate |
|---------|------|--------------|--------------|--------------|
| O14     | O    | 0.33379      | 0.79499      | 0.96347      |
| O15     | O    | 0.34119      | 0.16897      | 0.70157      |
| O16     | O    | 0.65581      | 0.48722      | 0.84403      |
| Zn17    | Zn   | 0.53552      | 0.71822      | 0.36488      |
| Zn18    | Zn   | 0.66907      | 0.02736      | 0.20688      |
| Zn19    | Zn   | 0.64093      | 0.30812      | 0.84451      |
| Zn20    | Zn   | 0.34297      | 0.16431      | 0.51336      |
| O21     | O    | 0.27398      | 0.46790      | 0.64933      |
| O22     | O    | 0.96347      | 0.33379      | 0.79499      |
| O23     | O    | 0.70157      | 0.34119      | 0.16897      |
| O24     | O    | 0.84403      | 0.65581      | 0.48722      |
| Zn25    | Zn   | 0.63512      | 0.46448      | 0.28178      |
| Zn26    | Zn   | 0.79312      | 0.33093      | 0.97264      |
| Zn27    | Zn   | 0.15549      | 0.35907      | 0.69188      |
| Zn28    | Zn   | 0.48664      | 0.65703      | 0.83569      |
| O29     | O    | 0.35067      | 0.72602      | 0.53210      |
| O30     | O    | 0.20501      | 0.03653      | 0.66621      |
| O31     | O    | 0.83103      | 0.29843      | 0.65881      |
| O32     | O    | 0.51278      | 0.15597      | 0.34419      |
| Zn33    | Zn   | 0.28178      | 0.63512      | 0.46448      |
| Zn34    | Zn   | 0.97264      | 0.79312      | 0.33093      |
| Zn35    | Zn   | 0.69188      | 0.15549      | 0.35907      |
| Zn36    | Zn   | 0.83569      | 0.48664      | 0.65703      |
| O37     | O    | 0.53210      | 0.35067      | 0.72602      |
| O38     | O    | 0.66621      | 0.20501      | 0.03653      |
| O39     | O    | 0.65881      | 0.83103      | 0.29843      |
| O40     | O    | 0.34419      | 0.51278      | 0.15597      |
| Zn41    | Zn   | 0.46448      | 0.28178      | 0.63512      |
| Zn42    | Zn   | 0.33093      | 0.97264      | 0.79312      |
| Zn43    | Zn   | 0.35907      | 0.69188      | 0.15549      |
| Zn44    | Zn   | 0.65703      | 0.83569      | 0.48664      |
| O45     | O    | 0.72602      | 0.53210      | 0.35067      |
| O46     | O    | 0.03653      | 0.66621      | 0.20501      |
| O47     | O    | 0.29843      | 0.65881      | 0.83103      |
| O48     | O    | 0.15597      | 0.34419      | 0.51278      |