Novel high-pressure monoclinic Fe₂O₃ polymorph revealed by single crystal synchrotron X-ray diffraction studies

E. Bykova^{a,b,*}, M. Bykov^b, V. Prakapenka^c, Z. Konôpková^d, H.-P. Liermann^d, N. Dubrovinskaia^b,
L. Dubrovinsky^a

^a*Bavarian Research Institute of Experimental Geochemistry and Geophysics, University of Bayreuth, Bayreuth, Germany;* ^b*Laboratory of Crystallography, University of Bayreuth, Bayreuth, Germany;* ^c*Center for Advanced Radiation Sources, University of Chicago, IL 60437, USA;* ^d*Photon Science, , DESY, Hamburg, Germany.*

A novel high-pressure polymorph of iron sesquioxide, *m*-Fe₂O₃, has been identified by means of single crystal synchrotron X-ray diffraction. Upon compression of a single crystal of hematite, α -Fe₂O₃, in a diamond anvil cell, the transition occurs at pressure of about 54 GPa and results in ~10 % volume reduction. The crystal structure of the new phase was solved by the direct method (monoclinic space group $P2_1/n$, $a = 4.588(3)$, $b = 4.945(2)$, $c = 6.679(7)$ Å and $\beta = 91.31(9)^\circ$) and refined to $R_1 \sim 11\%$. It belongs to the cryolite double-perovskite structure type and consists of corner-linked FeO₆ octahedra and FeO₆ trigonal prisms filling the free space between the octahedra. Upon compression up to ~71 GPa at ambient temperature no further phase transition were observed. Laser heating to $\sim 2100 \pm 100$ K promotes a transition to *Cmcm* CaIrO₃-type (post-perovskite, PPv) phase. The PPv-Fe₂O₃ crystal structure was refined by means of single crystal X-ray diffraction at ~65 GPa. On decompression the PPv-Fe₂O₃ phase fully transforms back to hematite at pressures between ~25 and 15 GPa.

Keywords: phase transition; iron sesquioxide; single crystal X-ray diffraction; laser heating; diamond anvil cell

*Corresponding author. Email: knilav@gmail.com.

1. Introduction

High pressure behavior of iron sesquioxide, Fe_2O_3 , has been a long-standing subject of research due to its importance for mineral physics as a proxy for modeling materials behavior in deep Earth's interiors. From the solid state physics point of view the compound is interesting since at pressures between 40 and 60 GPa it undergoes a series of transformations manifesting in structural changes (transition to an orthorhombic phase with a large volume discontinuity ($\sim 10\%$) [1,2]), a drop of the resistivity [3,4], a spin crossover of Fe^{3+} [5], and a disappearance of the ordered magnetic state [3]. The crystal structure of the Fe_2O_3 -orthorhombic phase, which might shed light on the physics of the observed pressure-induced phenomena, has remained controversial for a long time. Perovskite [2,6] and Rh_2O_3 -II structural types [1,3,7] were proposed based on Mössbauer spectroscopy and powder X-ray diffraction (XRD) data. Recent single crystal XRD studies demonstrated that compression of hematite to 40 GPa and laser heating to 2300 K results in formation of the Rh_2O_3 -II-type phase with a rather small volume change ($\sim 1.3\%$) [8]. The crystal structure of the phase(s) observed on compression above 50 GPa at ambient temperature [3, 5, 7] is still under question since only powder XRD data were available so far and Mössbauer and Raman spectroscopy studies cannot provide definitive structural information.

A reconstructive phase transition was reported to occur during laser heating of Fe_2O_3 compressed above 70 GPa [9–11]. Powder X-ray diffraction pattern was indexed in the CaIrO_3 structure type; however crystallographic data provided was based only on a Rietveld refinement of the powder pattern. The CaIrO_3 structural type has been assigned to the high pressure modification of $(\text{Mg,Al})(\text{Si,Fe})\text{O}_3$ perovskite, known as post-perovskite; the transition perovskite – post-perovskite is thought to be responsible for many anomalies of the D" layer, the lowest part of the Earth's mantle [12].

An ambiguity in the crystal structure of Fe_2O_3 in the 40–60 GPa pressure region and the absence of precise crystallographic data for the post-perovskite Fe_2O_3 phase encouraged us to perform a series of high-pressure and high-temperature XRD experiments on single crystals that provides a more accurate unit cell parameters a structure model and refinement.

Within, we report high pressure behavior of hematite up to 50 GPa based on a single crystals study and compare our results with previously available data. We found a structural transition to a novel monoclinic phase, $m\text{-Fe}_2\text{O}_3$, space group $P2_1/n$, and analyzed its relations with Rh_2O_3 -II and perovskite type structures. Upon laser heating at about 70 GPa the monoclinic phase transforms to post-perovskite (PPv- Fe_2O_3 , space group $Cmcm$). The structure of the latter was preserved upon decompression down to at least ~ 25 GPa.

2. Experimental

2.1. Samples preparation

In this study we used the same hematite single crystals which were described in the work by Schouwink *et al.* [13]. High-quality single crystals with an average size of $0.03 \times 0.03 \times 0.005 \text{ mm}^3$ were pre-selected on a 3-circle Bruker diffractometer equipped with a SMART APEX CCD detector and a high-brilliance Rigaku rotating anode (Rotor Flex FR-D, Mo-K α radiation) with Osmic focusing X-ray optics.

2.2. High-pressure experiments

All high-pressure experiments have been performed using the diamond anvil cell (DAC) technique. Pressure was generated by means of 4-screw-driven BX90 type DACs [14] equipped with Boehler-Almax [15] or spherical diamond [16] anvils (250 μm culet sizes). Rhenium gaskets were pre-indented to about 30 μm thickness and drilled with a 120 μm hole and placed between two diamonds to form a pressure chamber. The pressure chamber with the sample and a small ruby chip was loaded with Ne at ~ 1.5 kbar using the gas-loading system installed in Bayerisches Geoinstitut by means of mechanical closing of the DACs [17]. Pressure was determined using the ruby R_1 fluorescence line as a pressure marker and by measuring a position of the (111) X-ray diffraction line of Ne (<http://kantor.50webs.com/diffraction.htm>).

Upon compression of hematite up to 54 GPa at ambient temperature X-ray diffraction measurements were carried out in an angle-dispersive mode ($\lambda = 0.3344 \text{ \AA}$, the beam size $4 \times 8 \text{ }\mu\text{m}^2$) at the 13-IDD beamline at the Advanced Photon Source (APS), the Argonne National Laboratory. X-ray diffraction wide images (from -35 to $+35^\circ$ on omega) were collected with a MAR CCD detector at three different positions to increase a coverage of the reciprocal space. The sample was compressed from 12 to 40 GPa with a 5 to 7 GPa step and afterwards the pressure steps were decreased to ~ 2 GPa. For several pressure points a complete data collection was performed by narrow 1° omega-scanning in a range from -35 to $+35^\circ$.

Another set of experiments has been performed at the Extreme Conditions Beamline (P02.2) at PETRA III, Hamburg, Germany ($\lambda = 0.28978 \text{ \AA}$, beam size $2.3(\text{H}) \times 1.4(\text{V}) \text{ }\mu\text{m}^2$). Diffraction images were collected using a Perkin Elmer flat panel detector by 1° omega-scanning from -40 to $+40^\circ$. The first experiment with Fe_2O_3 was used to collect single crystal XRD data from 48 to 71 GPa with a 5 to 7 GPa step. The second one, compressed to 68 GPa, was heated for about 5 min with a NIR laser at $2100 \pm 100 \text{ K}$ and quenched afterwards. Then the sample was decompressed to 15 GPa with 5 to 10 GPa steps. At every step XRD wide images were obtained

(from -35 to $+35^\circ$ of omega), and for several pressure points a complete data collection was performed as described above.

The data treatment (integration and absorption corrections) collected at the Extreme Conditions Beamline was performed with the CrysAlis RED [18] software. The collection of intensities from wide-scan images collected at GSECARS the refinement of the unit cell parameters was done using GSE ADA software [19]. The structures were solved by the direct method and refined by full matrix least-squares using the SHELXS and SHELXL software [20], respectively, implemented in the X-Seed program package [21]. The results of the crystal structure refinement for $m\text{-Fe}_2\text{O}_3$ and $\text{PPv-Fe}_2\text{O}_3$ phases at 54.3(2) and 64.6(2) GPa, respectively, and ambient temperature are summarized in Table 1.

3. Results and discussion

3.1. Compression of hematite, $\alpha\text{-Fe}_2\text{O}_3$.

Figure 1a presents the pressure dependence of the normalized unit cell volume, V/Z , (V is the unit cell volume, Z is the number of formula units per a unit cell) for hematite and high-pressure modifications of Fe_2O_3 . The room temperature P – V data for hematite obtained in the present work agree well with those reported by Schouwink *et al.* [13], who compressed a single crystal up to 25 GPa (solid line in Fig. 1a corresponds to the equation of state from [13]). Combining Schouwink's *et al.* [13] data and our new results on compression of a single crystal of hematite to over 52 GPa, we have refined the 3rd order Birch-Murnaghan equation of state [23] keeping the value of $V_0 = 301.88(18) \text{ \AA}^3$ constant. Obtained $K = 201(4) \text{ GPa}$ and $K' = 4.3(2)$ are fairly close to the previously reported values ($K = 199(8) \text{ GPa}$, $K' = 5.3(9)$ [13]). The compressibility data reported for hematite powder samples [1,7] disagree with thus of Schouwink's *et al.* [13] and our new results. Latter may contributed to the non-hydrostatic stresses propagating though powder specimens. However, the variation of the ratio of the lattice parameters c/a with pressure (Fig. 1b) is similar for all the datasets; the c/a ratio decreases with pressure [1,7,8,10,13,24,25]. The same trend was observed in corundum-like V_2O_3 and Ti_2O_3 undergoing a pressure-induced insulator-to-metal transition [26], while corundum itself (Al_2O_3) displays a constant c/a ratio during compression, thus remaining an insulator [27].

3.2. Phase transformation upon compression at ambient temperature.

Upon compression, at 54.3(2) GPa we observed the appearance of new reflections (Fig. 2 *a, b*) that indicated a phase transformation. The transition pressure could be determined very accurately, since the transformation

was repeated within 0.3(2) GPa during two experiments at different high-pressure diffraction facilities. An inspection of the reciprocal space using “Ewald sphere explorer” available within the Crysalis software, revealed a formation of two pronounced twin domains rotated by $\sim 120^\circ$ (Fig. 1c). The formation of the similarly oriented twin domains was observed in two independent experiments. Overlapping of multiple peaks due to the specific orientation of the twin domains was successfully overcome by using small integration masks. Nevertheless, the reliable R_{int} values have been obtained only in one experiment conducted at pressure of ~ 54 GPa. This data set enabled us to solve the structure of the new phase, called $m\text{-Fe}_2\text{O}_3$, immediately after the phase transition. We found a monoclinic unit cell (space group $P2_1/n$) with $a = 4.588(3)$, $b = 4.945(2)$, $c = 6.679(7)$ Å and $\beta = 91.31(9)^\circ$ (see Table 1 for structural details).

The unit cell parameters of $m\text{-Fe}_2\text{O}_3$ are very close to those of the orthorhombic phase previously reported on compression of hematite at ambient temperature [1,2,7,11] in powder XRD experiments. The splitting of the reflections, reducing the symmetry to monoclinic, might have not been noticed earlier due to the broadening of the reflections accompanying the compression under non-hydrostatic conditions.

The crystal structure of $m\text{-Fe}_2\text{O}_3$ can be described as the so-called double perovskite structure with a general formula $A_2B'B''O_6$ [28]. Figure 3 illustrates relations between the monoclinic cryolite-type (space group $P2_1/n$) and orthorhombic GdFeO_3 -type (space group $Pbnm$) perovskite structures. Both are constructed of a 3-dimensional network of tilted corner-shared BO_6 octahedra (B site in the orthorhombic perovskite and crystallographically non-equivalent B' and B'' sites in the monoclinic double perovskite) with additional A -atoms located inside bicapped trigonal prismatic voids (A -site). In monoclinic cryolite-type double perovskites B' and B'' atoms have distinctly different atomic radii either due to an occupation with different atomic species (ex. $\text{Ca}_2\text{FeMoO}_6$, Ca_2MnWO_6 [29,30]) or with cations of alternating charges (ex. $\text{Ba}_2\text{Bi}^{3+}\text{Bi}^{5+}\text{O}_6$ [31]). In the case of Fe_2O_3 all metal sites are occupied by Fe but interatomic distances differ (see Table 2); $\text{Fe}_3\text{—O}$ (A site) distances are considerably larger than $\text{Fe}_1\text{—O}$ and especially $\text{Fe}_2\text{—O}$ are stretched (B' and B'' sites); a possible explanation for this phenomenon is described below. The A -void demonstrates a significant scatter of Fe—O distances, two of them (2.37(3) and 2.39(3) Å) are much larger in comparison to the remaining six distances (1.87(3)—2.196(16) Å). The six oxygen atoms form a trigonal prism around the Fe atom. If the two longer Fe—O contacts are included into the coordination polyhedron of Fe in the A -position, the polyhedron acquires a shape of a bicapped trigonal prism (Fig. 3).

The monoclinic cryolite-type structure can be described in terms of the parent orthorhombic perovskite structure plus a symmetry breaking structural distortion corresponding to the irreducible representation Γ_3^+ [32]. In the GdFeO_3 perovskite Fe_1 and Fe_2 atoms, as well as O_1 and O_2 atoms, are equivalent and related by a mirror

plane perpendicular to the c -axis (in $Pbnm$ setting), while Fe3 and O3 atoms are located on the mirror plane. The distortion moves the O3 atom from the mirror plane towards to Fe2 position which breaks mirror plane symmetry and results in two non-equivalent positions for both Fe and O atoms.

A reason for formation of Fe_2O_3 with the monoclinic double perovskite cryolite-type structure may be an alternation of the electronic (low-spin, LS, and high-spin, HS) state of the iron atoms. The Fe^{3+} ion in the low-spin state possesses a smaller atomic radius compared to that in the high-spin state, so that systematically shorter Fe2—O distances (1.74(4)—1.81(2) Å) compared to the Fe1—O ones (1.82(2)—1.92(3) Å) may indicate the spin crossover (the HS-to-LS transition) in Fe^{3+} at the Fe2 position associated with the atom shift responsible for the monoclinic distortion in the structure of Fe_2O_3 . The drastic volume reduction at ca. 54 GPa also supports this assumption. Structural transitions associated with the spin crossover in Fe^{3+} under pressure (in the same pressure region of about 50 GPa) are known for CaFe_2O_4 [33], FeOOH [34] and FeBO_3 (private communication with E. Greenberg). The Fe2—O distances in $m\text{-Fe}_2\text{O}_3$ are well consistent with the possible LS state of Fe2 if compared with the corresponding literature data (Fig. 4). However, the Fe1—O distances are rather short for HS Fe1 state, therefore the question about the spin state of iron in different structural positions in $m\text{-Fe}_2\text{O}_3$ cannot be presently answered unambiguously and requires further Mössbauer spectroscopy studies. Note that larger interatomic Fe—O distances 1.820(11)—2.146(19) Å reported for the Rh_2O_3 -II-type Fe_2O_3 phase [8] supported the HS state for Fe in this phase synthesized upon laser heating at about 40 GPa [8, 25] (Fig. 4).

Hematite and $m\text{-Fe}_2\text{O}_3$ structures are not connected by the group-subgroup relations. However, they consist of the common building blocks shown in Fig. 5. Hematite (corundum-type) structure can be considered as a set of layers of corner-shared FeO_6 octahedra stacked along the $[1\bar{1}2]$ direction with additional Fe atoms located in the octahedral voids. The layers are shifted with respect of each other in the (1-12) plane and connected via shared vertices of octahedra. In the $m\text{-Fe}_2\text{O}_3$ structure two layers are related with the mirror plane symmetry and, as a result, the void changes from octahedral to bicapped prismatic one. The distortion from the corundum to Rh_2O_3 -II-type structure has a rather different mechanism and, according to [35], requires altering a position of 1/6 of oxygen atoms. Both structures are considered as a combination of pairs of MO_6 octahedra with common faces [35], but in the corundum structure such pairs share three common edges and in Rh_2O_3 -II-type structure only two. The transformation of the corundum-type hematite structure to $m\text{-Fe}_2\text{O}_3$ destroys pairs of the FeO_6 octahedra and preserves only the corner-shared network.

3.3. Phase transformation of $m\text{-Fe}_2\text{O}_3$ into $\text{PPv-Fe}_2\text{O}_3$ upon laser heating above 70 GPa.

Formation of a new phase during laser heating above 2500 K of Fe_2O_3 compressed to 70 GPa was first observed by Ono *et al.* [9,10] by means of powder XRD in the DAC and the phase was assigned an orthorhombic cell (the $Cmcm$ space group), the CaIrO_3 structural type ($\text{PPv-Fe}_2\text{O}_3$). More recent studies were concentrated mostly on magnetic and electronic properties of the HP phase [11]; however no accurate data for atomic coordinates were reported so far. We observed a formation of $\text{PPv-Fe}_2\text{O}_3$ upon laser heating of $m\text{-Fe}_2\text{O}_3$ at 2100 ± 100 K compressed to ~ 68 GPa. Laser heating resulted in a formation of variety of closely-oriented single crystals (Fig. 6). Nevertheless the peaks remained sharp and well resolved; therefore the data integration using small masks provided appropriate results for data collected at 65 GPa. Upon decompression the number of domains decreased and at 25 GPa only two distinct domains mutually rotated by $\sim 5^\circ$ along the b axis remained.

Crystal structure of the $\text{PPv-Fe}_2\text{O}_3$ phase displays two independent positions for the iron atoms, namely Fe1 with the octahedral coordination and Fe2 with the bicapped trigonal prismatic (Table 2). Octahedra connect via common edges in rutile-like layers stacked along the b direction. The octahedral layers are interconnected by the face-shared bicapped trigonal prisms (Fig. 7). The Fe2—O interatomic distances in the prisms of $1.938(11)$ — $2.189(13)$ Å in $\text{PPv-Fe}_2\text{O}_3$ are longer than those in $m\text{-Fe}_2\text{O}_3$ suggesting the HS state of iron, while the distances in octahedra (three of $1.772(7)$ and three of $1.862(8)$ Å) are considerably smaller and suggest the LS state of the Fe^{3+} ions in the Fe1 position. Synchrotron nuclear forward scattering study and *ab initio* calculations performed by Shim *et al.* [11] suggested the HS state for Fe in the prism position in $\text{PPv-Fe}_2\text{O}_3$ while the spin assignment of iron in octahedra remained uncertain [11].

3.4. Compressional behavior of high-pressure polymorphs of Fe_2O_3 .

Among metal sesquioxides, $M_2\text{O}_3$, corundum, Al_2O_3 , and bixbyite, $(\text{Mn,Fe})_2\text{O}_3$, structural types are known to be common at ambient conditions. Corundum structure is composed of a hexagonal closest packing of oxygen atoms with $2/3$ of the octahedral voids being occupied by a metal atom. Each MO_6 polyhedron shares 3 edges with neighboring polyhedra forming honeycomb-like layers and, in addition one face with the polyhedron from the neighboring layer. Cubic bixbyite can be described as the CaF_2 -type structure with $1/4$ of oxygen being removed creating a network of MO_6 octahedra connected only through edges.

Compression of compounds induces a formation of phases with higher degree of the packing density. For the $M_2\text{O}_3$ family the coordination number of the cation can remain and the increase of the density is achieved through a strong distortion of the octahedra like in $\text{Rh}_2\text{O}_3\text{-II}$ [35]. Much more effective volume reduction in sesquioxides could be achieved through the increase of the metal coordination number. For example, so-called

A-RES and B-RES structural types, with 7-coordinated metal atoms appear during compression of Eu^{3+} -doped Y_2O_3 [36]. High-pressure and high-temperature treatment of B-RES-type phases of Sc_2O_3 and Y_2O_3 results in formation of the Gd_2S_3 -type structure with 7+8-fold coordination polyhedra [37,38]. At ~ 15 GPa and upon heating to ~ 1200 K Ti_2O_3 transforms into the Th_2S_3 -type phase with the metal coordination number varying from 6 to 8 [39,40]. So far, the transition to perovskite and post-perovskite structural types having 8-coordinated metal atoms in bicapped trigonal prisms has been reported only for Mn_2O_3 [41].

In our experiments the orthorhombic Fe_2O_3 (Rh_2O_3 -II-type) phase was not observed during compression up to 73 GPa at ambient temperature; a transformation to the monoclinic ($P2_1/n$) phase was detected at 54 GPa instead. The transition to the Rh_2O_3 -II-type phase [8] is accompanied with an abrupt volume decrease but it is relatively small ($\sim 1.3\%$) to be attributed to the HS-to-LS transition suggested previously [5]. Contrary, a significant difference in molar volumes of $m\text{-Fe}_2\text{O}_3$ and hematite ($\sim 10.2\%$) points toward the spin crossover upon transition accompanied with a structural change. The volume discontinuity in Fe_2O_3 of about 10 % at 50 GPa has been reported in [1,2], but the high-pressure phase was indexed in the orthorhombic unit cell. Although both Rh_2O_3 -II-type and $m\text{-Fe}_2\text{O}_3$ phases were observed at close P,T -conditions, it seems that the former appears only upon heating even at moderate pressures (~ 32 GPa and 800 K according to [25]), while the latter forms during compression above 54 GPa at ambient temperature (as observed in our single crystal X-ray diffraction experiments).

The laser heating at 68 GPa results in a transition to the orthorhombic ($Cmcm$) PPv- Fe_2O_3 phase. Studies of this phase performed on decompression for the first time unambiguously show that PPv- Fe_2O_3 can be preserved down to pressures of 25 GPa; any traces of the post-perovskite phase disappear upon pressure release to 15 GPa (Fig. 6, *c* and *d*).

The quality of the P — V data obtained in the current study on compression of $m\text{-Fe}_2\text{O}_3$ and on decompression of PPv- Fe_2O_3 appeared insufficient for accurate determination of the EOSs of these phases because of the multi-domain nature of samples and weak peaks intensities. However, available data suggest that the molar volumes of $m\text{-Fe}_2\text{O}_3$ and PPv- Fe_2O_3 are quite similar (Fig. 1). We would like to note that the molar volume difference between perovskite and post-perovskite phases for a number of compounds (namely, NaNiF_3 , NaZnF_3 , MgSiO_3 , MgGeO_3 , MnGeO_3 , CaSnO_3 , CaRuO_3 , CaRhO_3 , CaIrO_3) is just about 1.5% [42].

4. Conclusions

In the present work we describe in detail the structural changes that occur during the compression of single crystals of α -Fe₂O₃ and its transition to a double-perovskite-type phase with the monoclinic unit cell (space group P2₁/n) at about 54 GPa. The transition associated with a drastic volume reduction of 10.2 % unlike to the previously reported phase transition to the Rh₂O₃-II-type phase, which resulted in only a ~1.3 % volume change [8]. The analysis of the interatomic Fe—O distances in *m*-Fe₂O₃ suggests the HS-LS crossover in iron atoms located at least in one of the two octahedral positions. Based on available single crystal X-ray diffraction data we suggest that the iron sesquioxide undergoes a reconstructive transition to the Rh₂O₃-II-type phase only upon heating at pressures below 50 GPa, while at room temperature it transforms to the *m*-Fe₂O₃ phase at 54 GPa. Laser heating at 70 GPa provokes a transition to the post-perovskite (*Cmcm*) structure.

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Table 1. Crystallographic data for $P2_1/n$ (54.3(2) GPa) and $Cmcm$ (64.6(2) GPa) phases of Fe_2O_3 at room temperature.

	$P2_1/n$	$Cmcm$
a (Å)	4.588(3)	2.665(3)
b (Å)	4.945(2)	8.609(5)
c (Å)	6.679(7)	6.379(6)
β (°)	91.31(9)	90
V (Å ³)	151.5(2)	146.4(2)
Z	4	4
$F(000)$	304	304
Facility	ID-13D GSECARS, APS	P02.2 ECB, Petra III
Wavelength (Å)	0.33440	0.28978
Theta range for data collection (°)	2.51 to 10.81	2.33 to 10.31
Completeness to $d = 0.8$ Å (%)	54.6	79.0
Index ranges	$-4 < h < 4,$ $-5 < k < 5,$ $-5 < l < 6$	$-2 < h < 2,$ $-10 < k < 9,$ $-6 < l < 7$
Reflections collected	218	160
Independent reflections / R_{int}	124 / 0.0553	79 / 0.0638
Refinement method	Full matrix least squares on F^2	Full matrix least squares on F^2
Data / restraints / parameters	124 / 0 / 19	79 / 0 / 9
Goodness of fit on F^2	1.363	1.225
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.1111, wR_2 = 0.3068$	$R_1 = 0.0970, wR_2 = 0.2256$
R indices (all data)	$R_1 = 0.1195, wR_2 = 0.3241$	$R_1 = 0.1017, wR_2 = 0.2427$

Largest diff. peak and hole (e / Å ³)	1.746 and -1.813	3.645 and -4.298
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Atomic coordinates and equivalent isotropic displacement parameters (Å²)

Fe1 2 <i>a</i> (0, 0, 0, 0.027(3))	Fe1 4 <i>a</i> (0, 0, 0, 0.0070(19))
Fe2 2 <i>b</i> (0, 0, 0.5, 0.030(3))	Fe2 4 <i>c</i> (0, 0.2467(3), 0.25, 0.0059(19))
Fe3 4 <i>e</i> (0.5282(11), 0.0828(11), 0.7505(8), 0.030(3))	O1 4 <i>c</i> (0.5, 0.4102(17), 0.25, 0.010(4))
O1 4 <i>e</i> (0.338(5), 0.185(3), 0.072(4), 0.023(5))	O2 8 <i>f</i> (0.5, 0.1443(13), 0.060(2), 0.010(3))
O2 4 <i>e</i> (0.325(6), 0.181(3), 0.430(4), 0.036(6))	
O3 4 <i>e</i> (0.852(6), 0.063(3), 0.262(5), 0.030(6))	

Table 2. Interatomic distances (Å) in a double perovskite $P2_1/n$ (at 54.3(2) GPa) and post-perovskite $Cmcm$ (at 64.6(2) GPa) phases of Fe_2O_3 at ambient temperature.

$P2_1/n$		$Cmcm$	
Octahedron 1		Octahedron	
Fe1—O2	1.82(2)x2	Fe1—O1	1.772(6)x2
Fe1—O1	1.85(2)x2	Fe1—O2	1.861(8)x4
Fe1—O3	1.92(3)x2	Bicapped trigonal prism	
Octahedron 2		Fe2—O1	1.938(11)x2
Fe2—O3	1.74(4)x2	Fe2—O2	2.007(9)x4
Fe2—O1	1.796(15)x2	Fe2—O2	2.189(13)x2
Fe2—O2	1.81(2)x2		
Bicapped trigonal prism			
Fe3—O1	1.87(3)		
Fe3—O3	1.89(3)		
Fe3—O2	1.910(19)		
Fe3—O3	1.931(19)		
Fe3—O2	2.14(3)		
Fe3—O1	2.196(16)		
Fe3—O2	2.37(3)		
Fe3—O1	2.39(3)

Figure 1. Volume compressibilities for Fe_2O_3 polymorphs (a) and the c/a ratio of hematite as a function of pressure (b). All **black symbols** designate XRD experiments performed in the current work, **colored symbols** are for literature data [8,10,13,24,25]. The green dots correspond to the equation of state of hematite from [13]. Symbol's type indicates the crystal structure observed: $\diamond$ - $R\text{-}3c$ (hematite); $\circ$ - $Pbna$ (Rh_2O_3 -II structural type); $\triangle$ - $P2_1/n$ (double perovskite cryolite structural type); $\square$ - $Cmcm$ (post-perovskite structural type). Unsantanities in V/Z values are within the symbol size.

Figure 2. Rotation images of Fe_2O_3 at 52.4 GPa (a) and at 54.3 GPa (b). Squares show predicted positions of the Fe_2O_3 reflections based on the unit cell parameters. At 54.3 GPa the peaks split and in addition the new peaks appear that suggests a formation of a new phase. Inspection of the reciprocal space suggests 2 twin domains rotated by 120° .

Figure 3. Relations between orthorhombic GdFeO_3 -type perovskite (a) and double perovskite cryolite-type (b) structures. The perovskite structure contains a 3 dimensional network of corner-shared FeO_6 octahedra (*B*-position) and additional Fe atoms located in bicapped trigonal prismatic voids (*A*-position). In the double perovskite structure *B*-position is occupied by two alternating atomic species (Fe1 and Fe2 designated by darker and lighter colors). Fe3 atom possessing two significantly larger Fe3—O distances could be considered as having trigonal-prismatic coordination with two additional Fe—O bonds (c).

Figure 4. Average Fe-O distances in FeO₆ octahedra. All **black symbols** with the error-bars designate XRD results of the current work, **colored symbols** are for literature data [8,13,33,34]. Symbols type indicates on a crystal structure observed: ◇ - *R-3c* (hematite); ○ - *Pbna* (Rh₂O₃-II structural type); △ - *P2₁/n*; □ - *Cmcm* (post-perovskite structural type).

Figure 5. Similarity of building blocks in corundum-type (*a*) and double perovskite (*b*) structures. In the double perovskite structure *B*-position is occupied by Fe1 and Fe2 atoms (FeO_6 octahedra are designated by darker and lighter colors). The same fragments are marked at the corundum structure.

Figure 6. Central part of rotation images of Fe_2O_3 at 68.3 GPa ($P2_1/n$ phase) at ambient temperature (a) and at 68.8 GPa after laser annealing which induces the formation of the closely oriented crystals (b). During decompression intensity of the peaks belonging to the $Cmcm$ phase decreases (c) and they completely disappear to 15 GPa that indicates complete transformation back to the multi-domain hematite phase (d). Circles designate corresponding phases; diamond peaks and diffraction lines attributed to neon are not marked.

Figure 7. Crystal structure of the PPv- Fe_2O_3 ($Cmcm$) phase which possess two independent iron atoms, namely Fe1 with the octahedral coordination and Fe2 with the bicapped trigonal prismatic one.