LETTER

Cation disorder in dolomite, $CaMg(CO_3)_2$, and its influence on the aragonite + magnesite ↔ dolomite reaction boundary

SYTLE M. ANTAO,[1,*] WILLEM H. MULDER,[2] ISHMAEL HASSAN,[2] WILSON A. CRICHTON,[3] AND JOHN B. PARISE[1]

[1]Mineral Physics Institute & Department of Geosciences, State University of New York, Stony Brook, New York 11794-2100, U.S.A.
[2]Department of Chemistry, University of the West Indies, Mona, Kingston 7, Jamaica

ABSTRACT

The structure of dolomite, $CaMg(CO_3)_2$, was determined from 298 to 1466 K at a constant pressure of about 3 GPa using in situ synchrotron X-ray diffraction data to investigate the state of disorder. An order parameter s, defined as $2 x_{Ca} - 1$, varies from $s = 1$ (where $x_{Ca} = 1$) for a completely ordered dolomite to $s = 0$ (where $x_{Ca} = 0.5$) for a completely disordered dolomite. On heating, there is no measured change in s until the temperature is high enough to cause exchange of Ca^{2+} and Mg^{2+} cations. Significant disorder began to occur at about 1234 K [$s = 0.83(1)$] and increases along a smooth pathway to $T = 1466$ K [$s = 0.12(5)$]. The $R\overline{3} \leftrightarrow R\overline{3}c$ transition in dolomite is described by a modified Bragg-Williams thermodynamic model with the following molar free energy of disorder, $\overline{G}_d(T; s) = RT_c[1 - s^2 + \frac{1}{2} a(s^4 - 1) - (T/T_c) \{2 \ln 2 - (1+s) \ln(1 + s) - (1 - s) \ln(1 - s)\}]$. Using $T_c = 1466$ K and $a = -0.29$, this model provides an excellent agreement with experimental data. Moreover, the maximum enthalpy of disorder, $\overline{H}_d(s = 0) = RT_c(1 - \frac{1}{2} a) \sim 14$ kJ/mol, agrees with published calorimetric data. A thermodynamic description of the aragonite + magnesite ↔ dolomite reaction boundary is also presented and it reproduces the main qualitative features correctly.