Communication

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Computer Modelling of the Dolomite Structure Using a Mean Field Approach

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Abstract

The dolomite structure is modelled using interatomic potentials and the mean field approach, starting with the calcite structure. Good agreement between the calculated and experimental structure is observed, showing that this is a suitable method for predicting structural changes resulting from doping.

Keywords: dolomite; computer modelling; interatomic potentials; mean-field approach

1. Introduction & Background

Dolomite is the mineral name for calcium magnesium carbonate, chemical formula $CaMg(CO_3)_2$, with the Ca and Mg ions on alternate sites in an ordered structure.

The 'dolomite problem' refers to the fact that for 200 years, scientists were unable to grow dolomite in the laboratory under the conditions believed to have formed it naturally. It occurs abundantly in geological deposits, and structures have been determined and published [1]. Computer modelling, using a mean field approach with the calcite structure as a starting point has been used to model the structure, motivated by a recent experimental paper which succeeded in synthesising dolomite [2]. These authors used a synthesis process involving removal of defects as the crystal grows, using ideas developed from atomistic simulations.

In this study we have modelled dolomite in two ways – (i) using a mean field approach with the calcite structure as a starting point and substituting Mg at the Ca site up to a 50:50 distribution, and (ii) using the experimental structure as a starting point [1].

2. Methodology

Calculations were performed using the GULP code [3], which uses interatomic potentials and lattice energy minimisation to model structures and properties. Full details are given in the subsections below.

2.1. Interatomic Potentials

The computer modelling work presented here was performed using interatomic potentials. The Buckingham potential has been employed, augmented with a term to represent the electrostatic interactions between ions, and it has the following form:

$$V(r) = A \exp(-r/\rho) - Cr^{-6} + q_1 q_2 / r$$

In the equation, A, ρ and C are parameters to be obtained by empirical fitting, and q_1, q_2 are charges on the interacting ions with 'r' being the interionic distance. The carbonate group is treated as a molecular ion, and three-body terms describe bond-bending about each O-C-O bond, and four-body torsional terms retain the planarity of the CO_3^{2-} group. The potential parameters used are given in section 3.1, and were taken from [4].

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2.2. Lattice Energy Minimisation

Lattice energy minimisation can be used to calculate structures corresponding to a minimum in the lattice energy.

The total lattice energy E_{latt} is written as a sum of interactions between ions (described by interatomic potentials):

$$E_{latt} = \sum V(r)$$

Then, by adjusting the structure (either the lattice parameters or atomic positions or both), the minimum energy structure is obtained. Note that a well derived potential would be expected to reproduce the structure without significant structural adjustment.

2.3. Mean Field Calculations

The dolomite structure has alternating Ca and Mg ions, and it has been modelled by the mean field method, in which the cation site is represented by an average of Ca and Mg in varying ratios (50:50 for dolomite). The advantage of this approach is that the calcite structure can be used as a starting structure, and any Ca-Mg structure of interest modelled. The disadvantage is that an averaged structure is being modelled, so specific Ca-Mg configurations are not considered by this method.

3. Results & Discussion

3.1. Mean Field Calculations

Starting with the calcite structure [1], Mg ions are successively substituted at the Ca site, and the structure was energy minimised at each point. This enables the structure corresponding to any concentration of dopant to be predicted, with dolomite corresponding to a 50% concentration. Potentials derived by Jackson and Price [5] were used, given in Table 1. Table 2 gives the calculated structures as a function of dopant concentration.

Table 1. Interatomic potentials (from reference [4]).

Interaction	A(eV)	ρ(Å)	C(eV Å^6)
Ca-O	8839.3	0.23813	0.0
C-O	3088.4	0.12635	0.0
O-O	36010.8	0.19756	0.0

Charges (|e|): q(Ca) = 2.0, q(C) = 0 99805, q(O) = 0 99935
Bond bending constant k_3 = 9.3 179 eV rad^{-2}
Torsional constant k_4 = I.1392 eV

Table 2. Mean field calculations on calcite-dolomite.

% of Mg ions in $CaCO_3$	a=b / Å	c / Å
0	4.99	17.061
10	4.91	17.474
20	4.907	17.443
30	4.903	17.411
40	4.900	17.377
50	**4.896**	**17.341**
60	4.892	17.303
70	4.888	17.262
80	4.883	17.219
90	4.877	17.173

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100	4.872	17.122

From Table 2, the predicted dolomite structure corresponds to 50% Mg concentration, and is compared with the experimental structure in Table 3.

Table 3. Comparison of mean field calculation with experimental structures.

	a=b / Å	**c / Å**
Calculated (table 2)	4.896	17.341
Effenberger et al [1]	4.817	16.686
Althoff [5]	4.803	15,984

From Table 3 it is seen that the 'a' and 'b' parameters agree with the Effenberger results to within 2.0%, and the 'c' parameter to within 4.0%. Considering that the starting structure was that of pure calcite, this is an encouraging result.

3.2. Lattice Energy Minimisation Calculations on the Experimental Structure

Finally, a lattice energy minimisation calculation was performed using the Althoff structure as a starting point. Results are given in Table 4, where it can be seen that similar agreement is obtained as with the mean field generated structure.

Table 4. Comparison of lattice energy minimisation calculations with the experimental structure from Althoff [5].

	a=b / Å	**c / Å**
Calculated	4.817	16.686
Althoff [5]	4.803	15,984

Conclusions

The aim of this paper was to show that mean field calculations can be used to predict structures of complex materials if the structure of a related material is known. In this case the calcite structure was used, $CaCO_3$, to predict the structure of $CaMg(CO3)_2$.

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