Order in the Disordered State

Structural Entities in Complex Oxides

While materials at low temperatures are often characterized in terms of crystal chemical concepts, descriptions of their high-temperature properties are usually based on defect chemistry. Both approaches are obviously of great value but also have clear limitations. While the defect chemistry is often weakly linked to the crystal structure of the material and basically provides an ideal solution model where the solutes are either simple defects or defect clusters, crystal chemistry most often gives a static view of the material and tries to reduce the real complex structure to one in which the local structure does not vary throughout the crystal. Thus descriptions based on partial occupancy and random distributions of different species are frequently encountered. We approach the local and average structure of grossly disordered materials by configurational averaging using energies of individual configurations optimized by density functional theory or force-field models. We interpret the average structure observed experimentally at any temperature as a time and spatial average of the different local environments (corresponding to separate local minima on the potential energy surface) which are energetically accessible at that temperature. These environments are regarded as representing snapshots of small regions of the disordered material and thus to show local structural environments and structural correlations. Our alternative description bridges the two usual approaches for describing the structure of disordered materials and provides a unified picture of the main structural features of disordered oxides both at low and high temperatures.

Grossly non-stoichiometric perovskite-related A$_2$B$_2$O$_5$-oxides are used as our case. The distribution of oxygen vacancies is even at high temperatures far from random and relatively few configurations, associated with different arrangements of tetrahedral BO$_4$, square pyramidal BO$_5$ and octahedral BO$_6$ entities, are thermally accessible at most temperatures.

![Energy – degeneracy plot for a 2x2x2 supercell of Ba$_2$In$_2$O$_5$](image-url)
The Brownmillerite-type ground state structure is reproduced in simulations of both Ba$_2$In$_2$O$_5$ and Sr$_2$Fe$_2$O$_5$. In addition, many of the lower energy minima resemble this ground state structure in that they consist of alternating layers of BO$_4$-tetrahedra and BO$_6$-octahedra. These configurations differ in the *stacking sequences* of the tetrahedral layers, and in the type of *connectivity* within the tetrahedral layers.

Connectivity patterns within the tetrahedral layers of a 2x2x2 supercell of Ba$_2$In$_2$O$_5$

Other configurations i.e. the structures taken by Sr$_2$Mn$_2$O$_5$ and La$_2$Ni$_2$O$_5$ are also present on the energy hypersurface but higher in energy. The energies of the configurations are in general largely influenced by the large A atoms and thus by the A-O interactions. These interactions are easily characterized using bond valence sums which correlate well with the energy for selected groups of related CNC’s. The existence of a range of different CNCs close in energy rationalises the frequent observation of incompletely ordered structures even at room-temperature. At low temperatures the energy barriers from one minimum to another are thermally inaccessible. Complete long-range order is thus not easily achieved and frozen-in disorder results. Freezing of rapid oxygen orderings recently has been reported to give rise to glass-like transitions in perovskite-related oxides as well as in ZrWMoO$_8$.

**Order-disorder in grossly non-stoichiometric SrFeO$_{2.50}$: a simulation study**
E. Bakken, N.L. Allan, T.H.K. Barron, C.E. Mohn, I.T. Todorov, S. Stølen
*Physical Chemistry Chemical Physics* 2003, 5, 2237-2243.

**Order in the disordered state: local structural entities in the fast ion conductor Ba$_2$In$_2$O$_5$**
C.E. Mohn, N.L. Allan, C.L. Freeman, P. Ravindran, S. Stølen
*Journal of Solid State Chemistry*, in press

**Cations Size-mismatch Strain**
Short-range-order also results in mixed cation systems where cations of one type are shown to cluster in the first coordination sphere. Clustering minimizes the size mismatch strain energy that dominates in most systems.
Breakdown of Intermediate Range Order in Liquid GeSe₂ at High Pressures
The presence of structural entities and thus short-range-order is often encountered also for liquids and glasses. In many cases will the short-range order in the liquid be that observed in the corresponding crystalline phase. The crystal structures of the stable silicon and germanium disulfides and diselenides are all based on tetrahedra as the basic structural entity. These (Si/Ge)(S/Se)₄-tetrahedra share corners or edges and while the two silicon compounds are one-dimensional with edge-sharing tetrahedra only, the germanium disulfide only show corner-sharing tetrahedral and form a three-dimensional network structure. GeS₂ have 50% edge and 50% corner sharing tetrahedra and form a two-dimensional crystal structure.

These connectivity patterns give rise to what is termed intermediate-range-order and they may be present even in the liquid state. Recent investigations have revealed rich thermodynamic behaviour in such liquids with tetrahedral coordination that point to the occurrence of multiple liquids distinguished by density and local structure. A first order liquid-liquid transition, above the melting line, has only been observed for phosphorus. In systems with critical phenomena in the supercooled state, anomalous behaviour of the compressibility is also anticipated above the critical point, as shown by simulation of water. Liquid GeSe₂ is attractive in this respect due to the density minimum near the melting point and the open structure consisting of a 2D framework of corner and edge sharing GeSe₄-tetrahedra.

A melting point minimum is observed below 1 GPa. The structure of liquid GeSe₂ is sensitive to pressure and anomalous compressibility is expected. The connectivity of the liquid changes from...
2D to 3D with increasing pressure due to conversion of edge-sharing tetrahedra to corner-sharing tetrahedra and the breakdown of the intermediate range order is manifested by the complete loss of the “first-sharp-diffraction-peak” (FSDP). The gradual change in structure above the melting line may develop to a first order liquid-liquid transition in the supercooled regime.

**Breakdown of the intermediate-range order in liquid GeSe$_2$ at high pressures**
W.A. Crichton, M. Mezouar, T. Grande, S. Stølen, A. Grzechnik

**Metastable melting and pressure-induced amorphization of GeSe$_2$**
T. Grande, S. Stølen, A. Grzechnik, W.A. Crichton, M. Mezouar