Exploring co-substitution as a method to direct synthesis towards otherwise hypothetical polymorphs

Martijn A. Zwijnenburg
Department of Chemistry, University College London, 20 Gordon Street, London WC1H 0AJ, UK
E-mail: m.zwijnenburg@ucl.ac.uk

Most, if not all, inorganic solids are predicted to display a dense spectrum of hypothetical polymorphs [1-3]. Polymorphs that may differ in structure and properties of the polymorph(s) normally synthesized for a material [4], and where the reason that they are not observed experimentally appears related to the topography of the energy landscape that funnels towards the experimental polymorph [5]. This all raises the question how one could direct synthesis towards these hypothetical polymorphs and realise them experimentally.

Inspired by the case of zeolites, where co-substitution of silicon dioxide by aluminium and alkali metal atoms stabilises low-density polymorphs [6], we explored similar co-substitution in zinc oxide (ZnO) using basin-hopping global optimisation calculations [1,7]. In my contribution, I will discuss the outcome of these calculations, specifically how co-substitution of ZnO with Li and K/Rb indeed stabilises otherwise hypothetical polymorphs [8,9], as well as what we can learn about the possible use of co-substitution for other systems beyond ZnO, the computational challenges to overcome and what kind of properties such substiuted materials might have.

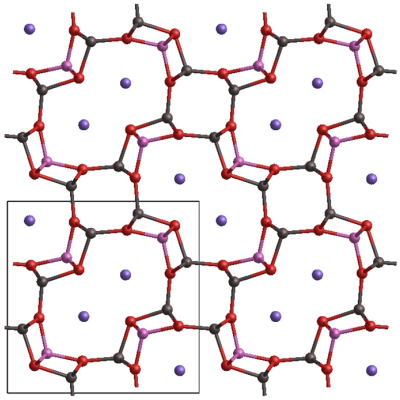

Figure 1. Structure of a Li/K co-substituted ZnO material.

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