Predicting the Influence of Growth Additives on the Morphology of Ionic Crystals

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Calcite surface energy and morphological changes observed in the presence of Mg^{2+} and Li^+ ions are predicted using atomistic simulation based on the Born model of solids.

The specific modification of crystal morphology in the presence of additives is of paramount importance to a wide variety of technological processes. Currently, most of these systems employ additives selected on an empirical basis using a general knowledge of the bonding and packing considerations of crystal structures. A quantitative treatment has been developed for molecular crystals[1,2] and the effects of solvents and additives on morphological modifications considered. However, although lattice simulation and surface relaxation approaches have been successfully applied in the prediction of the equilibrium morphology of pure ionic crystals,[3] the influence of modifiers on ionic surfaces has not to date been described in detail at the atomistic level. Previously we have calculated the heats of surface segregation of isovalent and aliovalent impurities in the corundum-structured oxides Al_2O_3 and Cr_2O_3.[4] These results indicated a modification of crystal habit according to relative changes in the surface energies of particular (*hkl*) faces. In this paper, we extend this approach to the study of the effect of simple cations (Li^+, Mg^{2+}) on the morphology of an ionic crystal containing an oxyanion ($CaCO_3$). Our predictions are consistent with experimental observations on the influence of Mg^{2+} and Li^+ on the morphology of calcite crystals grown from supersaturated hydrogencarbonate solutions at ambient temperature.[5,6]

A two-region approach was used in the atomistic modelling of calcite surfaces. The crystal surfaces must be electrically neutral and contain no orthogonal dipole moment. Ions close to the surface (region 1) were relaxed explicitly until there were no net forces acting on any of the ions. In contrast, ions further into the bulk (region 2) were kept in their lattice sites and constrained to relax only in a direction perpendicular to the interface. The final atomic positions gave the surface structure and the equilibrium surface energies were calculated from the differences in energy per unit area of atoms in the surface compared with those in the bulk. The interatomic potentials used for this simulation study were based on those developed by Jackson and Price.[7] They consist of Coulombic interactions between the ions; a short-range term which includes repulsive and attractive components; a three-body-bond bending term between O–C–O and a four-body torsional potential that ensures the carbonate ions remain planar during relaxation. The calculated surface energy μ^s per unit area for a given plane *hkl* can be defined as: $\mu^s = \Sigma_{\lambda=1}^{m}[\mu(\lambda) - \mu(m)]/A$ where the energy is summed over all ions in plane λ, m is the bulk plane and $\mu(m)$ is the bulk energy. In the presence of Mg^{2+} or Li^+, the defect surface energies were obtained by calculating the heats of surface segregation[8] and adding this value to the corresponding energy of the pure surface. The computer codes used in this work were CASCADE[9] which

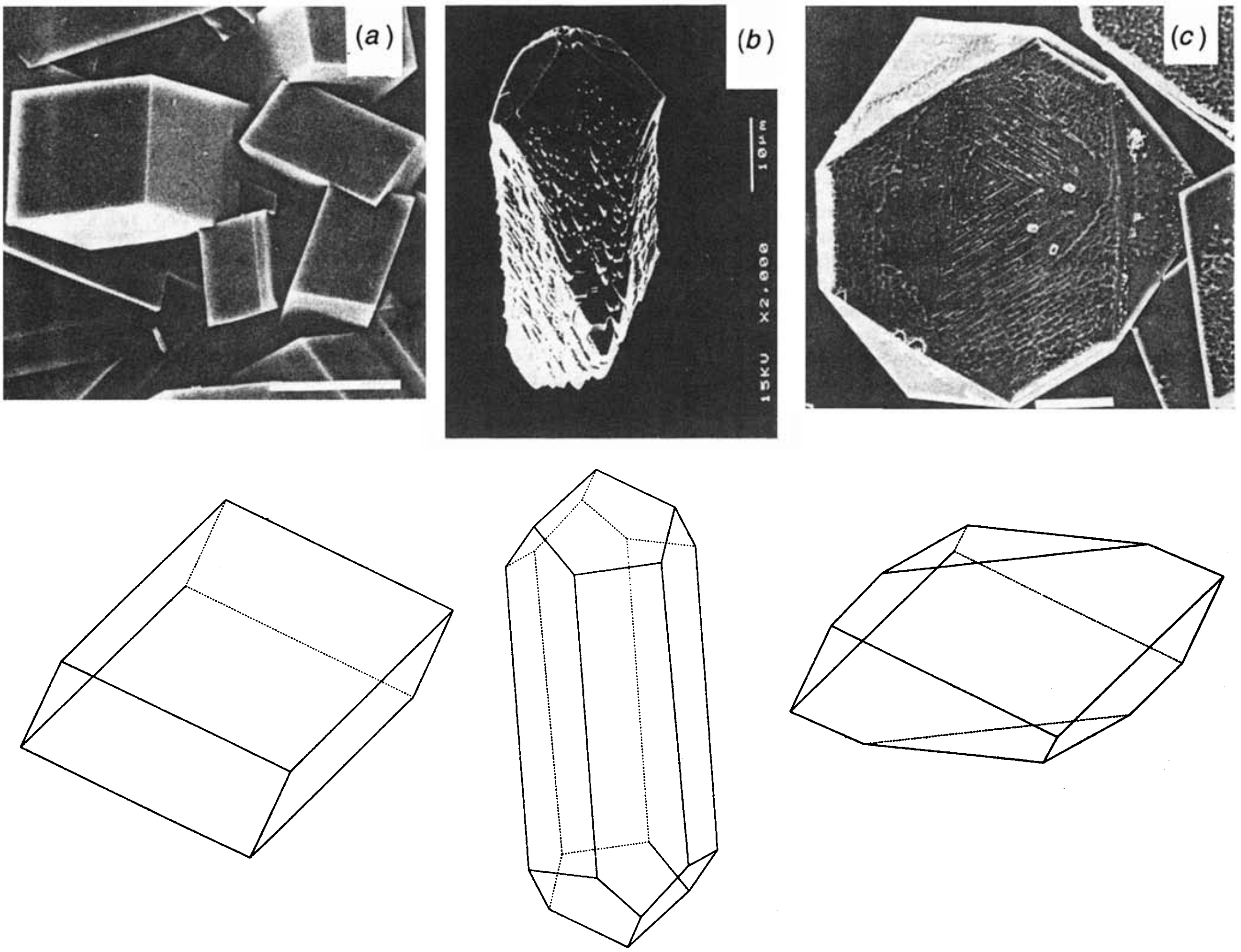

Fig. 1 Observed (top) and calculated (bottom) calcite morphology showing (*a*) {104} rhombohedral faces, (*b*) {100} faces stabilized with Mg^{2+} and (*c*) (001) faces stabilized with Li^+

evaluates the bulk defect energies and MIDAS[10] which models the surface energies and structures. Crystal faces of relatively low surface energy are stabilized with respect to growth. This is consequently expressed in the crystal habit according to Wulff's theorem[11] and hence calculations of surface energies lead directly to predictions of morphology.[4,12,13]

The surface energies of calcite were calculated for both pure and defective surfaces at 0 K. After relaxation, energies for the pure surfaces were in the order of stability: {104} > {100} > {110} > (001), where the {104} face was the most stable and showed no surface reconstruction on relaxation. In the absence of additives, therefore, the {104} surface was predicted to dominate the calcite morphology [Fig. 1(*a*)]. The resulting rhombohedral habit is consistent with experimental observations of calcite crystallization.

Table 1 Heats of segregation of Mg^{2+} ions to the calcite surface[a] from either bulk or solution

	100% coverage w.r.t.	
Surface	Bulk	Solution
{104}	163.6	−370.1
{100}	127.7	−405.9
{110}	151.8	−381.8
(001)	Failed to converge	

[a] Energies in kJ mol^{-1}, negative numbers indicate surface sites are energetically preferred.

Simulation of the effect of Mg^{2+} and Li^+ on the equilibrium morphology was achieved by replacing surface Ca^{2+} ions with Mg^{2+} and calculating the effect on the surface energy. The heats of segregation of Mg^{2+} at 100% coverage of different surfaces [except (001)] ranged from +127.7 to +163.6 kJ mol^{-1} (Table 1) indicating preferential dissolution of Mg^{2+} into the bulk calcite crystal lattice. Thus at thermodynamic equilibrium we would predict Ca–Mg solid solution behaviour with the surface consisting mainly of Ca^{2+} ions. This is inconsistent with the morphological effects observed experimentally which indicate a kinetic stabilization of {100} calcite faces in the presence of Mg^{2+} at room temperature. In this regard, we calculated, using the free energy perturbation method,[14] the heats of segregation of Mg^{2+} from solution as an indication of the strength of interaction of Mg^{2+}(aq) with various calcite surfaces. The calculations clearly showed a marked energetic preference particularly on the {100} face for Mg^{2+} adsorption. Thus it is reasonable to assume that under solution conditions, kinetic effects of surface-incorporated Mg^{2+} can readily give rise to morphological changes in calcite (Table 1). The simulations predicted that the addition of Mg^{2+} to the calcite surface preferentially lowered the defect surface energy of the first-order prismatic faces {100} with respect to dissolution of Mg^{2+} ions in the bulk lattice. The effect was such that the {100} faces became more stable than the {104} surfaces and the crystal morphology modified to a first-order prism capped with rhombohedral end faces [Fig. 1(*b*)]. This morphology is observed in experimental systems containing Mg^{2+} and it is surprising that our equilibrium calculations do in fact predict this type of solution behaviour. One possibility is that the energy calculation of a defective surface containing spatially constrained Mg^{2+} ions is analogous to a quasi-kinetic description of the crystallization process at the solution crystal interface. If this is correct (many further systems require testing), then atomistic simulation methods may be of relevance to a wide range of surface-controlled interactions involving solution additives and ionic crystals.

On substitution of Ca^{2+} ions with Li^+, the calculated defect surface energies showed that the polar (001) face became the most stable while all the other neutral faces were destabilized. The segregation energy of Li^+ ions on the (001) face was -776.1 kJ mol^{-1} with respect to the bulk and -407.9 kJ mol^{-1} in solution indicating the preference of lithium ions to remain at the calcite surface. The predicted morphology was tabular comprising basal (001) and {104} side faces [Fig. 1(*c*)]. This is in complete agreement with recent experimental studies of calcite crystallization in the presence of Li ions.[6] The simulations predicted that the surface Li^+ ions were accommodated in lattice and not interstitial sites at the crystal surface. Preliminary calculations suggested that sodium ions also stabilize the (001) face but to a lesser extent.

The prediction of calcite morphological modifications is a crucial step towards understanding the problems of controlled formation of this material in inorganic and biological systems. We are currently studying the effect of peptides on different faces of calcite. The accuracy of these results depends ultimately on the type of interatomic potentials used in the simulation. Studies on the derivation of $CaCO_3$ interatomic potentials are currently in progress.

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References

1 Z. Berkovitch-Yellin, *J. Am. Chem. Soc.*, 1985, **107**, 8239.
2 R. Docherty, K. J. Roberts, *J. Crystal Growth*, 1988, **88**, 159.
3 W. C. Mackrodt, *J. Chem. Soc., Faraday Trans. 2*, 1989, **85**, 541.
4 M. J. Davies, P. R. Kenway, P. J. Lawrence, S. C. Parker, W. C. Mackrodt and P. W. Tasker, *J. Chem. Soc., Faraday Trans. 2*, 1989, **85**, 555.
5 H. Leitmeier, *Neues Jahrb. Mineral. Abh.*, 1910, **1**, 49.
6 S. Rajam and S. Mann, *J. Chem. Soc., Chem. Commun.*, 1990, 1789.
7 R. A. Jackson and G. D. Price, in the press.
8 E. A. Colbourn, W. C. Mackrodt and P. W. Tasker, *J. Mater. Sci.*, 1983, **18**, 1917.
9 M. L. Leslie, Progam CASCADE: description of data set for use in crystal defect calculations, Daresbury Laboratory Technical Memorandum DL/SCI/TM31T, 1982.
10 P. W. Tasker, A guide to MIDAS: a program for studying defects and surfaces in ionic crystals, Harwell Report AERE-R9130, 1978.
11 G. Wulff, *Z. Kristallogr. Kristallgeom.*, 1901, **34**, 949.
12 P. J. Lawrence and S. C. Parker, in *Computer Modelling of Fluids, Polymers and Solids*, ed. C. R. A. Catlow, S. C. Parker and M. P. Allen, 1990, p. 219.
13 W. C. Mackrodt, R. J. Davey, S. N. Black and R. Docherty, *J. Crystal Growth*, 1987, **80**, 441.
14 DISCOVER, version 2.6.0 (August 1990), BIOSYM Technologies Inc.