

# Predicting Crystal Morphologies With *Crysalis* and *MetaMorph*

Properties of ceramic materials are strongly influenced by the presence of impurities and by surface structure and stability. To improve process and properties, it is crucial to know whether defects segregate to surfaces, or whether they remain in the bulk where they can lead to phase separation.

For example, surface segregation can give rise to lower surface energies - thereby providing a barrier to sintering, or, in other cases, leading to faceting of the surface.

The likelihood of surface segregation is dominated by energetic effects - particularly whether a defect is more stable at the surface than in the bulk. Measurement of segregation energies experimentally is a challenging task, requiring carefully purified materials and lengthy experimentation.

## A new approach - *Crysalis*

Increasingly, researchers are turning to their computers to give new insight and to predict properties which are hard to determine experimentally. Surface segregation is an area which ideally suited to a computational approach.

***Crysalis*** takes crystal data available from databases and allows you to generate bulk and surface crystal structures on your Silicon Graphics workstation. Introducing point defects like dopant ions is straightforward.

The simulation engine in ***Crysalis*** consists of a static lattice code, which quickly calculates defect energies and lattice relaxations around defects. Visualization and manipulation of the resulting structure can be carried out within ***Crysalis*** in a variety of display styles.

Static lattice simulations have been tested both in academe and industry over the past few years, and have a well-established track

record of producing useful results with minimal computational time. They use 2-body and higher potentials to describe the interactions between the ions; ***Crysalis*** is supplied with a standard database of potentials which have been tested and validated in the published literature.

Within minutes, therefore, you can predict defect energies at the surface and in the bulk.

THE RESULT? Improved understanding of the role of defects in ceramics

## Surface Segregation in Magnesia

One of the earliest good experimental measurements of surface segregation was for  $\text{Ca}^{2+}$  in MgO, by Wynblatt and McCune, who determined a free energy of segregation of -50.17 kJ/mole for an estimated 20% coverage of the surface. This has provided a benchmark against which the simulations can be tested, and work of Mackrodt, Tasker and colleagues has reproduced the experimental value well.

The free energy depends on both energetic and entropic contributions, where the configurational entropy is by far the more important.

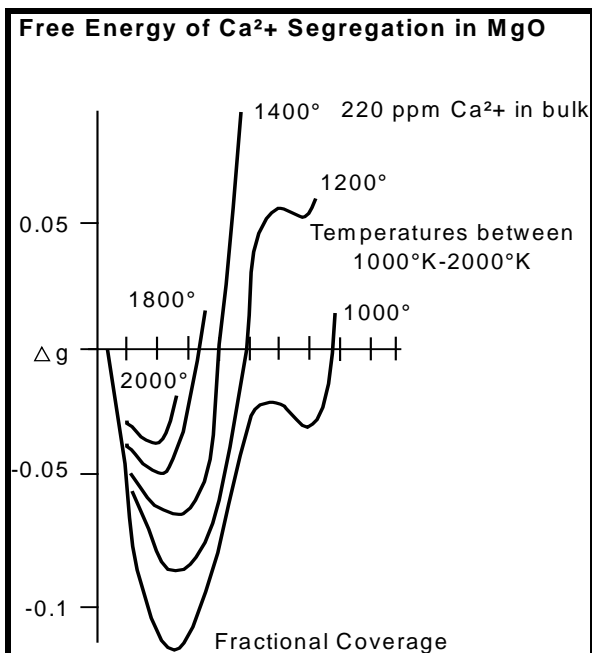
$$\Delta G = y \{ h(y) - kT [\ln(x/y) + (1-y)/y \ln((1-x)/(1-y))] \}$$

x	bulk concentration of impurity
y	surface concentration of impurity
h(y)	concentration-dependent enthalpy of segregation

Colbourn, Mackrodt and Tasker (*J Materials Science* **18** 1917 (1983)) report a formula (given in the box overleaf) for calculating the free energy of surface segregation which describes the segregation in terms of an enthalpy of segregation together with the temperature of the system.

The enthalpy of segregation can be approximated by the difference of two simple calculations - the defect energy in the bulk and the defect energy at the surface. The Defect Energy option within **Crysalis** gives this number automatically.

This expression includes the *configurational* entropic contribution to the free energy, but not that from the *vibrational* effects. However, other work by Masri and coworkers has shown that the vibrational contribution is relatively small, on the order of 3 kJ/mole.



Using **Crysalis** to calculate the enthalpy of segregation together with this expression for the configurational free energy, the free energy of segregation of  $\text{Ca}^{2+}$  in  $\text{MgO}$  has been calculated as 44 kJ/mole, in agreement with experimental values of 44 and 50 kJ/mole. The calculations also predict that the minimum in the free energy occurs at

about 20% coverage for a temperature of 1200C - again, in excellent agreement with the surface.

Larger dopants can also be considered - for example  $\text{Sr}^{2+}$  and  $\text{Ba}^{2+}$ . These large ions segregate strongly to the surface, causing a decrease in surface energy which provides a barrier to sintering. Thus, incorporation of defects can be important in controlling particle size. Segregation to various surfaces can be studied, and this has given important insights into faceting, for example.

### Surface Segregation in Alumina

Not only simple cubic oxides are accessible with **Crysalis** - more complicated structures such as  $\alpha$ -alumina can also be studied.

Again using the static lattice methodology which underlies **Crysalis**, Mackrodt and coworkers have studied the effect of dopants - both isovalent and aliovalent - in  $\text{Al}_2\text{O}_3$ . For aliovalent dopants, some charge compensation must be included, of course - as it would be in the real physical system.

### Conclusions

There is a driving force for the segregation of  $\text{Ca}^{2+}$  in  $\text{MgO}$ , which primarily results from the ability of the surface to reconstruct to accommodate the larger size calcium ion.

The calculated segregation energy is in excellent agreement with that observed from experiment, and the calculations took only minutes.

The same effect is seen for other ions, and for other oxide systems, meaning that static lattice calculations can be used to give rapid and reliable predictions of surface segregation.