

High-pressure and high-temperature behaviour of Fe_2O_3

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

^aBavarian Research Institute of Experimental Chemistry and Geophysics, University of Bayreuth, Bayreuth, Germany;

^bLaboratory of Crystallography / Material Physics and Technology, Department of Physics, University of Bayreuth, Bayreuth, Germany;

^cESRF, Grenoble, France;

^dGSECARS, ID-13D, APS, Argonne, USA;

^eP02.2 ECB, Petra III, Hamburg, Germany.

High pressure behavior of iron sesquioxide, Fe_2O_3 , has been a long-standing subject of research due to its high importance in understanding Earth interiors. Moreover, the compound is interesting from a physical point of view since at the pressures from 40 to 60 GPa it undergoes series of transformations with a diverse origin: structural transformation to an orthorhombic phase with large volume discontinuity (~10%) [1]; drop in the resistivity [2]; spin crossover of Fe^{3+} [3]; and disappearance of the ordered magnetic state [2]. The enigmatic crystal structure of the “orthorhombic phase” being able to shed light on the physics of the observed pressure-induced phenomena remained controversial for a long time. Perovskite and Rh_2O_3 -II structural types have been proposed as candidates and both were based on Mössbauer data supplemented with powder X-ray diffraction (XRD) [2,4]. Recent single crystal XRD studies unambiguously established that compression to 40 GPa and laser heating to 2300 K yields in formation Rh_2O_3 -II structural type phase, however the volume discontinuity was shown to be rather small (1.5 %) [5]. The crystal structure of the phase(s) observed on compression at ambient temperature above 50 GPa is still under the question since only powder XRD data were available so far, while Mössbauer and Raman spectroscopies studies cannot provide definitive structural information.

A reconstructive phase transition was reported to occur during a laser heating of Fe_2O_3 compressed at or above 70 GPa [6–8]. Powder diffraction pattern was indexed with CaIrO_3 type structure, crystallographic data provided was based only on a Rietveld refinement of the powder pattern. It is noteworthy that CaIrO_3 structural type is possessed by high pressure modification of $(\text{Mg,Al})(\text{Si,Fe})\text{O}_3$ perovskite known as a post-perovskite while the transition perovskite – post-perovskite is responsible for an abrupt increase of density in D" layer, the lowest part of the mantle [9].

An uncertainty in the crystal structure of Fe_2O_3 at 40–60 GPa pressure region and absence of crystallographic data for post-perovskite Fe_2O_3 phase encouraged us to perform a series of high-pressure and high-temperature XRD experiments on single crystals, since the powder XRD data have limitations both in accurate unit cell determination and in a structure solution and refinement. High-quality single crystals of Fe_2O_3 were placed inside diamond anvil cells, compressed up to 71 GPa, heated with the laser afterward and finally decompressed while single crystal XRD was measured concurrently.

We report finding of a novel high-pressure polymorph of Fe_2O_3 by means of the in situ high pressure single crystal XRD. The transition occurs under compression of the hematite to ~54 GPa yielding in the about 10 % of volume reduction. The phase crystallizes in a double perovskite structural type (space group $P2_1/n$, $a = 4.588(3)$, $b = 4.945(2)$, $c = 6.679(7)$ Å and $\beta = 91.31(9)^\circ$) (Fig.1) related by a distortion with the perovskite structure. No phase transition to the orthorhombic Rh_2O_3 -II has been observed upon compression at ambient temperature up to at least 71 GPa. Laser heating to $\sim 2100 \pm 100$ K at pressures above 70 GPa promotes a transition to $Cmcm$ CaIrO_3 -type phase. Decompression experiments show that the $Cmcm$ phase transforms back to the hematite between ~25 and 15 GPa.

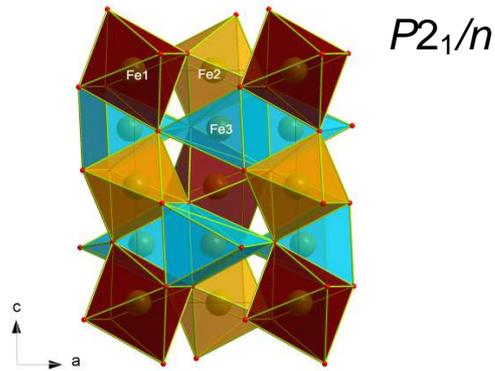


Figure 1: Double perovskite cryolite-type structure: B-position is occupied by 2 alternating atomic species (Fe1 and Fe2 designated by darker and lighter colors). Fe3 atom possessing 2 significantly larger Fe3—O distances could be considered as having trigonal-prismatic arrangement with 2 additional Fe—O bonds instead bipolar prismatic one.

References

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