Synthesis and Compression study of orthorhombic $Fe_7(C, Si)_3$: A possible constituent of the Earth’s core

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Abstract

Orthorhombic phase of Si-doped Fe carbide is synthesized at high pressures and temperatures using laser-heated diamond anvil cell (LHDAC), followed by its characterization using Transmission Electron Microscopy (TEM), Raman spectroscopy, and X-ray diffraction (XRD) measurements. High-pressure XRD measurements on the synthesized sample are carried out up to about 104 GPa at room temperature for determination of its equation of state (EOS) parameters. No structural change is observed, though two anomalies are observed in the compression behaviour of our sample at about 28 and 78 GPa, respectively. Pressure evolution of isothermal bulk modulus show elastic stiffening around 28 GPa followed by softening around 78 GPa. These anomalies are possibly related to two different magnetic transitions driven by pressure induced anisotropic strain in the unit cell. Extrapolation of the density profile of our study to the inner core conditions agrees within 2-3% with respect to PREM data.
I. INTRODUCTION

Over several decades composition of Earth’s core has been under extensive debate in scientific communities. Amongst several elements, Iron (Fe) and its alloys with Nickel (Ni) have been predicted to be the main components of the Earth’s core from X-ray diffraction experiments at extreme pressures. But densities of these materials are found to be significantly higher than that of Earth’s core obtained from seismic observations. In view of the above it has been suggested that a few percentages of light elements may be present along with Fe or Fe – Ni alloy. Initially, Carbon (C) was considered to be the leading light element along with Fe in the form Fe$_3$C at Earth’s core due to its high solar abundance, chemical affinity to iron at low pressures, and overall ability to lower the density of pure Fe or Fe – Ni alloy. Sata et al. did show that C is the most dominant constituent along with Fe in comparison with other light elements such as Si, O, S due to its minimal density deficit with respect to the PREM data at inner core conditions. However, theoretical studies predicted a non-magnetic Fe$_3$C with stiffer bulk modulus compared to the PREM data.

High pressure and high temperature experiments using both multi-anvil (MA) cell and LHDAC on Fe – C system resulted in crystallization of a new iron-carbide phase with chemical formula Fe$_7$C$_3$ at about 1500°C and 10 GPa, which is predicted to be a potential candidate of solid inner core. Several research groups indexed the synthesized phase to be of hexagonal crystal structure. Electronic structural calculations by Mookherjee et al. on hexagonal Fe$_7$C$_3$ at Earth’s core conditions proposed around 7% less density as compared to PREM data. Experimental work by Chen et al. proposed the density of hexagonal Fe$_7$C$_3$ to be about 5-10% higher with respect to PREM data at inner core pressure and temperature range 5000-7000 K. Recently, Prescher et al. synthesized an orthorhombic phase of Fe$_7$C$_3$ using MA apparatus. A theoretical simulation study by Das et al. comparing the hexagonal, orthorhombic pure phases of Fe$_7$C$_3$ and silicon (Si) doped hexagonal, orthorhombic phases of Fe$_7$C$_3$ showed that values of density and Poisson’s ratio of orthorhombic(o) Fe$_7$(C, Si)$_3$ at inner core to be very close to the PREM data. The above study proposed orthorhombic Si-doped Fe carbide (o – Fe$_7$(C, Si)$_3$) with 3.2 wt % of Si at C cite to be one of the most important component of the Earth’s inner core.

Depending on the current trends of the possible candidates for the core material, we
have successfully synthesized orthorhombic phase of $Si$-doped $Fe_7C_3$ at high pressures and high temperatures using $LHDAC$ facility present in our laboratory. We have characterized the above material by $TEM$, Raman, and $XRD$ measurements. We have also carried out the equation of state measurements on $Si$-doped $Fe_7C_3$ at room temperature. We have estimated the bulk modulus and the density at inner core conditions by extrapolating our results, which is found to be closest to the PREM data within error limits.

II. EXPERIMENTAL

We have prepared a homogeneous stoichiometric mother mixture of 2 gm taking appropriate amounts of Fe (CAS No: 7439-89-6, purity: >99.5% (RT), grain size: 5-9 micron), nano-diamond (CAS No: 7782-40-3, purity: >95% trace metal basis, grain size: 10 nm) and Si powders (CAS No: 7440-21-3, purity: >99% trace metal basis, grain size: 2-5 micron) having atomic ratio $Fe : C : Si = 70:25:5$, which is grinded over a long period of time in mortal pestle in alcohol. This provides us a very homogeneous mixture of the sample. Thin pellet of the above mixture of approximate diameter of about 60 - 80 $\mu$m, sandwiched between pellets of dried $NaCl$ (15 $\mu$m) are loaded in $LHDAC$. The $LHDAC$ consists of a plate type $DAC$ (Boehler-Almax design) of culet diameter 300 $\mu$m with a stainless steel gasket having a hole of diameter $\sim$ 100 $\mu$m pre-indented to a thickness of 45 $\mu$m. A few ruby chips of approximate size 5 $\mu$m are placed at the gasket edge to determine the pressure in the $LHDAC$ before and after heating using ruby fluorescence method$^{21}$. Heating of the sample is carried out using IPG photonics CW laser of wavelength 1.07 $\mu$m (maximum power of 100 Watt). Temperature of the sample is measured using spectra-radiometry technique$^{22,23}$ by fitting Planck's radiation function$^{24}$ to the collected flatfield corrected spectra. Three different heating runs are carried out on the sample at pressures of 8, 15, and 30 GPa at a temperature of the hotspot of the sample about 2200 K.

Raman measurements of the unheated and heated samples (after washing the retrieved sample using distilled water) are carried out with a micro-Raman spectrometer (Monovista CRS + from S&I) having 1500 grooves mm$^{-1}$ grating using 20 X long working distance objective (infinitely corrected) and the excitation wavelength of 532 nm with spectral resolution of 1 cm$^{-1}$. We have recorded bright field electron image of the retrieved sample using the $TEM$ operating at 200 kV. We have also carried out electron diffraction at selected area
to determine the crystal structure and elemental analysis to determine Si content. XRD measurements of all these retrieved samples have been carried out in P02.2 beamline of Petra-III synchrotron radiation facility of Hamburg, Germany using 42 keV X-ray source.

*In situ* high-pressure high-temperature X-Ray diffraction measurements also carried out in the above synchrotron source using the LHDAC facility consisting of membrane driven symmetric DAC of culet 150 µm. In this case dried MgO is used as a pressure transmitting medium as well as a pressure marker. A total number of four high pressure high temperature XRD measurements are performed. In all LHDAC heating experiments the laser spot is moved around in pre-determined grids for heating of the complete sample volume. We have carried out the heating run for 2-5 minutes at each pressure and temperature and continuously check the evolution of pattern during heating. Synchrotron powder diffraction measurements are carried out using monochromatic X-ray radiation of wavelength 0.29 Å collimated to 1.2 × 2.3 µm². Diffracted X-rays are detected using a Perkin-Emler 1681 detector aligned normal to the beam. The sample to detector distance is calibrated using CeO₂ standard. Collected two-dimensional diffraction images are integrated to intensity versus 2θ profile using Dioptas software available in the P02.2 beamline and then analyzed using the CRYSFIRE and Rietveld refinement program of GSAS.

**III. RESULTS AND DISCUSSION**

Raman spectra of unheated and recovered samples after heating at three different runs are shown in Supplementary Fig. 1. Raman spectrum of unheated sample reveals three peaks centered at 520, 1330 and 1580 cm⁻¹ corresponding to Si, D-band and G-band of nano-diamond. But Raman spectra of the heated sample do not show any prominent mode of the parent constituents. Disappearances of the Raman bands after heating excludes the presence of un-reacted elemental C and Si in the heated samples. After retrieving the sample from LHDAC, it was prepared for TEM measurements in the following manner: The retrieved sample is enclosed within MgO pressure transmitting medium. MgO is removed very carefully under microscope which itself takes a long time and hard work. Then the retrieved sample is polished to make it very thin suitable for TEM measurements. The mapping of the chemical composition of the quenched sample using TEM after heating at about 2200 K at 8 GPa reveals the presence of Fe, C, and Si in the synthesized compound.
at ratio \(Fe : C : Si = 71:26:4\) and are shown in Supplementary Fig. 2. Fig. 1 shows the selected area diffraction pattern (SADP) of the grain at the tip of the red arrow as shown in the inset. Analysis\textsuperscript{28} of SADP reveals orthorhombic phase of silicon doped \(Fe_7C_3\) in space group \(Pbc\) having two prominent Bragg planes (021) and (210) and it is indexed to a unit cell having lattice parameters \(a = 12.9(1)\), \(b = 4.9(1)\), and \(c = 14.2(2)\) Å.

Fig. 2(a) shows the XRD pattern of the above mentioned quenched sample. The pattern is indexed to an orthorhombic phase with lattice parameters \(a = 12.469(3)\), \(b = 4.509(1)\), and \(c = 14.591(3)\) Å in space group \(Pbc\). The Rietveld refinements of above XRD pattern are carried out using the atom positions from the pure phase of orthorhombic \(Fe_7C_3\)\textsuperscript{19}. Rietveld refinement shows an excellent fit as evident from the figure. Moreover, fractional occupancy of \(C\) and \(Si\) are found to be 83% and 17% at the \(C\) cite, respectively. This shows that 17% of \(C\) cite is replaced by the \(Si\) in the orthorhombic \(Fe_7C_3\) phase. In comparison to the pure orthorhombic phase of \(Fe_7C_3\) at room temperature and pressure as reported in the literature\textsuperscript{15,19}, we have observed 4%, 6%, and 10% increase in the values of \(a\), \(c\), and \(V\), respectively; while we obtain similar value of \(b\). This may due to large diameter of \(Si\) (2.10 Å) with respect to \(C\) (1.70 Å), and low electronegativity of \(Si\) (1.9) with respect to \(C\) (2.55) causes the expansion in the lattice parameters and hence in volume. Henceforth, we label our synthesized orthorhombic \(Si\)-doped \(Fe_7C_3\) as \(o−Fe_7(C, Si)_3\). In situ X-Ray diffraction measurements at higher pressures and higher temperatures in P02.2 beamline confirmed the presence of same phase of \(o−Fe_7(C, Si)_3\). We have carried out XRD measurements at much high pressures and high temperatures to look for any new modification of \(o−Fe_7(C, Si)_3\), however failed to obtain any phase other than the orthorhombic phase. In Fig. 2(b), we have shown the Rietveld refinement of the diffraction pattern collected at a pressure 32 GPa and temperature 2000 K in the orthorhombic phase and indexed each peak. Our high pressure XRD measurements on \(o−Fe_7(Si, C)_3\) at room temperature up to about 104 GPa do not show any structural phase transitions (Supplementary Fig. 3).

In Fig. 3(a) we have compared the pressure evolution of volume of the \(o−Fe_7(C, Si)_3\) at room temperature in our study with those reported in the literature for pure \(o−Fe_7C_3\)\textsuperscript{19} and \(Si\)-doped \(o−Fe_7C_3\).\textsuperscript{20} We have found 1-3% volume increment at high pressure (28-104 GPa) regime of our study in compared to above studies. The errors are calculated using the error obtained in pressure from \(MgO\) pressure marker. Volume error is obtained from the indexing of XRD patterns. Two anomalies are seen at about 28 GPa and 78
GPa, respectively. To understand the effect of strain on the compression behaviour of 
\( \alpha - Fe_T(C, Si)_3 \), we have plotted reduced pressure \( H = \frac{P}{\frac{3}{2}f_E(1+2f_E)^{5/2}} \) with respect to the 
finite Eulerian strain \( f_E = \frac{1}{2}[\left(\frac{V_0}{V}\right)^{2/3} - 1] \) in Fig. 3(b). The behaviour is expected to be 
linear as following equation\(^{31,32}\):

\[
H = K_0 + \frac{3}{2}K_0(K' - 4)f_E
\] (1)

where, \( V_0 \) is the volume at 1 bar and 300 K, \( V \) is the volume at pressure \( P \), \( K_0 \) is the 
bulk modulus, and \( K' \) is the first derivative of bulk modulus. However, the plot shows 
two distinct discontinuities at around 28 GPa and 78 GPa. In the pressure range 28-78 
GPa Eulerian strain shows almost 70% increment, indicating a large pressure induced strain 
in the lattice. The discontinuities in the \( H \) versus \( f_E \) plot have been previously observed 
in \( Fe_3C \) and \( h - Fe_T C_3 \) system during the magnetic transition with the absence of any 
structural transition\(^{12,18,33}\). Therefore, we have carried out separate 3\(^{rd}\)-order B-M EOS 
fitting in the three regions (i) 0-28 GPa, (ii) 28-78 GPa, and (iii) 78-104 GPa, respectively, 
which is shown in Fig. 3(a). The fitted values of \( V_0 \), \( K_0 \) (bulk modulus) and \( K' \) (first 
derivative of bulk modulus) in the pressure range (i) are 822(8) Å\(^3\), 72(7) GPa and 5.8(7), 
respectively. The value of \( K' \) is consistent with \( \epsilon - Fe \) and \( \alpha - Fe_T C_3\)\(^{1,2,19}\). The sample 
seems to be highly compressible up to 28 GPa. In the range-(ii), values of \( V_0 \), \( K_0 \) and \( K' \) are 
found to be 716(6) Å\(^3\), 294(17) GPa and 5.9(6), respectively. \( K_0 \) and \( K' \) are consistent with 
the hexagonal phases of \( Fe_T C_3 \) in their paramagnetic phase\(^{12,15,18}\). In this pressure range, 
the sample is less compressible than the range-(i). Above 78 GPa, the volume decreases 
faster with pressure indicating increase in compressibility. For being very narrow range of 
pressure in range (iii), we fit our P-V data in the range 78 to 104 GPa using 2\(^{nd}\)-order 
Birch-Murnaghan EOS and find the best fit for \( V_0 \) to be 830 Å\(^3\). Taking this initial \( V_0 \) we 
fit our data in this pressure range using 3\(^{rd}\)-order Birch-Murnaghan EOS floating \( K_0 \) and 
\( K' \) and find the best fit for \( K_0 = 141(9) \) and \( K' = 3.9(4) \). Value of \( K_0 \) seems to be low in 
comparison to that of the paramagnetic phase of \( h - Fe_T C_3\)\(^{12,15,18}\). However, the value of \( K' \) 
is consistent with the non-magnetic phases of iron carbide\(^{12,15}\). The lattice parameters and 
volume of the sample at each pressure points are presented in Table-I in the Supplementary 
information. Also, the atomic positions at each pressure point are tabulated in Table-III of 
the Supplementary information.

In Fig. 3(c) we have shown the pressure evolution of individual lattice parameters in
this study along with literature values for pure and Si-doped $o-Fe_7C_3^{12,19}$. Interestingly $a$ and $c$- axes show pressure behaviour similar to volume, but $b$-axis shows a single anomaly at 28 GPa. This behaviour indicates an anisotropic compression of the unit cell. The axial compression behavior ($\beta_0 = -\frac{(\delta l/\delta P)_{P=0}}{l_0}$, where $l_0$ is the lattice parameters at 1 bar and 300 K) for each axis is estimated by fitting pressure dependence of each axis to a 3rd-order B-M EOS$^{34}$ and is shown in the figure. A single EOS function could not be used to fit the data in the complete pressure range: (1) three distinct EOS parameters for $a$ and $c$ - axes and (2) two distinct EOS parameters for $b$- axis. The obtained axial compressibility values are given in Table-II of the Supplementary information. In the pressure range 0 - 28 GPa, $b$- axis seems to be least compressible. In the pressure range 28 - 75 GPa, compressibility of $c$- axis reduces drastically compared to the other two axes. At high pressures above 75 GPa, the compressibility along all the axes almost behave similarly. Such a different linear compressibility has not been reported in the literature for other iron-carbide phases$^{12,15,18,19}$.

High-pressure Mossbauer spectroscopic study of $Fe_3C$ shows a ferro-to-paramagnetic transition around 8-10 GPa and a spin transition at about 22 GPa$^{33}$. Other high pressure experiments on hexagonal $Fe_7C_3$ have shown two anomalies in the compression curve at around 7-18 GPa and 53 GPa corresponding to the ferro-to-paramagnetic and para-to-non-magnetic phase transition, respectively$^{12,18}$. In $o - Fe_7C_3$, Prescher et al.$^{19}$ have observed a ferromagnetic to paramagnetic phase transition at around 16 GPa and a paramagnetic to non-magnetic phase transition at 70 GPa, which is reflected in the mean $C$ to $Fe$ atom distance with pressure. In all possibility these magnetic transitions are reflected in our volume as well as axial compressibility behavior.

The elastic hardening of $o - Fe_7(C, Si)_3$ is observed at 28 GPa as indicated by a sharp increment of bulk modulus ($K_0$) followed by an elastic softening at 78 GPa as evident from the drop of $K_0$ value at 78 GPa as shown in Fig. 4(a). This surprising elastic hardening at low-pressure range and softening at higher pressure can be attributed to magnetic transitions as observed in the case of reported high pressure phase of $Fe_7C_3^{12,13,18,19}$. Though we have not performed any magnetic measurements on our sample, we propose the anomalies observed in the compressional behaviour of $o - Fe_7(C, Si)_3$ unit cell are probably related to the above magnetic transitions in comparison with literature$^{12,13,16,18,19,33}$. Possibly the pressure induced anisotropic strain induces these magnetic transitions. We have compared our isothermal bulk modulus ($K_0$) extrapolated to inner core pressure at 300 K with that
of other phases of \( \text{Fe}_7\text{C}_3 \) calculated using \( EOS \) fitted parameters and PREM data in the inset of Fig. 4(a). As evident from the inset of Fig. 4(a), our \( K \) values approach very close to the PREM data among all having non-magnetic phase. The value seems to be 13-15\% less than the that of PREM data in the shown pressure range and is better matched with respect to other reported values for non-magnetic phase.

We have estimated the density of \( \text{o} - \text{Fe}_7(\text{C},\text{Si})_3 \) from 104 GPa to inner core pressure at 300 K taking into account the \( EOS \) parameters of the range-(iii) in our study and compared with that of pure \( \text{Fe} \), PREM data, and other phases of \( \text{Fe}_7\text{C}_3 \) in Fig. 4(b). We have assigned the errors in the density (Fig. 4) from the errors in the measurement of the mass of the mother mixture at ambient pressure and errors in the volume from the 3\textquoteleft\text{d}-order Birch-Murnaghan EOS using standard deviation of the EOS parameters obtained from the fitting of P-V data in the range 78-104 GPa. The overall error in the density measurement is found to be \( \pm 2\% \) at the core pressure. We have found around 5\% higher density of our \( \text{o} - \text{Fe}_7(\text{C},\text{Si})_3 \) at 300 K in comparison to PREM data. The inner core temperature ranges from 5000 to 7000 K as estimated by \( \text{Boehler}^{35} \). We have estimated the temperature effect on our density value from the thermal pressure following the equation \( P(V,T) = P(V,T_0) + P_{th}(T) \); where \( P(V,T_0) \) is the B-M EOS and \( P_{th}(T) = \alpha K_T \Delta T \), where \( \alpha \) is thermal expansion coefficient and \( K_T \) is the bulk modulus and \( \Delta T = T - T_0 \) is the thermal pressure. Thermal pressure \( P_{th}(T) \) is the pressure that would be created by increasing temperature from \( T_0 \) to \( T \) at constant volume. Since we have used \( \text{MgO} \) as pressure standard and observed the pressure before heating, during heating and after heating around 2000 K in few runs, we can assess the effect of temperature from thermal pressure on density. We have plotted temperature versus thermal pressure and is shown in Fig. 4 in the supplementary information. We have found 10 GPa of thermal pressure at a temperature 2000 K from \( \text{MgO EOS} \), which in turns provides, \( \alpha K_T = 0.0058 (5) \) GPa\(^{-1} \). Extrapolation of the density profile of the range (iii) in our study to the inner core pressures at 7000 K is found to 2\% higher than PREM data\(^2\). Among all the reported densities at the Earth\’s core pressures and temperatures, extrapolation of the density profile of the range (iii) at 7000 K to the inner core pressures agrees very well with the PREM data\(^1,3,12,15,18,19 \). Therefore, we propose that \( \text{o} - \text{Fe}_7(\text{C},\text{Si})_3 \) can be a strong contender for the composition of Earth inner core. More measurements are also necessary to resolve the inner core constituent.
IV. CONCLUSIONS

We have successfully synthesized $o \text{-- Fe}_7(C, Si)_3$, followed by characterization using TEM, Raman, and XRD measurements. High-pressure XRD measurements reveal no structure transition up to 104 GPa at room temperature, the highest pressure in this study. High-pressure compression behaviour of our sample reveals two anomalies around 28 and 78 GPa and anisotropic compression of the unit cell. Isothermal bulk modulus shows elastic stiffening around 28 GPa followed by an elastic softening around 78 GPa. We attribute these anomalies to the magnetic transitions. We have estimated the bulk modulus to the inner core pressures and density to the inner core pressures and temperatures by extrapolating our results. The bulk modulus approaches very close to the PREM data. Also our estimated density of the inner core at 7000 K seems to have excellent match with PREM data.

ACKNOWLEDGMENTS

GDM wishes to thank Ministry of Earth Sciences, Government of India for financial support under the project grant no. MoES/16/25/10-RDEAS. PS wishes to thank DST, INSPIRE program by Department of Science and Technology, Government of India for financial support. We acknowledge DESY (Hamburg, Germany), a member of the Helmholtz Association HGF, for the provision of experimental facilities. Parts of this research were carried out at PETRA III and we would like to thank beamline scientists for assistance in using P02.2 beamline. GDM and PS are gratefully acknowledge the financial support from Department of Science and Technology, Government of India for DST-DESY project to carry out the proposed experiment on DESY, Germany.

Author Contributions All authors have equal contribution. All authors reviewed the manuscript.
V. ADDITIONAL INFORMATION

Competing Financial Interests: The authors declare no competing financial interests.

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Figure 1. The Selected area diffraction pattern (SADP) of the grain at the tip of red arrow shown in inset. The pattern is indexed to a \( P\overline{b}ca \) space group of orthorhombic phase with unit cell parameters \( a = 12.9(1) \text{ Å} \), \( b = 4.9(1) \text{ Å} \), and \( c = 14.2(2) \text{ Å} \).
Figure 2. (a) Fitted X-ray diffraction pattern of the recovered sample heated at a pressure 8 GPa and temperature around 2200 K using laser heated diamond anvil cell facility using Reitveld refinement program of GSAS. (b) X-ray diffraction pattern of the sample during heating at 32 GPa and 2000 K using LHDAC with its Reitveld refinement fitting.
Figure 3. (a) Comparison of compression behaviour of $\text{o} - \text{Fe}_7(C, \text{Si})_3$ at 300 K up to 104 GPa (All filled symbols) with $\text{Si}$-free (Black unfilled square symbols) and $\text{Si}$-doped (Black unfilled triangular symbols) $\text{o} - \text{Fe}_7\text{C}_3$. Different runs in this study are presented with separate filled symbols and colors. Dashed blue, red, and green curve represent 3$^{\text{rd}}$-order $B - M$ EOS fitting for three distinct ranges of pressure. (b) The reduced pressure with respect to the finite Eulerian strain reveals change in the slope at two pressure points to its linear behavior around 28 GPa and 78 GPa. (c) Axial compression behaviour of $\text{o} - \text{Fe}_7(C, \text{Si})_3$ (All filled symbols) at 300 K along with $\text{Si}$-free (Black unfilled square symbols) and $\text{Si}$-doped (Black unfilled triangular symbols) $\text{o} - \text{Fe}_7\text{C}_3$ as a function of pressure. Separate filled symbols and colors represent $a$, $b$, and $c$ lattice parameters with pressure in different runs. Blue, red, and green dashed lines are fitting to 3$^{\text{rd}}$-order $B - M$ EOS of our data at three different ranges of pressure.
Figure 4. (a) $K$ value of $\sigma - Fe_7(C, Si)_3$ at 300 K as a function of pressure, estimated using parameters obtained from fitted $3^{rd}$-order $B - M$ EOS in our study (blue lines), ferromagnetic (fm)- phase of $h - Fe_7C_3$ (green short dashed line, Nakajima et al.15), paramagnetic(pm)-phase of $h - Fe_7C_3$ (cyan dotted line, Chen et al.12), and nonmagnetic (nm)-phase of $h - Fe_7C_3$ (red dotted line, Chen et al.12). Inset: $K$ extrapolated to core pressure at 300 K of our study (blue line), pm-phase of $h - Fe_7C_3$ (cyan short dotted line, Nakajima et al.15), nm-phase of $h - Fe_7C_3$ (red dotted line, Chen et al.12), nm-phase of $o - Fe_7C_3$ (olive dashed line, Prescher et al.10), PREM data (Magenta short dashed line, Dziewonski & Anderson3). (b) Comparison of densities of $\epsilon - Fe$, $Fe_7C_3$, and $o - Fe_7(C, Si)_3$ at the Earth’s core pressures. Green short dashed line is density profile of PREM13. Violet and purple solid curves represent isothermal density profile $\epsilon - Fe$ at temperatures 5000 K and 7000 K14. Orange and wine short dotted lines show density profile of pm-$h - Fe_7C_3$ at 300 K15 and 6230 K15. Pink and cyan short dashed lines are the density profile of nm-$h - Fe_7C_3$ at 5000 K and 7000 K12. Magenta short dashed line represents density profile of nm $o - Fe_7C_3$ at 300 K10. Filled green squares, red circles, and blue diamonds represent the density profile at 300 K, 5000 K, and 7000 K in our study obtained by extrapolating the density at range (iii).
Supporting Information

Contents

1. Text S1

2. Figures 5 to 8

3. Tables 1 to 3

Text S1

In this Supplementary information, figures and tables are provided in the support of the main manuscript. We have added four figures and three tables here. Raman spectra of unheated and heated recovered samples at three different runs are compared in Figure 5. Three prominent peaks are observed in the unheated sample at around 520, 1330 and 1580 cm$^{-1}$ corresponding to Silicon and D-band and G-band of nanodiamond. But the Raman spectra of the heated sample do not show any prominent peak of the parent constituents, which excludes the presence of un-reacted elemental C and Si in the heated samples. Figure 6 represents the image of mapping of the chemical composition of the retrieved sample, which reveals that our retrieved sample contains iron, carbon, and silicon. The high percentage of the carbon is evident from the image, which is due to the use of carbon coated copper grid during TEM measurements. The corrected percentage of Fe, C, and Si in the synthesized compound is found to be at atomic weight ratio Fe : C : Si = 71 : 26 : 4, which is very close to the starting materials. In the Figure 7, we have plotted the evolution of the XRD patterns of $o$ – $Fe_7(C, Si)_3$ at selected pressure points of different runs, which show the shifting of the Bragg peaks to higher 2$\theta$-values with pressure. No new Bragg peak is observed up to highest pressure in our study up to 104 GPa. In Figure 8, we have shown the effect of temperature on the pressure of the sample that acts as negative pressure. Lattice parameters and volume of $o$ – $Fe_7(C, Si)_3$ are tabulated in Table-SI. In Table-SII, the axial compressibility for each axis are listed for three different pressure ranges. The atomic positions at each pressure point of $o$ – $Fe_7(C, Si)_3$ are tabulated in Table-SIII.
Figure 5. Raman spectra of unheated and heated sample at three different pressure points around 2000 K.
Figure 6. The image of mapping of the chemical composition on the recovered sample heated at a pressure 8 GPa and temperature around 2200 K taken using TEM operating at 200 kV.
Figure 7. Evolution of selected diffraction patterns with pressure at 300 K up to 104 GPa of \( \alpha - Fe_T(C,Si)_3 \). Inset: Image of loaded LHDAC around 53 GPa containing synthesized \( \alpha - Fe_T(C,Si)_3 \) and \( MgO \) as pressure transmitting medium in the central hole of diameter around 65 \( \mu m \).
Figure 8. Thermal pressure \( P_{th}(T) = \alpha K_T \Delta T \) with temperature \( \Delta T = T - T_0 \). Red solid fitted line yields \( \alpha K_T = 0.0058 (5) \) GPa\(^{-1} \)
Table I. Lattice parameters and volume of the $o-Fe_7(C, Si)_3$ structure obtained from high-pressure powder X-ray diffraction measurements.

| Run no. | P(GPa) | a(Å)   | b(Å)   | c(Å)   | v(Å³)  |
|---------|--------|--------|--------|--------|--------|
| Run-1   | 0      | 12.469(2) | 4.589(1) | 14.591(1) | 820(3)  |
|         | 3.0(5) | 12.352(1) | 4.491(1) | 14.281(1) | 792(3)  |
|         | 8.5(5) | 12.133(1) | 4.436(1) | 13.946(1) | 751(3)  |
|         | 9.4(5) | 12.096(2) | 4.401(1) | 13.891(1) | 739(3)  |
|         | 12.0(5)| 11.970(1) | 4.387(2) | 13.902(1) | 730(3)  |
|         | 14.9(5)| 11.921(1) | 4.371(1) | 13.806(2) | 719(3)  |
| Run-2   | 24(1)  | 11.646(1) | 4.327(1) | 13.360(2) | 673(3)  |
|         | 28(1)  | 11.592(1) | 4.310(1) | 13.405(1) | 670(3)  |
|         | 29(1)  | 11.562(1) | 4.300(1) | 13.365(1) | 664(3)  |
|         | 30(1)  | 11.538(1) | 4.292(1) | 13.345(2) | 661(3)  |
|         | 33(2)  | 11.504(1) | 4.283(1) | 13.337(1) | 657(4)  |
|         | 33(2)  | 11.445(2) | 4.278(1) | 13.322(1) | 652(4)  |
| Run-3   | 37(2)  | 11.398(1) | 4.261(1) | 13.316(2) | 647(4)  |
|         | 43(3)  | 11.368(2) | 4.253(2) | 13.285(2) | 642(4)  |
|         | 48(3)  | 11.331(1) | 4.234(1) | 13.248(1) | 636(4)  |
|         | 49(3)  | 11.329(1) | 4.231(1) | 13.245(1) | 635(4)  |
|         | 53(3)  | 11.321(2) | 4.225(2) | 13.233(1) | 633(4)  |
|         | 58(3)  | 11.293(1) | 4.207(1) | 13.205(1) | 627(4)  |
|         | 63(4)  | 11.271(1) | 4.189(1) | 13.177(2) | 622(5)  |
|         | 72(4)  | 11.228(1) | 4.160(2) | 13.136(2) | 614(5)  |
|         | 75(4)  | 11.218(2) | 4.153(2) | 13.114(1) | 611(5)  |
|         | 79(4)  | 11.181(1) | 4.149(1) | 13.143(2) | 610(5)  |
|         | 86(4)  | 11.176(1) | 4.126(1) | 13.034(2) | 601(5)  |
|         | 90(5)  | 11.136(2) | 4.108(2) | 13.022(1) | 596(6)  |
|         | 92(5)  | 11.119(1) | 4.096(1) | 12.995(1) | 592(6)  |
|         | 94(5)  | 11.098(1) | 4.0950(2) | 12.928(2) | 588(6)  |
|         | 98(5)  | 11.067(1) | 4.063(1) | 12.898(1) | 584(6)  |
|         | 101(5) | 11.040(2) | 4.085(1) | 12.871(2) | 580(6)  |
|         | 104(5) | 11.008(2) | 4.083(2) | 12.832(1) | 576(6)  |
Table II. The values of linear compressibility ($\beta$) along three lattice parameters at three different regions of the axial compression data of $\sigma-Fc7(C, Si)_3$. $\beta$ is represented in units of GPa$^{-1}$.

| Pressure range 0 to 28 GPa | 28 to 78 GPa | 78 to 104 GPa |
|---------------------------|--------------|---------------|
| $\beta_0^a$               | 0.00421(3)   | 0.00262(2)    | 0.00099(2)    |
| $\beta_0^b$               | 0.00192(2)   | 0.00166(3)    | 0.00166(3)    |
| $\beta_0^c$               | 0.00558(3)   | 0.00098(2)    | 0.00104(2)    |
Table III. Fractional atomic positions for $o - Fe_7(C, Si)_3$ structure derived from Rietveld analysis of high-pressure X-ray diffraction data at selected pressure points.

|       | 0 GPa | 3.0(5) GPa | 8.5(5) GPa | 9.4(5) GPa | 12.0(5) GPa | 18(1) GPa |
|-------|-------|------------|------------|------------|-------------|-----------|
| Fe1   |       |            |            |            |             |           |
| x     | 0.8180(8) | 0.8158(10) | 0.8047(15) | 0.7903(17) | 0.79075(75)| 0.7969(30)|
| y     | 0.0453(10) | 0.0593(28) | 0.0663(56) | 0.0804(35) | 0.0764(12)| 0.0118(39)|
| z     | 0.7193(11) | 0.7169(32) | 0.7156(10) | 0.7232(20) | 0.7207(6) | 0.7254(24)|
| Fe2   |       |            |            |            |             |           |
| x     | 0.6330(10) | 0.6257(10) | 0.6230(17) | 0.6319(30) | 0.63785(32)| 0.6355(34)|
| y     | 0.0535(20) | 0.0488(25) | 0.0302(44) | 0.0352(63) | 0.0367(26)| 0.0220(47)|
| z     | 0.6283(25) | 0.6231(30) | 0.6215(17) | 0.6446(35) | 0.6461(6) | 0.6211(21)|
| Fe3   |       |            |            |            |             |           |
| x     | 0.8036(9)  | 0.8132(12) | 0.8102(5)  | 0.8157(11) | 0.81557(36)| 0.8111(19)|
| y     | 0.09327(12)| 0.0794(21) | 0.0750(19) | 0.0848(24) | 0.0857(8) | 0.0297(26)|
| z     | 0.5346(16) | 0.5295(28) | 0.5297(6)  | 0.5276(11) | 0.5251(4) | 0.5472(17)|
| Fe4   |       |            |            |            |             |           |
| x     | 0.9006(15)| 0.9180(12) | 0.9205(7)  | 0.9205(10) | 0.91918(40)| 0.9226(21)|
| y     | 0.2625(26) | 0.2544(28) | 0.2648(30) | 0.2742(61) | 0.2764(15)| 0.2865(50)|
| z     | 0.8609(15)| 0.8746(30) | 0.8737(11) | 0.8651(21) | 0.8652(4) | 0.8811(22)|
| Fe5   |       |            |            |            |             |           |
| x     | 1.0293(6) | 1.0235(10) | 1.0241(4)  | 1.0262(10) | 1.02532(31)| 1.0034(24)|
| y     | 0.2225(18) | 0.2269(25) | 0.2174(18) | 0.2286(19) | 0.2210(8) | 0.2403(38)|
| z     | 0.7202(20)| 0.7164(32) | 0.7147(4)  | 0.7183(10) | 0.7170(4) | 0.7038(22)|
| Fe6   |       |            |            |            |             |           |
| x     | 0.5138(22)| 0.5202(14) | 0.5223(9)  | 0.5177(16) | 0.51792(67)| 0.5367(19)|
| y     | 0.2180(23)| 0.2516(26) | 0.2522(33) | 0.2287(43) | 0.2266(16)| 0.2720(37)|
| z     | 0.4618(18)| 0.4694(30) | 0.4694(7)  | 0.4597(22) | 0.4595(6) | 0.4530(20)|
| Fe7   |       |            |            |            |             |           |
| x     | 0.7298(11)| 0.7300(10) | 0.7120(7)  | 0.7128(14) | 0.71120(47)| 0.6923(19)|
| y     | 0.2450(12)| 0.2495(24) | 0.2612(23) | 0.2674(21) | 0.2567(10)| 0.2268(36)|
| z     | 0.8695(24)| 0.8759(32) | 0.8776(7)  | 0.8841(12) | 0.8833(4) | 0.8935(17)|
| C1 & Si1 | x   | 0.8416(11)| 0.8416(10)| 0.833(10)  | 0.819(6)  | 0.8134(27)| 0.811(10)|
|       |       |            |            |            |             |           |
|       | y     | 0.5303(26)| 0.5304(25)| 0.445(27)  | 0.506(15) | 0.506(4) | 0.503(25)|
|       | z     | 0.4915(18)| 0.4915(28)| 0.729(7)   | 0.730(6)  | 0.7288(23)| 0.738(5)|
| C2 & Si2 | x   | 0.5337(21)| 0.5637(14)| 0.592(9)   | 0.534(9)  | 0.5187(30)| 0.552(11)|
|       |       |            |            |            |             |           |
|       | y     | 0.4654(16)| 0.4655(25)| 0.483(12)  | 0.511(18) | 0.494(5) | 0.482(20)|
|       | z     | 0.6235(23)| 0.6235(36)| 0.610(8)   | 0.612(8)  | 0.6120(25)| 0.628(10)|
| C3 & Si3 | x   | 0.8331(15)| 0.8331(15)| 0.841(7)   | 0.815(6)  | 0.8046(31)| 0.807(9)|
|       |       |            |            |            |             |           |
|       | y     | 0.4608(25)| 0.4607(32)| 0.451(18)  | 0.456(18) | 0.440(5) | 0.445(19)|
|       | z     | 0.7521(25)| 0.7522(38)| 0.488(6)   | 0.473(7)  | 0.4732(22)| 0.479(9)|
|   | 24(1) GPa | 28(1) GPa | 30(1) GPa | 33(2) GPa | 372(1) GPa | 43(3) GPa |
|---|-----------|-----------|-----------|-----------|------------|-----------|
| Fe1 | x | 0.8037(14) | 0.835(5) | 0.8103(7) | 0.8358(11) | 0.795(11) | 0.816(5) |
|    | y | 0.095(5) | 0.092(8) | 0.061(7) | 0.0844(31) | 0.042(13) | 0.077(8) |
|    | z | 0.7133(18) | 0.720(4) | 0.7071(9) | 0.7129(11) | 0.6855(48) | 0.7332(34) |
| Fe2 | x | 0.6339(12) | 0.658(6) | 0.6311(10) | 0.6441(16) | 0.662(15) | 0.621(8) |
|    | y | 0.098(5) | 0.071(10) | 0.052(5) | 0.0973(45) | 0.064(24) | 0.124(11) |
|    | z | 0.6333(17) | 0.637(4) | 0.6375(7) | 0.6332(13) | 0.6288(72) | 0.6233(41) |
| Fe3 | x | 0.8107(16) | 0.776(6) | 0.8068(5) | 0.7639(20) | 0.810(7) | 0.801(10) |
|    | y | 0.030(5) | 0.021(12) | 0.052(5) | 0.0271(30) | 0.106(8) | 0.015(17) |
|    | z | 0.5276(18) | 0.542(4) | 0.5355(10) | 0.5425(14) | 0.5378(33) | 0.5374(35) |
| Fe4 | x | 0.9059(16) | 0.935(8) | 0.9118(8) | 0.9509(18) | 0.912(11) | 0.908(10) |
|    | y | 0.240(10) | 0.204(13) | 0.257(6) | 0.2324(45) | 0.357(13) | 0.330(20) |
|    | z | 0.9015(16) | 0.876(5) | 0.8758(11) | 0.8690(14) | 0.8675(40) | 0.8614(41) |
| Fe5 | x | 1.0247(16) | 1.035(8) | 1.0271(9) | 1.0297(11) | 0.998(9) | 1.010(6) |
|    | y | 0.215(10) | 0.233(12) | 0.233(5) | 0.2794(31) | 0.240(7) | 0.286(9) |
|    | z | 0.7074(21) | 0.715(6) | 0.7130(10) | 0.7145(12) | 0.7117(23) | 0.7227(32) |
| Fe6 | x | 0.5192(12) | 0.472(6) | 0.5106(10) | 0.4713(13) | 0.454(13) | 0.459(6) |
|    | y | 0.240(9) | 0.235(11) | 0.238(7) | 0.1994(31) | 0.216(13) | 0.188(7) |
|    | z | 0.4635(17) | 0.464(4) | 0.4725(9) | 0.4575(11) | 0.4848(54) | 0.4569(33) |
| Fe7 | x | 0.6971(13) | 0.725(6) | 0.7194(10) | 0.7365(11) | 0.702(8) | 0.739(4) |
|    | y | 0.249(6) | 0.256(8) | 0.226(4) | 0.2509(23) | 0.310(12) | 0.225(9) |
|    | z | 0.8677(19) | 0.846(4) | 0.8570(8) | 0.8608(13) | 0.8814(34) | 0.8516(27) |
| C1 & Si1 | x | 0.928(9) | 0.898(9) | 0.8224(26) | 0.8255(5) | 0.8968(12) | 0.835(7) |
|      | y | 0.290(6) | 0.556(5) | 0.523(27) | 0.4927(9) | 0.605(7) | 0.462(6) |
|      | z | 0.826(7) | 0.715(7) | 0.7683(37) | 0.7725(7) | 0.7878(18) | 0.764(5) |
| C2 & Si2 | x | 0.540(9) | 0.611(9) | 0.5762(41) | 0.5865(6) | 0.4914(9) | 0.563(6) |
|      | y | 0.550(5) | 0.560(5) | 0.551(24) | 0.5466(6) | 0.385(8) | 0.464(10) |
|      | z | 0.591(6) | 0.550(9) | 0.5636(38) | 0.5631(10) | 0.573(11) | 0.6193(12) |
| C3 & Si3 | x | 0.855(9) | 0.842(9) | 0.8505(37) | 0.8502(10) | 0.824(8) | 0.841(7) |
|      | y | 0.290(5) | 0.456(6) | 0.330(24) | 0.3325(8) | 0.743(34) | 0.486(8) |
|      | z | 0.455(11) | 0.478(8) | 0.4700(27) | 0.4712(10) | 0.427(14) | 0.483(6) |
|    | C1 & Si1 | Fe1 | Fe2 | Fe3 | Fe4 | Fe5 | Fe6 | Fe7 | C2 & Si2 | C3 & Si3 |
|----|---------|-----|-----|-----|-----|-----|-----|-----|---------|---------|
| x  | 0.7785(15) | 0.8198(35) | 0.6218(48) | 0.7656(60) | 1.0322(36) | 0.4793(43) | 0.7430(38) | 0.6092(10) | 0.8831(8) |
| y  | 0.9099(12) | 0.8376(22) | 0.6238(19) | 0.7736(15) | 1.0267(19) | 0.4773(17) | 0.7402(15) | 0.6899(19) | 0.9249(19) |
| z  | 0.791(11)  | 0.8283(20) | 0.6194(17) | 0.7725(27) | 1.0264(13) | 0.4806(17) | 0.7398(15) | 0.6178(18) | 0.9099(12) |

|    | C1 & Si1 | Fe1 | Fe2 | Fe3 | Fe4 | Fe5 | Fe6 | Fe7 | C2 & Si2 | C3 & Si3 |
|----|---------|-----|-----|-----|-----|-----|-----|-----|---------|---------|
| x  | 0.7211(14) | 0.8295(5)  | 0.6139(26) | 0.7728(28) | 1.0224(21) | 0.5024(38) | 0.7393(4)  | 0.6238(19) | 0.930(11) |
| y  | 0.776(12)  | 0.831(8)   | 0.6139(26) | 0.7720(8)  | 1.0239(4)  | 0.5024(38) | 0.7330(4)  | 0.6238(19) | 0.930(11) |
| z  | 0.7745(14) | 0.8295(5)  | 0.6139(26) | 0.7720(8)  | 1.0239(4)  | 0.5024(38) | 0.7330(4)  | 0.6238(19) | 0.930(11) |

|    | C1 & Si1 | Fe1 | Fe2 | Fe3 | Fe4 | Fe5 | Fe6 | Fe7 | C2 & Si2 | C3 & Si3 |
|----|---------|-----|-----|-----|-----|-----|-----|-----|---------|---------|
| x  | 0.791(11)  | 0.8283(20) | 0.6194(17) | 0.7725(27) | 1.0264(13) | 0.4806(17) | 0.7398(15) | 0.6178(18) | 0.9099(12) |
| y  | 0.776(12)  | 0.8295(5)  | 0.6139(26) | 0.7720(8)  | 1.0239(4)  | 0.5024(38) | 0.7330(4)  | 0.6238(19) | 0.930(11) |
| z  | 0.7745(14) | 0.8295(5)  | 0.6139(26) | 0.7720(8)  | 1.0239(4)  | 0.5024(38) | 0.7330(4)  | 0.6238(19) | 0.930(11) |
|   | 86(4) GPa | 90(5) GPa | 94(5) GPa | 98(5) GPa | 101(5) GPa | 104(5) GPa |
|---|-----------|-----------|-----------|-----------|------------|------------|
| Fe1 | x | 0.8190(10) | 0.8194(5) | 0.8193(10) | 0.8223(10) | 0.8219(8) | 0.8236(11) |
|    | y | 0.0339(24) | 0.0308(16) | 0.0290(24) | 0.0271(27) | 0.0287(21) | 0.0301(27) |
|    | z | 0.7169(9)  | 0.7152(6)  | 0.7153(10) | 0.7178(8)  | 0.7153(7)  | 0.7171(9)  |
| Fe2 | x | 0.6317(20) | 0.6314(11) | 0.6274(16) | 0.6177(17) | 0.6187(10) | 0.6146(16) |
|    | y | 0.0528(29) | 0.0500(18) | 0.0297(30) | 0.0155(35) | 0.0063(22) | 0.0040(38) |
|    | z | 0.6230(9)  | 0.6235(6)  | 0.6257(12) | 0.6234(13) | 0.6229(10) | 0.6224(11) |
| Fe3 | x | 0.7541(17) | 0.7532(9)  | 0.7590(14) | 0.7601(13) | 0.7593(11) | 0.7573(10) |
|    | y | 0.0798(25) | 0.0780(10) | 0.0696(18) | 0.0641(23) | 0.0611(15) | 0.0584(20) |
|    | z | 0.5383(10) | 0.5386(7)  | 0.5402(15) | 0.5390(12) | 0.5385(9)  | 0.5429(18) |
| Fe4 | x | 0.9162(13) | 0.9167(9)  | 0.9157(19) | 0.9187(19) | 0.9192(8)  | 0.9174(8)  |
|    | y | 0.2016(27) | 0.2002(15) | 0.1861(36) | 0.1868(29) | 0.1825(21) | 0.1895(26) |
|    | z | 0.8736(8)  | 0.8746(4)  | 0.8788(11) | 0.8823(9)  | 0.8813(9)  | 0.8820(14) |
| Fe5 | x | 1.0453(18) | 1.0468(7)  | 1.0573(15) | 1.0586(15) | 1.0581(6)  | 1.0598(8)  |
|    | y | 0.3002(31) | 0.2977(14) | 0.2987(21) | 0.3070(26) | 0.3106(16) | 0.3142(21) |
|    | z | 0.7124(10) | 0.7123(6)  | 0.7089(8)  | 0.7077(9)  | 0.7074(7)  | 0.7065(9)  |
| Fe6 | x | 0.5044(18) | 0.5042(11) | 0.4951(14) | 0.4924(14) | 0.4920(9)  | 0.4924(13) |
|    | y | 0.2077(27) | 0.2089(14) | 0.2097(23) | 0.2153(33) | 0.2149(21) | 0.2177(23) |
|    | z | 0.4632(9)  | 0.4640(5)  | 0.4669(17) | 0.4683(10) | 0.4659(7)  | 0.4635(12) |
| Fe7 | x | 0.7347(16) | 0.7344(10) | 0.7383(15) | 0.7344(14) | 0.7334(9)  | 0.7325(7)  |
|    | y | 0.1819(12) | 0.1822(8)  | 0.1760(13) | 0.1777(14) | 0.1758(8)  | 0.1783(11) |
|    | z | 0.8668(9)  | 0.8665(7)  | 0.8695(12) | 0.8665(11) | 0.8714(11) | 0.8741(13) |
| C1 & Si1 | x | 0.781(5)  | 0.7879(19) | 0.7892(47) | 0.7789(54) | 0.7751(27) | 0.7799(22) |
|    | y | 0.747(10) | 0.740(5)  | 0.722(9)  | 0.708(8)  | 0.706(4)  | 0.709(5)  |
|    | z | 0.9690(25) | 0.9763(15) | 0.9728(32) | 0.9750(27) | 0.9769(18) | 0.9785(20) |
| C2 & Si2 | x | 0.651(5)  | 0.6371(25) | 0.6326(43) | 0.6166(39) | 0.6145(26) | 0.6109(30) |
|    | y | 0.649(11) | 0.635(5)  | 0.644(6)  | 0.657(6)  | 0.652(4)  | 0.655(5)  |
|    | z | 1.0351(28) | 1.0371(15) | 1.0290(38) | 1.0333(43) | 1.0320(22) | 1.0307(23) |
| C3 & Si3 | x | 1.001(4)  | 0.9970(26) | 0.9928(34) | 1.0003(27) | 0.9958(30) | 1.0045(23) |
|    | y | 0.682(12) | 0.667(4)  | 0.661(6)  | 0.678(11) | 0.669(5)  | 0.663(5)  |
|    | z | 0.6302(33) | 0.6236(14) | 0.6288(32) | 0.6364(29) | 0.6321(21) | 0.6346(20) |