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Discovery of Fe_7O_9: a new iron oxide with a complex monoclinic structure

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Ryosuke Sinmyo[1], Elena Bykova[1,2], Sergey V. Ovsyannikov[1], Catherine McCammon[1], Ilya Kupenko[3], Leyla Ismailova[1,2] & Leonid Dubrovinsky[1]

Iron oxides are fundamentally important compounds for basic and applied sciences as well as in numerous industrial applications. In this work we report the synthesis and investigation of a new binary iron oxide with the hitherto unknown stoichiometry of Fe_7O_9. This new oxide was synthesized at high-pressure high-temperature (HP-HT) conditions, and its black single crystals were successfully recovered at ambient conditions. By means of single crystal X-ray diffraction we determined that Fe_7O_9 adopts a monoclinic *C2/m* lattice with the most distorted crystal structure among the binary iron oxides known to date. The synthesis of Fe_7O_9 opens a new portal to exotic iron-rich $(M,Fe)_7O_9$ oxides with unusual stoichiometry and distorted crystal structures. Moreover, the crystal structure and phase relations of such new iron oxide groups may provide new insight into the cycling of volatiles in the Earth's interior.

Iron oxides have great importance for all natural sciences as well as numerous industrial applications. Considering the high abundance of oxygen and iron in the Earth's crust and the mantle, binary iron oxides and their derivatives are important endmembers of phases that make a significant contribution to properties of the Earth. Many studies have been devoted to investigations of various properties of iron oxides at conditions relevant to the Earth's interior, i.e., at high pressure or at high pressure combined with high temperature (HP-HT). These studies reported a number of remarkable findings for the three basic iron oxides, $Fe_{1-x}O$ wüstite[1,2], α-Fe_2O_3 hematite[3–8], and Fe_3O_4 magnetite[9–11]. Meanwhile, several experimental and theoretical studies indicated that the chemistry of iron oxides at extreme conditions of high pressure and high temperature may extend to intriguing behavior beyond these three well-known oxides[12–15]. For instance, recent experimental HP-HT investigations in the pressure range of 10–20 GPa reported two new orthorhombic *Cmcm* polymorphs with Fe_4O_5[13] and Fe_5O_6[14] stoichiometry, i.e., between Fe_3O_4 and $Fe_{1-x}O$, and hence, with mixed Fe^{2+} and Fe^{3+} oxidation states. More interestingly, using modern theoretical methods an opposite tendency in the stoichiometry changes in Fe-O systems was found, suggesting an extended stability of ferric hematite and a gradual shift to Fe^{4+}–bearing oxides at megabar pressures[15]. In particular, these studies predicted the existence of a new exotic FeO_2 oxide with highly charged Fe^{4+} ions that should have an extended range of stability against decomposition under megabar pressures[15]. Recently, a number of experimental studies have shown the important role of the iron oxides under HP-HT conditions in the Earth's deep interior[16–19]. Decomposition reactions of iron oxides and oxyhydroxides may induce the release of oxygen or hydrogen in the Earth's lower mantle[17,18].

In addition to their obvious and primary importance for geosciences, iron oxides play crucial roles in many technological processes and applications, and remain among a handful of key materials with significant impact on the fundamental behavior of materials, including charge carrier transfer and interactions, spin dynamics of electrons, and other central topics. In other words, iron oxides are important prototype materials. For instance, the oldest-known natural magnet, magnetite, demonstrates a fascinating 'metal-insulator'-type transition near 120–125 K[20], named later as the 'Verwey transition' after its discovery in 1939. This Verwey transition was believed to be related to charge ordering on octahedral sites in the spinel structure, and has been hotly debated for decades. Only recently it was revealed that this transition is linked to formation of hitherto unknown 'quasiparticles' consisting of three bonded Fe ions called 'trimerons'[21]. In hematite another landmark transition was discovered near 255 K with a related abrupt and drastic reorientation of spins of Fe^{3+} ions, named afterwards as a

[1]Bayerisches Geoinstitut, Universität Bayreuth, D-95440 Bayreuth, Germany. [2]Laboratory of Crystallography, Universität Bayreuth, D-95447 Bayreuth, Germany. [3]European Synchrotron Radiation Facility, BP220, F-38043 Grenoble, France. Correspondence and requests for materials should be addressed to R.S. (email: ryosuke.sinmyo@elsi.jp)

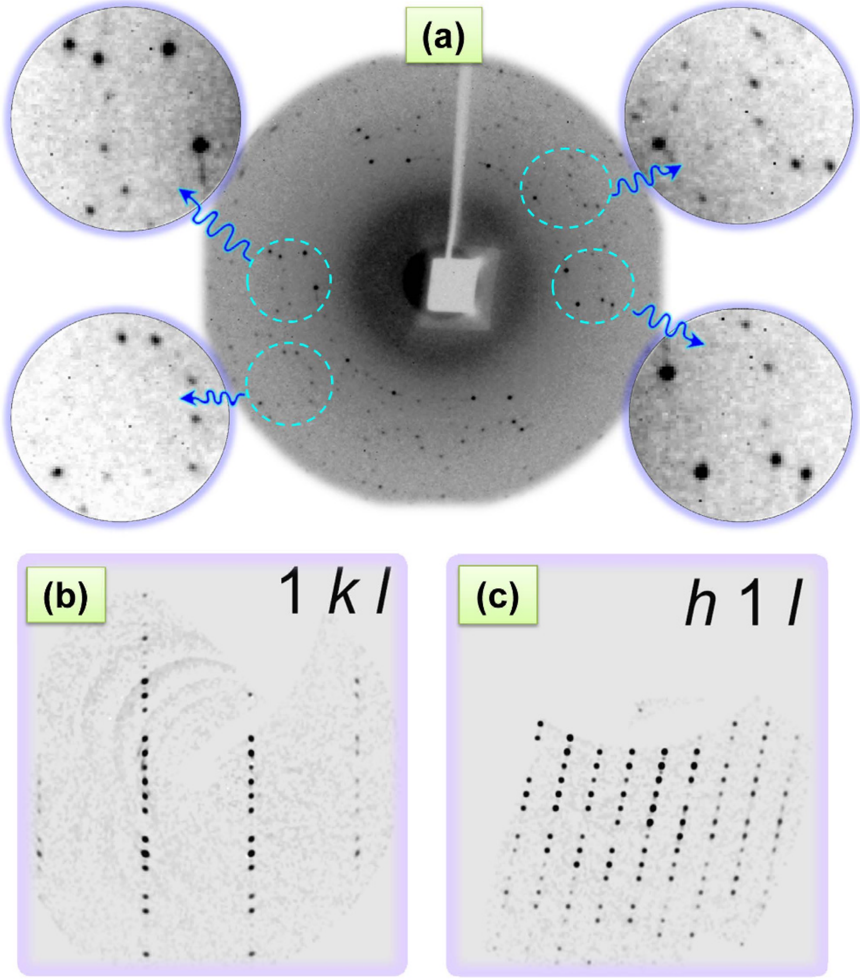

Figure 1. X-ray diffraction images. (**a**) Example of X-ray diffraction image of microscopic single crystal of $(Mg,Fe)_3Fe_4O_9$ collected at ambient conditions under rotation of a sample over 360 degrees in a beam. This image contains several hundreds of small well-resolved reflections. Insets show selected magnified areas of this image that better show indistinct reflections. (**b**,**c**) Projections of these X-ray diffraction data in reciprocal space, for two selected planes, *1kl* (**b**) and *h1l* (**c**).

'spin-flop' or Morin transition[22]. Also iron-deficient wüstite, $Fe_{1-x}O$, displays puzzling complexities with regard to stoichiometry, defect structure, and elastic and physical properties[23–28], and serves as a prototype for systems with non-stoichiometry. Recently it was experimentally demonstrated that, similar to magnetite, the newly-discovered Fe_4O_5[13] also undergoes an unprecedented 'metal-insulator'–type transition upon cooling below 150 K with competing dimeric and trimeric ordering in the Fe chains, leading to strong structural modulations[29]. Therefore, synthesis of new iron oxides with both mixed Fe^{2+} and Fe^{3+} valences and bearing highly charged Fe^{4+} ions is of significant interest for many scientific fields.

In the present work we investigated the phase stability of iron oxides at HP-HT conditions (see Methods) and discovered in samples recovered at ambient conditions the presence of crystals of a new iron oxide with unusual Fe_7O_9 stoichiometry. Fe_7O_9 with its ratio of Fe/O ~ 0.777 lies between Fe_3O_4 and newly-discovered Fe_4O_5[13], but in contrast to both, it is non-magnetic at ambient conditions and adopts a monoclinic crystal structure with four sites for Fe cations. These observations combined with the difference in Fe^{3+}/Fe^{2+} ratios ($^4/_3$ in Fe_7O_9 *versus* 2 in Fe_3O_4 and 1 in Fe_4O_5) suggest that the physical properties of Fe_7O_9 may be remarkably different. In addition, we also synthesized Fe_7O_9 containing a significant amount of Mg and discuss possible geological implications for this new polymorph.

Results and Discussion

Single crystal XRD measurements. The single crystals of pure Fe_7O_9 and Mg-doped $(Mg,Fe^{2+})_3Fe^{3+}{}_4O_9$ had sizes less than 50 μm in their linear dimensions that restricted detailed investigations of their properties. The chemical composition of the samples was determined using conventional electron microprobe methods and from single crystal X-ray diffraction data. We also collected Mössbauer spectra from these samples to determine the oxidation states of the Fe ions.

By means of single crystal X-ray diffraction on the crystals (Fig. 1 and Supplementary Figure 1) we solved and refined the crystal structures of Fe_7O_9 and $(Mg,Fe^{2+})_3Fe^{3+}{}_4O_9$ at ambient conditions and confirmed their

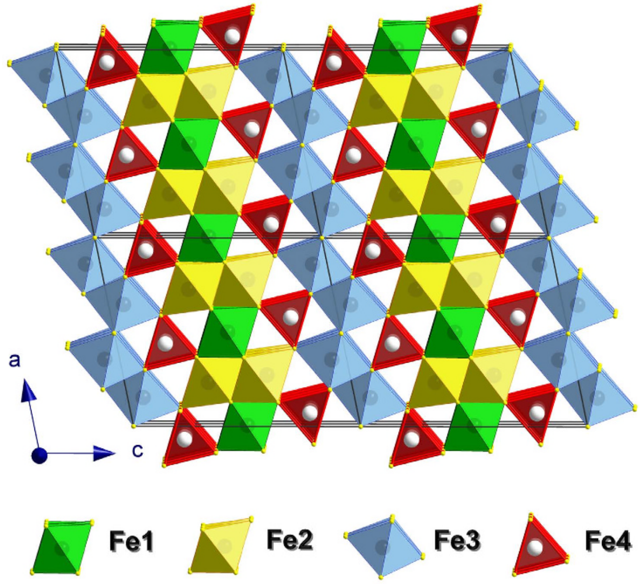

Figure 2. The crystal structure of Fe_7O_9. This structure corresponds to ambient conditions and is shown in a projection along the *b* axis.

stoichiometry. Crystals of Fe_7O_9 and $(Mg, Fe^{2+})_3Fe^{3+}{}_4O_9$ had no pronounced asymmetry in their shape, but were rather small ($0.03 \times 0.02 \times 0.01$ and $0.03 \times 0.02 \times 0.02\,mm^3$), so it was not possible to perform an analytical absorption correction based on crystal shape. Crystals of Fe_7O_9 appeared to be twinned, and due to the high degree of peak overlap (>50%), we had to integrate both twin domains simultaneously to perform a refinement of the crystal structure against HKLF5 data (BASF value was about 49.8%). The twinning could also influence the quality of determination of the anisotropic parameters. For consistency, we also refined the structure in an isotropic approximation and demonstrated a negligible influence on the atomic positions (CIF-files in the Supplementary Materials). Technical details of the structure determinations are summarized in Tables S1 and S2 in the Supplementary Materials. We established that both compounds adopt the same monoclinic structure of the $C2/m$ space group. The unit cell parameters in Fe_7O_9 are as follows: $a = 9.696(2)$ Å, $b = 2.8947(6)$ Å, $c = 11.428(3)$ Å, $\beta = 101.69(2)°$, $V = 314.10(12)$ Å^3, and $Z = 2$ (Fig. 2, and Tables S1 and S2 and CIF-files in the Supplementary Materials). The crystal structure of Fe_7O_9 has four different crystallographic sites for cations, three (Fe1, Fe2, Fe3) are octahedrally–coordinated and connected in a 3D network, while the fourth, Fe4, has a trigonal-prismatic arrangement (Fig. 2 and Table S2 in the Supplementary Materials). By analyzing the Fe-O bond distances in this polymorph using a bond valence sums (BVS) method[30], we established the average oxidation state for Fe ions occupying the Fe1, Fe2, Fe3, and Fe4 sites to be +2.74, +2.72, +2.82, and +2.10, respectively. Thus, we conclude that the Fe4 sites are occupied almost exclusively by Fe^{2+} ions (Fig. 2). The other octahedral sites participate in electronic exchange between Fe^{2+} and Fe^{3+} ions through the polaron hopping mechanism, similar to the octahedral network of magnetite[20] and other Fe-bearing oxides[31]. Thus, the BVS method shows the average charge for each of the Fe1-Fe3 sites. We note that various considerations lead to octahedral sites in the recently-discovered Fe_4O_5 phase having different charges[29].

Mg-doped Fe_7O_9 crystals adopt the same crystal structure as Fe_7O_9 with similar unit cell parameters: $a = 9.6901(12)$ Å, $b = 2.8943(5)$ Å, $c = 11.4397(15)$ Å, $\beta = 102.045(14)°$, $V = 313.77(8)$ Å^3, and $Z = 2$ (Fig. 2 and Table S1 in the Supplementary Materials). Electron microprobe analysis established their chemical composition to be $Mg_{1.06}Fe_{5.94}O_9$, i.e., nearly 15% of Fe ions are substituted by Mg. We used this chemical composition in the crystal structure refinement and found that Mg^{2+} ions occupy all four Fe sites, but with a noticeable preference for (*i*) the spacious Fe4 sites that are occupied by the larger Fe^{2+} ions in Fe_7O_9, and (*ii*) the Fe1 sites, located between the Fe4 sites (Fig. 2, Table S2 in the Supplementary Materials). In the case of Mg doping of Fe_4O_5, Mg ions were also found to occupy all Fe sites in the structure[32]. Repeating the same BVS analysis[30] as above for Fe_7O_9 taking into account the Mg atom distribution determined by single crystal X-ray diffraction (Table S2 in the Supplementary Materials), we confirmed the ferrous nature of Fe4 ions and detected a minor increase in the BVS of all other octahedrally coordinated Fe ions as +2.81, +2.78, and +2.87 for the Fe1, Fe2, and Fe3 sites, respectively (Fig. 2). Thus, the results of BVS analysis suggest the persistence of charge transfer in the 3D octahedral network with the distributed Mg ions. However, these Mg impurities should dramatically lower the mobility of hopping polarons, and hence, the bulk electrical conductivity of Mg-doped Fe_7O_9 is expected to be much lower than that of Fe_7O_9.

Mössbauer spectroscopy. Both Fe_7O_9 and $(Mg,Fe)_7O_9$ samples were analyzed by Mössbauer spectroscopy using a synchrotron Mössbauer source that gave excellent signal to noise ratios (Fig. 3 and Table S3 in the Supplementary Materials). We did not observe any magnetic component in these spectra, and hence conclude that these materials are non-magnetic at ambient conditions. The spectrum of Fe_7O_9 (Fig. 3a) could be fitted by

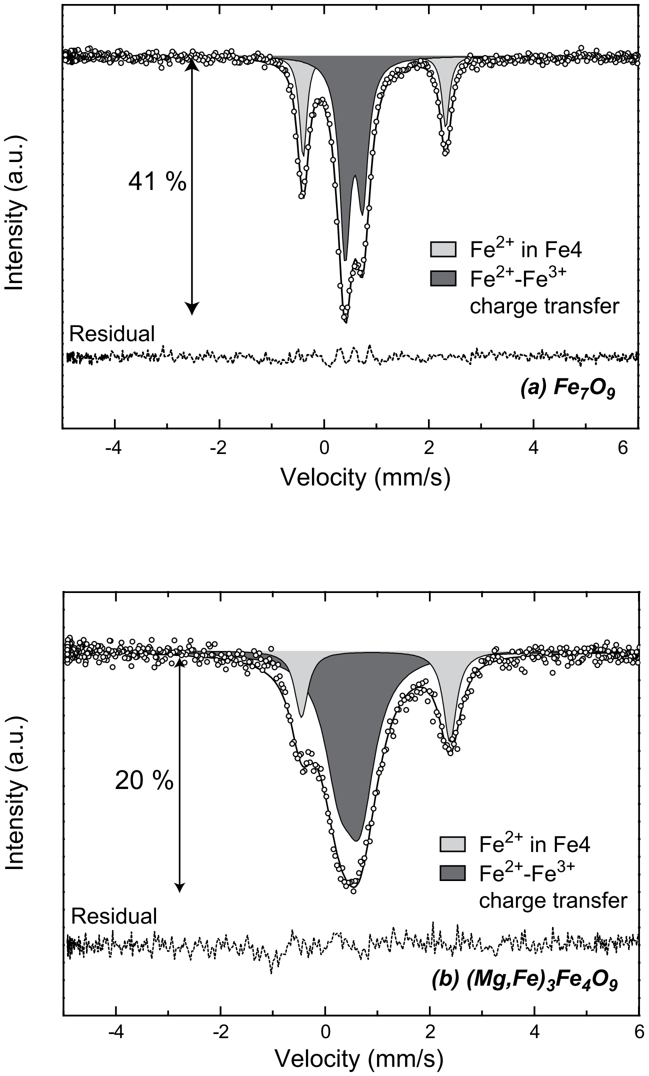

Figure 3. Mössbauer spectra of Fe_7O_9 samples. (**a**) Single crystal of Fe_7O_9. (**b**) Single crystal of $(Mg,Fe)_3Fe_4O_9$. Both spectra were collected at ambient conditions. Black open circles, experimental spectrum; lines, fitted spectra; broken line, residual.

a superposition of two basic components, including (*i*) Fe^{2+} ions at the prismatically-coordinated Fe4 sites in the crystal structure (Fig. 2) and (*ii*) a merged component related to octahedrally-coordinated Fe1, Fe2, and Fe3 ions with an average oxidation state of $Fe^{2.8+}$ (Fig. 3a and Table S3 in the Supplementary Materials). We note that this $Fe^{2.8+}$ component is an average because of the above-mentioned rapid charge exchange between Fe^{2+} and Fe^{3+} ions at the octahedral sites, similarly to Fe_3O_4[33]. This finding is in excellent agreement with the above BVS oxidation states of the Fe ions obtained from the single crystal XRD data. It should be noted here that the three slightly structurally-inequivalent Fe1, Fe2 and Fe3 sites (Fig. 2) give similar contributions to the Mössbauer spectrum because of the very similar environment (edge-sharing FeO_6 polyhedron) of the Fe ions, so it is not possible to separate their individual components in the spectrum (Fig. 3a). Spectra obtained from $(Mg,Fe)_7O_9$ were quite similar to Fe_7O_9 (Fig. 3b), while the merged component in the Mg-bearing sample spectrum shows a slightly higher average oxidation state of $Fe^{2.9+}$ due to incorporation of Mg.

Discussion

In our work we synthesized Fe_7O_9 and $(Mg,Fe^{2+})_3Fe^{3+}{}_4O_9$ crystals at high pressures around 24–26 GPa. In previous studies the orthorhombic polymorphs of Fe_4O_5[13] and Fe_5O_6[14] were prepared at substantially lower pressures, between 10 and 20 GPa. It is interesting to note that the first pressure-driven structural phase transitions in the known iron oxides were detected at similar pressures around 20–25 GPa. For instance, at room temperature cubic $Fe_{1-x}O$ wüstite with the rocksalt structure transforms to a rhombohedral lattice above 20 GPa[1], while at high temperatures the rocksalt structure of $Fe_{1-x}O$ is stable to at least 60 GPa[1,2]. High temperature-assisted phase transitions in Fe_3O_4 from cubic spinel to an orthorhombic phase[34,35], and from corundum-type α-Fe_2O_3 to an orthorhombic Rh_2O_3(II)-type or to other phases[4–8] were also observed in some studies already above 20–25 GPa, although these phase transitions are still hotly debated. These observations suggest that all conventional iron oxides (α-Fe_2O_3, Fe_3O_4, and $Fe_{1-x}O$) become unstable with respect to structural transformations in approximately

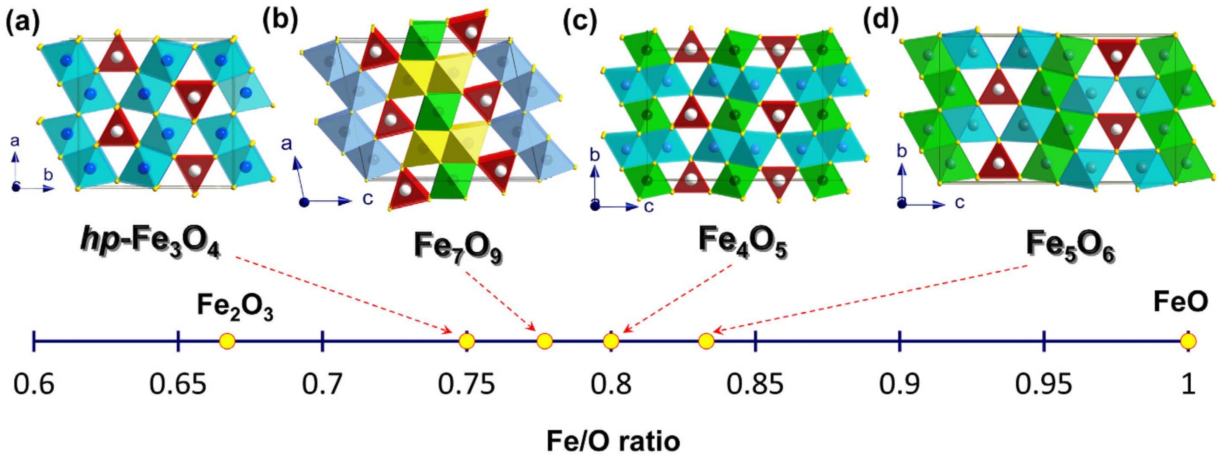

Figure 4. Comparison of unit cells of crystal structures of iron oxides. (**a**) High-pressure orthorhombic polymorph of Fe_3O_4[34], (**b**) Monoclinic Fe_7O_9 polymorph discovered in the present work. (**c**) Orthorhombic *Cmcm* polymorph of Fe_4O_5 discovered in ref. 13. (**d**) Orthorhombic *Cmcm* polymorph of Fe_5O_6 discovered in ref. 14. Different colors of the octahedra denote different crystallographic sites for Fe ions.

similar pressure ranges that might be related to similar shortening of Fe-O bond lengths in their structures. Hence, the resultant high-pressure polymorph of a compressed and heated iron oxide could depend on its stoichiometry, thereby suggesting chemical tuning as a route to new structural phases. In general, one could expect that a minor tuning in stoichiometry could lead either to structures with vacancies (ordered or disordered) or to modified, Fe_3O_4-like or Fe_2O_3-like high-pressure phases in new oxides. Likewise, significant shifts from known stoichiometry could potentially lead to hitherto unknown structures. For instance, the newly-discovered orthorhombic *Cmcm* polymorphs of Fe_4O_5[13] and Fe_5O_6[14] crystalize in structures that are linked to the high-pressure orthorhombic polymorph of Fe_3O_4[34,35] (Fig. 4). By analogy with the existing family of calcium ferrites, $CaFe_n^{2+}Fe_2^{3+}O_{4+n}$[36], it was proposed that iron oxides with this *Cmcm* structure could also form such a family as $Fe_{1+n}^{2+}Fe_2^{3+}O_{4+n}$[37], which includes Fe_3O_4, Fe_4O_5[13] and Fe_5O_6[14]. However, the present discovery of Fe_7O_9 that does not belong to this family on the one hand, but having a certain structural similarity with the above oxides on the other hand (Fig. 4), suggests that the family of iron oxides that are structurally linked to the high-pressure polymorph of Fe_3O_4 may be more broad, e.g., like $Fe_{3\pm n}^{2+}Fe_4^{3+}O_{9\pm n}$, thereby suggesting a potentially greater diversity than in the calcium ferrite oxides. For instance, Fe_9O_{11} ($n = 2$) or $Fe_{11}O_{13}$ ($n = 3$) might be hypothetically stable under certain HP-HT conditions.

At the moment the stability field of this new Fe_7O_9 polymorph is not well defined, although it appears to lie at pressures higher than those of Fe_4O_5[13] and Fe_5O_6[14]. The chemical compositions and the structural phases of iron-magnesium oxides in the Earth's mantle remain a disputed issue that requires *in situ* investigations at HP-HT conditions under different oxygen fugacities. In this regard, the unexpected discovery of a Fe_7O_9 polymorph provides new insight into possible compositions of mantle phases, and provides a new type compound that may play a key role in determining physical and chemical properties.

The new oxide, Fe_7O_9, is a compound with a ratio of Fe^{3+}/Fe^{2+} intermediate between those of Fe_3O_4 and Fe_4O_5 (Fig. 4). Both Fe_3O_4 and Fe_4O_5 are model systems for investigations of Fe^{2+}–Fe^{3+} interactions in solids, demonstrating enigmatic low-temperature phase transitions of 'metal-insulator'-type that lead to the formation of exotic 'trimeron quasiparticles' in Fe_3O_4[21] or to even more intricate ordering patterns in Fe_4O_5[29]. We note that the low-temperature Verwey transition in Fe_3O_4 has had a strong impact on solid state physics and chemistry for decades. Thus, Fe_7O_9 presents an exciting compound that promises important implications for geosciences, solid state physics and chemistry with potential for industrial applications.

The recently discovered iron oxides may play important roles in the cycling of volatiles in the Earth's deep interior[16–19]. For instance, oxygen could be released in the deeper part of the lower mantle via decomposition reactions of Fe_2O_3 and Fe_3O_4 into Fe_5O_7 and $Fe_{25}O_{32}$ above 60 GPa[17]. Further, it was recently reported that FeO_2 could be formed in the lower mantle as a product of FeOOH goethite decomposition[18]. Moreover, this reaction could supply hydrogen to the surrounding mantle[18]. Physical and chemical properties of the newly-discovered iron oxides can therefore provide novel insights into the chemical evolution of the Earth's interior.

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Author Contributions

The samples were synthesized by R.S. and S.V.O. E.B. and L.I. conducted the single crystal XRD measurements. Mössbauer spectra were obtained and analyzed by S.V.O., C.M., I.K. and L.D. Microprobe analysis were carried out by R.S. R.S., S.V.O. and L.D. designed the research project. The manuscript was written by R.S., S.V.O. and C.M. with contributions from all co-authors.

Additional Information

Supplementary information accompanies this paper at http://www.nature.com/srep

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