Fe\textsuperscript{3+} spin transition in CaFe\textsubscript{2}O\textsubscript{4} at high pressure

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ABSTRACT

Single-crystal diffraction data collected for CaFe\textsubscript{2}O\textsubscript{4} at high pressure reveal above 50 GPa an isosymmetric phase transition (i.e., no change in symmetry) marked by a volume decrease of 8.4%. X-ray emission spectroscopic data at ambient and high pressure confirm that the nature of the phase transition is related to the Fe\textsuperscript{3+} high-spin/low-spin transition. The bulk modulus \( K_0 \) calculated with a Birch Murnaghan EoS (\( K' = 4 \)) is remarkably different \( K_0 = 159(2) \) GPa for CaFe\textsubscript{2}O\textsubscript{4} “high spin” and \( K_0 = 235(10) \) GPa for CaFe\textsubscript{2}O\textsubscript{4} “low spin”). Crystal structure refinements reveal a decrease of 12% of the Fe\textsuperscript{3+} crystallographic site volume. The geometrical features of the low-spin Fe\textsuperscript{3+} crystallographic site at high pressure (bond lengths, volume) indicate a relevant decrease of Fe\textsuperscript{3+}-O bond lengths, and the results are in agreement with tabulated values for crystal radii of Fe\textsuperscript{3+} in high- and low-spin state. The reduced crystal size of Fe\textsuperscript{3+} in the low-spin state suggest that in lower mantle assemblages, Fe\textsuperscript{3+} partitioning in crystallographic sites should be strongly affected by the iron spin state.

Keywords: CaFe\textsubscript{2}O\textsubscript{4}, high pressure, spin transition, single crystal

INTRODUCTION

The mineralogical and geophysical interest in the CaFe\textsubscript{2}O\textsubscript{4} structure (\( Pbnm, a = 10.716, \ b = 9.237, \ c = 3.021 \) Å) arises, because at the mantle transition zone the spinel structure is no longer stable and transforms to a CaFe\textsubscript{2}O\textsubscript{4} type structure (i.e., Irifune et al. 1991). The crystal structure of CaFe\textsubscript{2}O\textsubscript{4} consists of hexagonal arrays of oxygen atoms, parallel to \( a-b \) plane, but with only 1/3 of the positions filled. Within the layers, two different sixfold-coordinated cation sites are occupied by Fe, and an eightfold-coordinated site is filled by Ca (Fig. 1). The Ca-ferrite structure (or slightly distorted modifications, such as CaTi\textsubscript{2}O\textsubscript{4} or CaMn\textsubscript{2}O\textsubscript{4} structure) is expected to be stable for all of the \( P \) and \( T \) conditions of the lower mantle. In basaltic compositions (Perrillat et al. 2006), the CaFe\textsubscript{2}O\textsubscript{4} structure is enriched in NaAlSiO\textsubscript{4} component, and coexists with MgSiO\textsubscript{3} perovskite, CaSiO\textsubscript{3} perovskite, stishovite, and the NAL phase (Akaogi et al. 1999; Miura et al. 2000), a Na-Al-Ca- and K-bearing phase. The NAL phase is not stable above 40 GPa and it seems to dissolve into the Ca-ferrite phase. For this reason, Ca-ferrite is a potential geochemical reservoir in the mantle for alkaline and other large cations. The CaFe\textsubscript{2}O\textsubscript{4} structure is also an excellent model structure to investigate the behavior of Fe\textsuperscript{3+} in oxide structures at lower mantle conditions. Iron is normally present in the high-spin state in terrestrial minerals at ambient conditions, but can transform to a low-spin state at extremely high pressure, the pressure depending on the iron valence state and the particular crystal structure (Cohen et al. 1997). The presence of iron in the low-spin state in lower mantle minerals dramatically changes the thermodynamic properties and the crystal chemistry of oxide and silicate phases. In fact, whereas high-spin Fe\textsuperscript{3+} is expected to substitute easily for Mg\textsuperscript{2+} and similar cations, low-spin Fe\textsuperscript{3+}, because of its smaller size, comparable to Al\textsuperscript{3+}, could eventually enter crystallographic sites usually filled by smaller cations, Si\textsuperscript{4+} in particular. As a consequence, all thermodynamic properties (bulk properties, element partitioning, electric and

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0003-004X/10/0001–200S05.00/DOI: 10.2138/am.2010.3347 200

FIGURE 1. Crystal structure of CaFe\textsubscript{2}O\textsubscript{4}, showing the coordination polyhedra (Fe-O\textsubscript{6}: light gray; Ca-O\textsubscript{8}: dark gray).