Thermodynamics of cation ordering in karrooite (MgTi_2O_5)

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ABSTRACT

A thermodynamic model of non-convergent cation-ordering in karrooite (MgTi_2O_5) has been calibrated from the single-crystal X-ray structure refinements of Yang and Hazen (1998) and from estimates of the dependence of the bulk modulus on ordering state (Hazen and Yang 1997). Derived values of the Gibbs free energy, enthalpy, entropy, and heat capacity of disordering of karrooite are reported as a function of temperature at 1 bar and at elevated pressures.

INTRODUCTION

In this paper we develop a thermodynamic model that describes cation ordering as a function of temperature and pressure in the karrooite (MgTi_2O_5) end-member of the armacolite solid-solution series. The model is constructed utilizing techniques first developed by Thompson (1969, 1970) to describe cation order-disorder phenomena in minerals in terms of the principle of homogeneous equilibrium. The present study was prompted by the recent completion (Yang and Hazen 1998) of high quality, one-atmosphere X-ray structure refinements of single crystals of synthetic karrooite, which were equilibrated prior to analysis at temperatures over the range 600–1400 °C. The results of the study of Yang and Hazen (1998) are at odds with previous estimates of the equilibrium ordering state of karrooite (especially at elevated temperatures) and, consequently, existing formulations of the thermodynamics of cation ordering in this phase (Brown and Navrotsky 1989) require reevaluation in light of the recent results. We take this opportunity to develop a thermodynamic model that accounts for the recent measurements, and incorporate into the formulation a pressure dependence of this cation-ordering phenomena by accounting for the effect of ordering on the compressibility estimates of Hazen and Yang (1997).

THERMODYNAMIC ANALYSIS

A description of the karrooite structure and its relationship to other pseudobrookite-type oxide solid solutions is summarized by Waychunas (1991). For the present purpose, it is sufficient to understand that the Mg^{2+} and Ti^{4+} cations are distributed over two types of octahedral sites, M1 and M2, which are present in the ratio 1:2, respectively. The cation ordering, which is consequently of non-convergent type, therefore can be quantified by inventorying the proportion of Mg^{2+} or Ti^{4+} occupying either site. We may define an ordering parameter, s, to accomplish this task:

\[ s = X_{Mg}^{M1} - 2X_{Mg}^{M2} \]  

where \( X_{Mg}^{M1} \) denotes the mole fraction of Mg^{2+} on the M1 octahedral site and \( X_{Mg}^{M2} \) denotes the mole fraction of Mg^{2+} on the M2 octahedral site. The experimental evidence demonstrates that s is a function of both temperature and pressure. Note that the order parameter defined in Equation 1 is different from that adopted by Brown and Navrotsky (1989) or by Yang and Hazen (1998). Our choice is motivated by a desire to simplify the thermodynamic treatment by generating an order parameter that assumes values over the range 1 to –1 in proceeding from the fully ordered ( \( X_{Mg}^{M1} = 1, X_{Mg}^{M2} = 0 \); \( s = 1 \) ) to the fully antiondered ( \( X_{Mg}^{M1} = 0, X_{Mg}^{M2} = 1/2 \); \( s = -1 \) ) state. The algebraic simplification with this definition is considerable. It should also be noted that a random cation configuration is given by \( X_{Mg}^{M1} = X_{Mg}^{M2} = 1/3; s = -1/3 \). From Equation 1 it follows that:

\[ X_{Mg}^{M1} = \frac{1 + s}{2} \]  
\[ X_{Mg}^{M2} = \frac{1 - s}{4} \]  
\[ X_{Ti}^{M1} = \frac{1 - s}{2} \]  
\[ X_{Ti}^{M2} = \frac{3 + s}{4} \]  

The configurational entropy (\( \Delta S_{conf} \)) associated with the degree of cation order is:

\[ \Delta S_{conf} = -R \left( X_{Mg}^{M1} \ln X_{Mg}^{M1} + X_{Mg}^{M2} \ln X_{Mg}^{M2} + 2X_{Mg}^{M1} \ln X_{Ti}^{M1} + 2X_{Mg}^{M2} \ln X_{Ti}^{M2} \right) \]  

which, via Equations 2a–d may be written as a function solely of the order parameter, s:

\[ \Delta S_{conf} = -R \left( \frac{1 + s}{2} \ln \frac{1 + s}{2} + \frac{1 - s}{2} \ln \frac{1 - s}{2} + \frac{1 - s}{4} \ln \frac{1 - s}{4} + \frac{3 + s}{4} \ln \frac{3 + s}{4} \right) \]  

We construct a thermodynamic model for karrooite ordering by writing an expression for the molar Gibbs free energy (\( G \)) of the phase in terms of configurational (\( -T \Delta S_{conf} \)) and lattice vibrational (\( G^\nu \)) contributions: