

Thermodynamics and stability of pseudobrookite-type MgTi_2O_5 (karrooite)

DIMITRIOS XIROUCHAKIS,^{1,2,*} ALEXANDER SMIRNOV,³ KELLY WOODY,³ DONALD H. LINDSLEY,³ AND DAVID J. ANDERSEN⁴

¹Office of Astromaterials Research and Exploration Science, NASA JSC, Mail Code SA13, Houston, Texas 77058, U.S.A.

²Department of Chemistry, Texas Southern University, 3100 Cleburne Avenue, Houston, Texas 77004, U.S.A.

³Department of Geosciences and Center for High Pressure Research, State University of New York at Stony Brook, Stony Brook, New York 11794-2100, U.S.A.

⁴MDProductivity, 12710 Research Blvd., Ste. 205, Austin, Texas 78759, U.S.A.

ABSTRACT

Pseudobrookite-type MgTi_2O_5 (karrooite) is a synthetic crystalline phase with the *Bbmm* structure and a component in orthorhombic oxide solid solutions, $\text{R}^{2+}\text{Ti}_2\text{O}_5\text{-R}_2^{3+}\text{TiO}_5$, which are present as accessory minerals in lunar and terrestrial rocks. In this study, we present a model for the molar Gibbs free energy of MgTi_2O_5 as a function of T , P , and the order parameter $s = X_{\text{Mg}}^{\text{M}_1} - 2X_{\text{Mg}}^{\text{M}_2}$, ($-1 \leq s \leq 1$). We describe the molar Gibbs free energy, (\bar{G}), with the equation: $\bar{G} = \bar{g}_0 + \bar{g}_1 \cdot (1 - s) + 3/2 \bar{g}_2 \cdot (1 - s^2) - T \cdot \bar{S}_{\text{config}}$, and take parameter g_0 to represent the molar Gibbs free energy of ordered MgTi_2O_5 ($s = 1$), whereas parameters g_1 and g_2 may represent cation-disorder contributions. We used powder and single-crystal X-ray diffraction, and high-temperature relative enthalpy data, to calibrate the disorder contribution to the volume ($b_0 = 7.3822 \cdot 10^{-3}$ J/bar), and the model parameters g_1 (7370.8 J/mol) and g_2 (3576.1 J/mol), and heat capacity and volume equation coefficients. We also optimized standard state thermodynamic data from the elements for ordered MgTi_2O_5 , ($\Delta H^0 = -2498.51528$ J/mol, $S^0 = 149.55$ J/(mol·K), $\Delta G^0 = -2362.18172$ J/mol, $V^0 = 5.445$ J/bar) consistent with the model parameters and equations, the thermodynamic data in QUILF, and phase-equilibrium experiments involving MgTi_2O_5 , geikelite, rutile, orthoenstatite, and forsterite in the range 973 to 1673 K and 0.0001 to 2.0 GPa. Finally, we investigate theoretically the stability of MgTi_2O_5 (karrooite) with respect to geikelite, rutile, diopside, enstatite, and forsterite in the $\text{CaO-MgO-TiO}_2\text{-SiO}_2$ system. We find that diopside- and titanite-bearing reactions require extremely high temperatures, and are thus not stable with respect to liquid. The inferred phase relations can be of help in understanding the stability of MgTi_2O_5 with respect to rutile, geikelite, forsterite, and orthoenstatite, and by extrapolation that of armalcolite relative to rutile, ilmenite, olivine, and orthopyroxene in terrestrial mantle rocks and high-Ti lunar basalts.