

Structure prediction and solid solutions with evolutionary algorithms

Scott Woodley

UCL, London, UK

The recent explosion of interest in the synthesis and characterisation of nano-clusters has been driven in part by the wide-ranging applications of nano-particulate materials in catalysis, electronics and energy conversion. The field has been further stimulated by the increasing need to obtain atomic level models of crystal nucleation and the early stages of growth, which also involve the formation and evolution of nano-clusters. However, elucidation of the structures and properties of nano-particulate matter is fraught with difficulties. Structure determination from experiment is often highly problematic. Diffraction may be of little if any value; small angle scattering and X-ray absorption spectroscopy can provide useful information, which, however, falls short of a detailed structural model; high resolution electron microscopy can in a number of cases provide detailed images of cluster structures, but is often difficult to apply. A range of spectroscopic techniques may be employed, but the information they give is generally incomplete and indirect. These difficulties can be related to the differing behaviour of particles of different sizes. For example, structural and optical properties of zinc oxide are crucially determined by the size of the particles. Three regimes, or length scales are recognized (cf. work on ZnO by Wood et al. [1]): Macroscopic: Particles maintain the crystal structure of the bulk; the optical band gap is practically constant, while point defects and surfaces give rise to specific size-independent phenomena, e.g. UV, blue-green, yellow-orange and red luminescence; Quantum dots: At least in one dimension, the particle size is of the order of the exciton radius, 1530\AA . (which could be still greater by one to two orders of magnitude in materials with high dielectric constant). In this regime, the bulk crystal structure is preserved even though the X-ray diffraction lines broaden, while the order of stability between the phases could change, and the optical absorption bands shift and deform, owing to quantum-size effects; Nano-Clusters: The structure of the particles may differ significantly from that of the bulk phases. Moreover, no clear diffraction patterns are obtainable, and optical properties cannot be directly correlated with those of the bulk. Indeed, for ZnO, as for other materials, there has not yet appeared an experimental technique capable of reliable characterization of the local structure; and this regime is understood least.

In my presentation I will discuss recent progress we have made [2-6] within this last size regime, namely the application of global optimisation techniques [7] as applied to predicting the atomic structure of low energy nano-clusters of inorganic compounds, the first essential step before investigating physical or electronic properties. The global search is applied to the energy landscape defined by a rigid ion and/or Shell Model (IP-landscapes), as implemented within the GULP software, as well as that defined by electronic structure techniques, as provided by the FHI-AIMS software

(the latter also being applied as a second stage for refining/re-ranking structures when searching the IP-landscapes). Our approach has recently been automated in the form of the “Knowledge Lead Master Code (KLMC)”, which manages the data and calls/reads back from external software including GULP and FHI-AIMS. Initial results from KLMC will be shown, which includes results where we have investigated the cation and vacancy ordering in bulk zinc oxide.

- [1] A. Wood, M. Giersig, M. Hilgendorff, A. Vilas-Campos, L.M. Liz-Marzan and P. Mulvaney, *Aust. J. Chem.* 56 1051 (2003)
- [2] C.R.A. Catlow, S.T. Bromley, S. Hamad, M. Mora-Fonz, A.A. Sokol and S.W. Woodley, *Phys. Chem. Chem. Phys.* 12 786 (2010)
- [3] S.M. Woodley, A.A. Sokol and C.R.A. Catlow, *Z. Anorg. Allg. Chem.* 630, 2343 (2004)
- [4] S. Hamad, C.R.A. Catlow, S.M. Woodley S. Lago and J.A. Mejias, *J. Phys. Chem. B* 109, 15741 (2005)
- [5] A.A. Al-Sunaidi, A.A. Sokol, C.R.A. Catlow and S.M. Woodley, *J. Phys. Chem. C* 112, 18860 (2008)
- [6] A. Walsh and S.M. Woodley, *Phys. Chem. Chem. Phys.* 12 8446 (2010)
- [7] S.M. Woodley and C.R.A. Catlow, *Nat. Mater.* 7 937 (2008)