

A shell model for the simulation of rhombohedral carbonate minerals and their point defects

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ABSTRACT

The electronic polarization of oxygen ions has been explicitly incorporated in a shell model to better simulate the structure of calcite and related rhombohedral carbonate minerals. Pair-potentials for Ca^{2+} ions and C and O comprising the carbonate molecular ion were simultaneously fitted to experimental lattice, elastic, dielectric, and vibrational data for calcite, and the structure and elastic properties of aragonite. The resulting potential parameters for the CO_3^{2-} group were then transferred to models for the structures and bulk moduli of the carbonate minerals incorporating Mn, Fe, Mg, Ni, Zn, Co, Cd, and thus a fully consistent set of interaction parameters for calculating the properties of the carbonate minerals was obtained. Defect energies for doping the divalent cations into the calcite structure, and for calcium and carbonate ion vacancies were calculated. In addition, various disorder types for dolomite, including anti-site defects, stacking defects, and the energy related to increasing the Ca/Mg ratio in the dolomite structure were simulated. The theoretical enthalpy for dolomite ordering (34.4 kJ/mol) compares very well with experimental measurements.