

The free energy of formation of Mg_2TiO_4 (synthetic qandilite), an inverse spinel with configurational entropy

HUGH ST. C. O'NEILL* and DEAN R. SCOTT

Research School of Earth Sciences, Australian National University, Canberra, ACT 0200, Australia

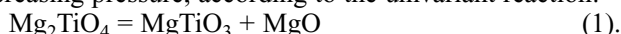
Abstract: Synthetic qandilite (Mg_2TiO_4) is an inverse spinel in which random mixing of Mg and Ti on the octahedral site should give rise to a configurational entropy of $11.5 \text{ J K}^{-1} \text{ mol}^{-1}$. The free energy of formation of Mg_2TiO_4 has been determined from the location of the univariant reaction $\text{MgTiO}_3 + \text{MgO} = \text{Mg}_2\text{TiO}_4$ in pressure-temperature space between 0 and 20 kbar; together with literature data for MgTiO_3 and MgO , the results give $S_{(298\text{K})}^\circ = 111.2 \pm 0.6 \text{ J K}^{-1} \text{ mol}^{-1}$ for Mg_2TiO_4 . This entropy is only $7.6 \pm 0.9 \text{ J K}^{-1} \text{ mol}^{-1}$ more than the calorimetrically determined value of $103.6 \pm 0.7 \text{ J K}^{-1} \text{ mol}^{-1}$. The discrepancy implies either considerable short-range order of Mg and Ti in Mg_2TiO_4 , or perhaps an error in the high-temperature heat-capacity data for MgTiO_3 caused by disordering in this substance.

Key-words: spinel, thermodynamic data, order-disorder, phase equilibria.

Introduction

A recent experimental investigation of the significance of Ti substitution into forsterite (Mg_2SiO_4) in the system $\text{MgO-SiO}_2\text{-TiO}_2$ (Hermann *et al.*, in press) has raised the need for accurate thermodynamic data for Mg_2TiO_4 spinel (the mineral qandilite). At present there exist some calorimetric data for this substance (reviewed by Eriksson & Pelton, 1993), but these data are insufficient to give the free energy of formation, as Mg_2TiO_4 is an inverse spinel which is expected to have configurational entropy from mixing of Mg and Ti on the octahedral sites of the spinel structure (O'Neill *et al.*, 2003b). Full development of this configurational entropy would contribute 11.5 J/K.mol in Mg_2TiO_4 , but this may be reduced if there is short-range ordering. Since Mg_2TiO_4 with the usual cubic spinel structure ($Fd\bar{3}m$) is known to undergo a phase transition on cooling at $\sim 1000^\circ\text{C}$ to a tetragonal modification ($P4_122$), in which Mg and Ti are ordered onto distinct octahedral sites (Wechsler & Navrotsky, 1984; Millard *et al.*, 1995), some short-range ordering is a possibility.

Akimoto & Syono (1967) found that Mg_2TiO_4 breaks down to MgTiO_3 (geikielite) plus MgO (periclase) with increasing pressure, according to the univariant reaction:



Since this reaction occurs in an experimentally easily accessible region of P-T space, and since there are complete calorimetric data for MgTiO_3 and MgO (which are both nearly pure, stoichiometric phases in the system MgO-TiO_2), this reaction provides an excellent means of

determining the free energy of formation of Mg_2TiO_4 , which moreover can be done over an adequate temperature span to test whether the full configurational entropy of Mg-Ti mixing is developed. However, the study of Akimoto & Syono (1967) is really only reconnaissance work, in that their results do not bracket the reaction particularly snugly (see Fig. 1). Hence the purpose of this study is to reinvestigate reaction (1), applying modern piston-cylinder methods to obtain reversals that bracket the reaction with better precision than that achieved by Akimoto & Syono (1967), and probably also with better accuracy as regards temperature and pressure measurement.

Experimental

Starting materials consisted of synthetic Mg_2TiO_4 (material from the study of O'Neill *et al.*, 2003b) and MgTiO_3 , synthesised, similarly to Mg_2TiO_4 , from a stoichiometric mixture of MgO and TiO_2 , ground under acetone in an agate mortar, pressed into pellets, and reacted at 1400°C in air in a box furnace. MgO was from BDH (Analar grade), fired at 1200°C in air before use. A starting mixture consisting of all three phases in the molar ratio of 1 Mg_2TiO_4 to 1 MgTiO_3 to 2 MgO (*i.e.* MgO in excess of that required by the stoichiometry of reaction 1) was then prepared.

Experiments at atmospheric pressure were made in a vertical tube furnace in air with a type B thermocouple positioned directly above the sample, ensuring that the

*E-mail: hugh.oneill@anu.edu.au