American Mineralogist, Volume 95, pages 200–203, 2010

LETTER

Fe^{3+} spin transition in $CaFe_2O_4$ at high pressure

MARCO MERLINI,[1,2,*] MICHAEL HANFLAND,[1] MAURO GEMMI,[2] SIMO HUOTARI,[1]
LAURA SIMONELLI,[1] AND PIERRE STROBEL[3]

[1]ESRF—European Synchrotron Radiation Facility, 6 rue Jules Horowitz, BP220, 38043 Grenoble CEDEX, France
[2]Dipartimento di Scienze della Terra, Università degli Studi di Milano, Via Botticelli 23, 20133 Milano, Italy
[3]Institut Néel, CNRS and Université Joseph Fourier, BP166, 38042 Grenoble Cedex 9, France

ABSTRACT

Single-crystal diffraction data collected for $CaFe_2O_4$ 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^{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 $CaFe_2O_4$ "high spin" and $K_0 = 235(10)$ GPa for $CaFe_2O_4$ "low spin"]. Crystal structure refinements reveal a decrease of 12% of the Fe^{3+} crystallographic site volume. The geometrical features of the low-spin Fe^{3+} crystallographic site at high pressure (bond lengths, volume) indicate a relevant decrease of Fe^{3+}-O bond lengths, and the results are in agreement with tabulated values for crystal radii of Fe^{3+} in high- and low-spin state. The reduced crystal size of Fe^{3+} in the low-spin state suggest that in lower mantle assemblages, Fe^{3+} partitioning in crystallographic sites should be strongly affected by the iron spin state.

Keywords: $CaFe_2O_4$, high pressure, spin transition, single crystal