Calorimetric study of the surface energy of forsterite

SHUSHU CHEN AND ALEXANDRA NAVROTSKY*

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Abstract

Surface energies are an important factor in determining surface reactivity, sintering, and transformation, yet, until recently, there have been few direct measurements for rock-forming mineral phases. Using calorimetric methodology we developed and first applied to aluminum and iron oxides, we present here the first direct measurement of the surface enthalpy of forsterite, Mg$_2$SiO$_4$, based on high-temperature oxide melt solution calorimetry and water adsorption calorimetry. The measured surface enthalpies of hydrated and anhydrous Mg$_2$SiO$_4$ particles are 3.37 ± 0.21 and 4.41 ± 0.21 J/m$^2$, respectively. The measured water adsorption enthalpies for approximately first and second monolayer coverage are ~102 and ~79 kJ per mole of H$_2$O (liquid water reference state). Both the surface enthalpy and water adsorption enthalpy values agree well with values from atomistic simulations. The relatively high surface enthalpy of forsterite is greater than that of γ-alumina, maghemite (γ-Fe$_2$O$_3$), and MgAl$_2$O$_4$ spinel. This suggests that the surface energy of ringwoodite may be lower than that of forsterite, and that surface energy effects may thermodynamically favor the olivine-spinel transition, bringing it to lower pressures for small grains.

Keywords: Forsterite, calorimetry, surface energy, thermodynamics

Introduction

Olivine is a common rock-forming mineral and is considered to comprise a large fraction of the Earth’s upper mantle. Forsterite, Mg$_2$SiO$_4$, is the Mg end-member of the complete olivine solid-solution system Mg$_2$SiO$_4$–Fe$_2$SiO$_4$. At elevated pressure and temperature, two other polymorphs of exist: wadsleyite, which was previously called modified spinel, and ringwoodite with a spinel structure (Moore and Smith 1970). Besides its geological importance, the extremely low electrical conductivity, high melting point, and low thermal expansion of forsterite make it a useful ceramic and refractory. In both ceramic processing and in the Earth, surfaces of and interfaces between grains are the locus of most chemical reactivity. Reduction of surface area is the driving force for sintering, grain growth, and densification. Thus, the surface energy is an important parameter for understanding such processes, and differences in surface energy among different polymorphs can affect phase stability, especially of nanoscale particles (McHale et al. 1997; Navrotsky et al. 2008). Although extensive computational research has been performed to investigate the structure and stability of forsterite surfaces as well as the effect of water on the surfaces (Deju and Bhappu 1966; de Leeuw et al. 2000; Stimpfl et al. 2006), no experimental study of forsterite surface energetics is available. By using oxide melt solution calorimetry, Shearer and Kleppa (1973) and Akaogi et al. (1984, 1989) have studied the enthalpies of formation and phase transition in micrometer-sized forsterite. In the present study, the surface energy of forsterite was measured using a similar high-temperature oxide melt calorimetric method, and water adsorption enthalpy was measured using recently developed methodology (Ushakov and Navrotsky 2005). Enthalpies of anhydrous (dry) and hydrated (wet) surfaces of forsterite were obtained. The values are compared to computational results and implications for the olivine-spinel transition are discussed.

Experimental Methods

Synthesis of nanocrystalline Mg$_2$SiO$_4$

Nanocrystalline Mg$_2$SiO$_4$ powder was synthesized using an aqueous solution of magnesium nitrate, colloidal silica, and sucrose (Saberi et al. 2007). Magnesium nitrate (0.0142 mol) [Mg(NO$_3$)$_2$·6H$_2$O, Alfa Aesar, Ward Hill, Massachusetts], 0.0568 mol of sucrose (Aldrich, St. Louis, Missouri), and 0.0071 mol polyvinyl alcohol (Alfa Aesar, Ward Hill, Massachusetts) were dissolved in deionized water separately and then mixed with 0.0071 mol of colloidal silica (40 wt%, Aldrich, St. Louis, Missouri) to form an aqueous solution. The solution was stirred in an oil bath at 80 °C until it became clear. It was then heated on a hot plate at about 150 °C while stirring until it became a black-brown low-density foam (precursor). This mass was then ground into a powder and subjected to calcination at different temperatures to produce forsterite crystals of different sizes. To achieve a pure forsterite phase, a minimum calcination temperature of 850 °C was required. Calcination at a temperature below 850 °C produced a mixture of MgO, amorphous silica, and Mg$_2$SiO$_4$. Micrometer-grained Mg$_2$SiO$_4$ powder was achieved by calcining the precursor at 1200 °C for 24 h. Nanocrystalline Mg$_2$SiO$_4$ powder was exposed to air in the calorimetry laboratory, which has a controlled environment (23 ± 1 °C and 55 ± 2% relative humidity) for 6 days to achieve equilibrium in hygroscopic nanopowders.

Characterization

Powder X-ray diffraction (XRD) patterns were collected using a Bruker AXS D8 advance diffractometer (CuKα radiation) operated at 40 kV and 40 mA with a 0.02° step size. Microstructural characterization was made on nanograined powder using a Philips CM12 transmission electron microscope operated at 120 kV. The magnification calibration was performed with Ted Pella, Inc. 603 replica and the estimated uncertainty in size measurements is 10–15%.

The water content of the “hydrated” nanopowders was determined by thermogravimetric analysis (TGA), surface area measurement, and drop solution calorimetry. The goal of this equilibration was to provide a well-defined water content for these hygroscopic nanopowders.

* E-mail: anavrotsky@ucdavis.edu