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1 Introduction

Iron(III) oxide is a typical representative of compounds exhibiting polymorphism, i.e., a feature manifested by existence of two or more phases which are isochemical but have distinct crystal structures imparting them with different physical properties. Due to different physical properties driven by different crystal structures, all the iron(III) oxide polymorphs have been found effective and/or promising in a miscellaneous scale of practical applications mainly in the field of nanotechnologies. Recently, β -Fe₂O₃ has been identified as a chloroform sensor or as a suitable candidate for preparation of an anode in lithium-ion batteries. Up to now, there are no reports on high-pressure transformations of rare β - and ϵ -Fe₂O₃ phases. Here, we monitor in-situ high-pressure transformations of rare β -Fe₂O₃ for the first time.

2 Experiment

β -Fe₂O₃ nanoparticles were synthesized by a thermally induced solid-state reaction of NaCl with Fe₂(SO₄)₃ in air followed by post-processing separation based on dissolution of all byproducts in water. High-pressure X-ray powder diffraction experiments with synchrotron radiation were performed using a diamond anvil cell high-pressure apparatus. Powdered β -Fe₂O₃ sample was loaded into a 50–100 μ m diameter hole that was drilled into a rhenium gasket. Several ruby crystals were also put into the sample chamber. No pressure transmitting medium was used in this study. The pressure was determined from the fluorescence line of ruby. The pressure applied varied from 0 to 64.4 GPa in an increasing regime, stopping at the required value. At each pressure set, the sample was probed using an angle-dispersive X-ray diffraction technique at the synchrotron beam line NE1A, KEK. A monochromatic incident X-ray beam with a wavelength of $\lambda \approx 0.41$ Å was used. The X-ray beams were collimated to a diameter of 30 μ m, and the angle-dispersive X-ray diffraction patterns were obtained on an imaging plate (Rigaku). The observed intensities on the imaging plates were integrated as a function of 2θ in order to obtain conventional, one-dimensional diffraction profiles. Rietveld analyses of the synchrotron X-ray diffraction patterns were performed using the PDXL Integrated X-ray powder diffraction software of Rigaku, Japan.

3 Results and Discussion

The purity and structural features of the synthesized β -Fe₂O₃ sample before pressure treatment were checked employing conventional X-ray powder diffraction and

Mössbauer spectroscopy techniques. The pressure effect on the crystal structure of β -Fe₂O₃ was investigated using high-pressure synchrotron radiation XRD measurements. On lowering the temperature, β -Fe₂O₃ passes from paramagnetic to magnetically ordered regime, adopting an antiferromagnetic state below ~ 110 K (the Néel temperature). The X-ray synchrotron data presented in this study show that upon high-pressure treatment of β -Fe₂O₃ above 40 GPa, a new iron(III) oxide polymorph assigned as ζ -Fe₂O₃ is evolved (Fig. 1), being surprisingly stable even after the pressure release and at room temperature, thus extending the line of four existing iron(III) oxide forms. It turns out that ζ -Fe₂O₃ has a monoclinic structure with C2/c space group and six nonequivalent cation sites (two regular and four distorted octahedral sites) and, following magnetization measurements, behaves in an antiferromagnetic manner at temperatures below ~ 70 K [1]. Its stability is most probably favored by surface energy imparted from smaller β -Fe₂O₃ nanoparticles and convenient chemical potential altered during pressure treatment.

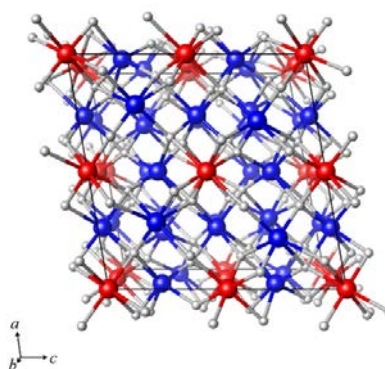


Fig. 1: Crystal structure of ζ -Fe₂O₃ (monoclinic, C2/c space group) after pressure release, projected along the b-axis. Red, blue, and gray balls represent regular octahedral Fe sites (Fe1, Fe4), distorted octahedral Fe sites (Fe2, Fe3, Fe5, Fe6), and oxygen sites, respectively.

References

[1] J. Tuček *et al.*, *Scientific Reports* **5**, 15091 (2015).

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