The thermal equation of state of FeTiO₃, ilmenite based on in situ X-ray diffraction at high pressures and temperatures


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ABSTRACT

We present in situ measurements of the unit-cell volume of a natural terrestrial ilmenite (Jagersfontein mine, South Africa) and a synthetic reduced ilmenite (FeTiO₃) at simultaneous high pressure and high temperature up to 16 GPa and 1273 K. Unit-cell volumes were determined using energy-dispersive synchrotron X-ray diffraction in a multi-anvil press. Mössbauer analyses show that the synthetic sample contained insignificant amounts of Fe³⁺ both before and after the experiment. Results were fit to Birch-Murnaghan equations of state, which reproduce the experimental data to within 0.5 and 0.7 GPa for the synthetic and natural samples, respectively. At ambient conditions, the unit-cell volume of the natural sample \[ V_0 = 314.75 \pm 0.23 \text{ (1σ A}^3 \text{)} \] is significantly smaller than that of the synthetic sample \[ V_0 = 319.12 \pm 0.26 \text{ A}^3 \text{]. The difference can be attributed to the presence of impurities and Fe³⁺ in the natural sample. The 1 bar isothermal bulk moduli \[ K_{0 B} \] for the reduced ilmenite is slightly larger than for the natural ilmenite (181 ± 7 and 165 ± 6 GPa, respectively), with pressure derivatives \[ K^\prime_0 = 3 \pm 1 \text{. Our results, combined with literature data, suggest that the unit-cell volume of reduced ilmenite is significantly larger than that of oxidized ilmenite, whereas their thermoelastic parameters are similar. Our data provide more appropriate input parameters for thermo-chemical models of lunar interior evolution, in which reduced ilmenite plays a critical role.}

Keywords: Ilmenite, equation of state, X-ray diffraction, lunar magma ocean

INTRODUCTION

Ilmenite (nominal composition FeTiO₃) plays a pivotal role in current models of the thermal and magmatic evolution of the Moon (e.g., Shearer et al. 2006; Klemme et al. 2006), although it is only found as an accessory phase in terrestrial crustal and upper mantle rocks. Its crystallization during the later stages of the solidification of a global lunar magma ocean resulted in a gravitationally unstable mineral stratification in the lunar mantle (e.g., Taylor 1982; Snyder et al. 1992), prompting a large-scale mantle overturn (e.g., Hess and Parmentier 1995; de Vries et al. 2010). The thermal effects associated with this overturn are believed to have triggered the formation and eruption of the lunar mare basalts that cover a significant part of the lunar near-side surface (e.g., Lucey et al. 2006).

Thermo-chemical models of the internal evolution of the Moon thus require accurate knowledge of the density of ilmenite as a function of pressure (\( P \)), temperature (\( T \)), and chemical composition. Due to its limited importance for the dynamics of the interior of the Earth, the thermal equation of state of FeTiO₃ ilmenite has not been studied extensively. As a result, the temperature dependence of the bulk modulus, and pressure dependence of thermal expansivity are poorly constrained. In addition, the reducing conditions on the Moon lead to the absence of Fe³⁺ in lunar ilmenite, whereas in terrestrial ilmenite 15–30% of iron is trivalent (e.g., Virgo et al. 1988). The effects of oxidation state on ilmenite’s density evolution are not known.

In this paper, we compare the \( P-T \) variation of the unit-cell volume of a synthetic Fe³⁺-free ilmenite with that of a natural terrestrial ilmenite at simultaneous high \( P-T \), to determine the thermal equation of state of ilmenite and its dependence on the valence state of iron.

PREVIOUS WORK

Ilmenite (FeTiO₃) is an iron-titanium oxide crystallizing in the trigonal system (space group \( R3 \)). Its structure was first studied by Barth and Posnjak (1934) and was found to be equivalent to the corundum structure. Detailed crystal-structural data at ambient pressure-temperature conditions have since been reported for natural terrestrial ilmenite (Raymond and Wenk 1971; Bayer et al. 1972; Liu 1975; Thorpe et al. 1977; Ming et al. 2006), synthetic ilmenite (Shirane et al. 1962; Syono et al. 1981; Wechsler and Prewitt 1984), and lunar ilmenite (Raymond and Wenk 1971;