Pressure-induced spin transition in FeCO₃-siderite studied by X-ray diffraction measurements

T Nagai¹, T Ishido¹, Y Seto², D Nishio-Hamane³, N Sata⁴, K Fujino⁵

¹ Department of Natural History Sciences, Hokkaido University, N10W8, Sapporo 060-0810, Japan
² Department of Earth and Planetary Sciences, Kobe University, 1-1 Rokkodai-cho, Nada, Kobe 657-8501, Japan
³ Institute for Solid State Physics, University of Tokyo, 5-1-5 Kashiwanoha, Kashiwa 277-8581, Japan
⁴ Japan Agency for Marine-Earth Science and Technology, Yokosuka, Kanagawa 237-0061, Japan
⁵ Geodynamics Research Center, Ehime University, 2-5 Bunkyo-cho, Matsuyama 790-8577, Japan

E-mail: nagai@mail.sci.hokudai.ac.jp

Abstract. We have collected synchrotron X-ray diffraction patterns of FeCO₃-siderite after or in-situ laser heating at high pressures to 66 GPa. Diffraction peaks of FeCO₃ in all diffraction patterns obtained can be indexed as a trigonal cell. However, calculated cell volumes show an abrupt decrease (about 6.5%) between 47 and 50 GPa at room temperature. This abrupt change of the cell volume on FeCO₃ is possibly due to a pressure-induced spin transition of ferrous Fe (HS: high-spin → LS: low-spin). Because cell parameters obtained at high temperature and at pressures above 50 GPa suggest HS state rather than LS state, the Clapeyron slope of the HS-to-LS transition of FeCO₃ should be positive.

Introduction

FeCO₃-siderite is an isostructural mineral of CaCO₃-calcite and MgCO₃-magnesite. FeCO₃ has \( R\bar{3}c \) space group in the crystal system of trigonal. The ferrous Fe is in 6-coordination with O atoms of the CO₃ group. The C atoms lie in the plane surrounded by its three neighboring O atoms, that is normal to the c axis. Corner-sharing FeO₆ octahedra and CO₃ trigonal units build the crystal structure of FeCO₃-siderite as shown in Figure 1. Recently, a pressure-induced spin transition from high spin state (HS) to low spin state (LS) for ferrous iron in FeCO₃ has been proposed by x-ray emission spectroscopy (XES) [1] and first-principles calculations [2]. The XES study indicates the spin transition took place roughly at 50 GPa and room temperature. First-principles calculations proposed that the spin transition was with a volume collapse of about 10% and also accompanied by increase in bulk modulus, but the transition pressure at around 28 GPa was underestimated with respect to the XES experiment. Although a number of reports have been published on compression behaviours of calcite and magnesite, relatively few diffraction experiments on FeCO₃ at high pressure could be found in...
literature. Zhang et al. [3] reported compression data of FeCO$_3$ to 8.9 GPa and 1073 K. Santillán and Williams [4] reported X-ray diffraction patterns of FeCO$_3$ collected at room temperature before and after in-situ laser heating at pressures. They indicated the calcite structure of FeCO$_3$ is stable to about 50 GPa, which is below the spin transition pressure suggested by the XES experiment. In this study, we report new compression data on FeCO$_3$ using a diamond anvil cell technique up to 66 GPa with synchrotron monochromatized X-ray and in-situ laser heating. The experiments aimed to determine the cell parameters change associated with the spin transition and the effect of temperature on the spin transition.

**Experimental**

Natural mineral sample of FeCO$_3$-siderite (occurrence unkown) was used. Cell parameters determined from X-ray diffraction patterns ($a=4.6925(3)$ Å, $c=15.388(3)$ Å) are in good agreement with the data in JCPDS card (No. 29-696). Chemical composition of this sample is Fe$_{0.73}$Mg$_{0.22}$Mn$_{0.05}$CO$_3$. Compression experiments were performed using diamond anvil cells with 0.3 mm culet diamonds. Powdered sample of FeCO$_3$ were loaded with or without a small amount of gold powder into the sample chamber (about 100 μmΦ) of a pre-indented rhenium gasket. Argon was used as pressure transmitting medium, thermal insulating medium and also internal pressure standard by its equation of state [5]. It is difficult to apply gold pressure scales to determine the generated pressure in the range from 40 to 60 GPa, because diffraction peaks of gold are almost overlapped with those of Ar [e.g., 6].

Angle dispersive synchrotron X-ray diffraction patterns were recorded on an imaging plate (IP) at BL10XU beamline in the SPring8, Japan. Monochromatized X-ray beam (wavelength=0.4125 Å) was focused (15μmΦ) on the center of the sample chamber in the diamond anvil cell. Double sided YAG laser heating treatments at about 1500 K were conducted for annealing after increasing pressure at room temperature. Some diffraction patterns were collected at high pressure and high temperature of about 1500 K. The two-dimensional diffraction pattern recorded on an IP was converted to the conventional one-dimensional 2θ-intensity diffraction pattern with IPAnalyzer software [7].

**Results and Discussion**

All diffraction patterns of FeCO$_3$ obtained in this study could be indexed as the trigonal cell, $R\overline{3}c$. Figure 2(a) shows the compression curve of FeCO$_3$. Cell volumes at a room temperature suddenly decrease between 47 and 50 GPa. The third-order Birch-Murnaghan equation of state was applied for the cell volume data up to 47 GPa at room temperature as shown in Figure 2(a). The isothermal bulk modulus, $K_0$ and its pressure derivative at 300 K, $K_0'$. are obtained as 120(3) GPa and 4.3(3), respectively. This value is good agreement with values ($K_0=117$ GPa, $K_0'=4$ fixed for the end member of FeCO$_3$-siderite) obtained by Zhang et al. [3] and with values ($K_0=114$ GPa, $K_0'=3.99$) calculated by Shi et al. [2].

The cell volume collapse of about 6.5% between 47 and 50 GPa seems to be due to the spin transition, because the pressure at which the abrupt collapse of cell volume is observed, is as almost
same as the pressure at which the spin transition was determined by X-ray emission spectroscopy [1]. The cell volume collapse of about 6.5% is a little smaller than that accompanied by the spin transition proposed by first-principles calculations (~10%) [2]. Since optimized cell volume by first-principles calculations for pure FeCO3 should be different from the present sample with 22 mol% MgO content, it seems that the cell volume collapse of about 6.5% also suggests the spin transition of FeCO3. The pressure-induced spin transition has been also reported for Fe-bearing silicate perovskite and magnesiowüstite, and showed gradual transitions through a mixed-spin state or an intermediate-spin state [e.g., 8,9]. However, the spin transition on FeCO3 seems to occur in relatively narrow pressure range at 300 K. It is the first evidence that the crystal structure of FeCO3-siderite is preserved after the spin transition; nevertheless the transition is accompanied by sudden cell volume collapse of about 6.5%. Santillán and Williams [4] reported no transition up to 50 GPa. However, it has been indicated that the amount of the FeO content in magnesiowüstite strongly affects the spin transition pressure, which increases with the FeO content [e.g., 10]. Indeed, because the FeO content in FeCO3-siderite sample used in Santillán and Williams [4] was larger than that in this study, the spin transition pressure possibly shifted to a higher pressure.

The relative axial compressibilities of $a/a_0$, $c/c_0$ and the axial ratio of $c/a$ on FeCO3 are plotted as a function of pressure. Black and red dots represent the data obtained at 300 K and at 1500 K, respectively. Blue dots represent the data obtained at 300 K and correspond to the LS state. Errors are within the dots. The dotted curve in (a) represents the best fit to the compression data up to 47 GPa with the third-order Birch-Murnaghan equation of state. The dotted curves in (b) are just guide for

![Figure 2](image.png)
Figure 3. The parameter $t$ increases with pressure, because the $c$ axis is more compressible than the $a$ axis as shown in Figure 2(b). No obvious discontinuity is shown at around the spin transition pressure between 47 and 50 GPa and the parameter $t$ approaches to one at about 70 GPa. The parameter $t=1$ means that Fe atoms and the CO$_3$ groups are arranged in a manner of an ideal NaCl structure.

Fe and C atoms are sitting on the origin (0,0,0) and the position of (0,0,1/4) in the crystal structure of FeCO$_3$-siderite (a hexagonal setting), respectively. O atoms are sitting on the position of $(u,0,1/4)$, where $u$ is an atomic coordinate. Previous compression data for some carbonate minerals suggested the CO$_3$ groups are rigid units and essentially incompressible [12,13]. Thus, the $u$ parameter and the Fe-O distance can be calculated under an assumption that the C-O distance of 1.29 Å is constant at pressures. The Fe-O distances calculated before the spin transition ($a=4.500(4)$ Å and $c=13.22(6)$ Å at 47 GPa) and after the spin transition ($a=4.396(3)$ Å and $c=12.83(2)$ Å at 50 GPa) should be 1.955(3) Å at $u=0.2867$ and 1.891(1) Å at $u=0.2935$, respectively. The difference of the Fe(LS)-O distance from the Fe(HS)-O is estimated at about 0.064 Å. This value is much smaller than the difference in effective ionic radii between octahedrally coordinated HS and LS Fe$^{2+}$ of 0.16 Å at ambient pressure.

Some diffraction patterns were measured at high pressure and high temperature (~1500 K). The cell volumes, the relative axial compressibilities of $a/a_0$, $c/c_0$ and the axial ratio of $c/a$ are quite different from the compression data for LS-FeCO$_3$ obtained at almost same pressure and at 300 K, and rather close to the extrapolation curve of the compression data up to 47 GPa for HS-FeCO$_3$ as shown in Figure 2(a), (b). This should be the evidence that HS-FeCO$_3$ is stable at higher pressure at high temperature. It could be explained as the effect of thermal expansion that the cell volumes at high temperature are above the extrapolation curve of the compression data up to 47 GPa and at 300 K. The first-principles calculation on magnesiowüstite also suggested that the stability field of a high spin state of Fe$^{2+}$ shifts to higher pressure at high temperature [14].

In summary, X-ray diffraction studies confirm that the pressure-induced spin transition of FeCO$_3$ between 47 and 50 GPa is accompanied by abrupt collapse of cell volume (~6.5%). In-situ observation of X-ray diffraction patterns at high pressure and high temperature suggest that the spin transition occurs at higher pressure at high temperature.
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