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In-situ high-pressure x-ray diffraction study of zinc ferrite nanoparticles

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ABSTRACT

We have studied the high-pressure structural behavior of zinc ferrite ($ZnFe_2O_4$) nanoparticles by powder X-ray diffraction measurements up to 47 GPa. We found that the cubic spinel structure of $ZnFe_2O_4$ remains up to 33 GPa and a phase transition is induced beyond this pressure. The high-pressure phase is indexed to an orthorhombic $CaMn_2O_4$-type structure. Upon decompression the low- and high-pressure phases coexist. The compressibility of both structures was also investigated. We have observed that the lattice parameters of the high-pressure phase behave anisotropically upon compression. Further, we predict possible phase transition around 55 GPa. For comparison, we also studied the compression behavior of magnetite (Fe_3O_4) nanoparticles by X-ray diffraction up to 23 GPa. Spinel-type $ZnFe_2O_4$ and Fe_3O_4 nanoparticles have a bulk modulus of 172 (20) GPa and 152 (9) GPa, respectively. This indicates that in both cases the nanoparticles do not undergo a Hall-Petch strengthening.

1. Introduction

Spinel-structured oxides belong to a large family of compounds which include more than eighty different oxides [1]. These oxides are relevant for many technological applications. Zinc ferrite ($ZnFe_2O_4$), the mineral Franklinite, is one of the members of this family. At ambient pressure (P), $ZnFe_2O_4$ has a cubic spinel structure (space group $Fd\bar{3}m$) [2], which is shown on the left side of Fig. 1. $ZnFe_2O_4$ is a normal spinel, which has a unit cell with 32 oxygen atoms in a close cubic packing arrangement, and 8 tetrahedral (T) and 16 octahedral (M) sites, occupied by Zn^{2+} and Fe^{3+} atoms, respectively.

There is a large interest on the study of spinel oxides under compression. The high pressure (HP) study of $ZnFe_2O_4$ has attracted attention for nearly half a century, since it was proposed that superparamagnetism can be induced by squeezing zinc ferrite [3]. In particular, $ZnFe_2O_4$ has been one of the first compounds where the HP orthorhombic post-spinel structure has been determined [4]. For this compound, the equation of state [1,5] and other mechanical properties, such as elastic moduli, have been reported [6–8].

Although many high-pressure studies have been performed on bulk spinel oxides, investigation of nanoparticles under pressure is scarce. Indeed, one of the few compounds already studied at high pressure in the nanoparticle form is $CoFe_2O_4$ [10]. It is a very well-known fact, that due to the high surface-to-volume ratio, nanomaterials might show a different high-pressure behavior than bulk materials [11,12]. In particular the transition-pressure, the HP structural sequence, and properties like compressibility maybe different. The above described facts suggest that it is important to explore the HP behavior of $ZnFe_2O_4$ nanoparticles to check the structural stability and the possible occurrence of a Hall-Petch strengthening [13]. Hence, we performed synchrotron room-temperature powder X-ray diffraction (XRD) experiments on $ZnFe_2O_4$ nanoparticles up to 47 GPa. These studies allowed us to determine the equation of state (EOS) of the low-pressure phase, the identification of a phase pressure-induced transition at 33 GPa, and the crystal structure of the HP phase, which is shown on the

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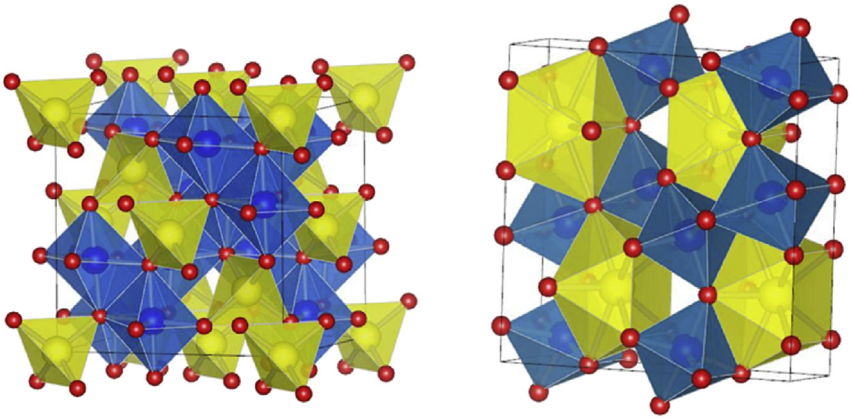

Fig. 1. (Left) Schematic view of the cubic spinel structure of $ZnFe_2O_4$ with octahedral (*blue*) and tetrahedral (*yellow*) units. Oxygen atoms are represented in red. (Right) Schematic view of the orthorhombic HP phase ($CaMn_2O_4$-like) of $ZnFe_2O_4$ with octahedral (*blue*) and dodecahedral (*yellow*) units. Oxygen atoms are also represented in red. Structural representations made with VESTA [9]. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

right side of Fig. 1. For comparison, we further performed similar studies on the low-pressure phase of magnetite (Fe_3O_4), an inverse spinel, up to 23 GPa. The results obtained for the nanoparticles are compared with the bulk and the high-pressure behavior of cobalt ferrite nanoparticles [10].

2. Experimental details

Zinc ferrite nanoparticles were synthesized by the sol-gel method and magnetite nanoparticles were synthesized by the co-precipitation method. Details of synthesis as well as the crystal structure and magnetic properties at ambient pressure have been reported elsewhere [14]. The resulting cubic $ZnFe_2O_4$ powder has a unit-cell parameter of 8.439 (1) Å and a grain size of 46 (3) nm. The magnetite powder has a lattice parameter of 8.389 (1) Å and a grain size of 55 (9) nm. Room-temperature HP angle-dispersive XRD studies were conducted in a symmetric-type diamond-anvil cell (DAC) with Ne as pressure-transmitting medium (PTM). The diamond cell was equipped with 300 μm-culet diamonds. The samples were loaded in a 100 micron-diameter hole of a rhenium gasket pre-indented to a thickness of 30 μm. Synchrotron radiation from beamline 16-IDB of the HPCAT at Advanced Photon Source (Argonne National Laboratory) was used as X-ray source. The applied pressure was determined by the ruby fluorescence technique with an accuracy of 0.05 GPa. The monochromatic x-rays ($\lambda = 0.3738$ Å) from the beamline were focused using Kirkpatrick-Baez mirrors to 10×10 μm^2. XRD patterns were collected using a Pilatus 1M-F detector. For $ZnFe_2O_4$ pressures from 1.3 GPa to 47 GPa (21 steps) were applied during compression, and four pressures (40.5, 34.6, 12.1 and 0.7 GPa) were measured during decompression. For magnetite, pressures were applied from 3.6 GPa to 23 GPa (9 steps) during compression using the same experimental set up. In addition, one pressure point was measured at 0.1 GPa after decompression. The two-dimensional XRD images were the integrated with FIT2D [15] into one-dimensional diffraction patterns. The patterns were analyzed using MAUD [16]. The extracted pressure versus unit-cell volume (V) data was analyzed using the EOS-fit [17].

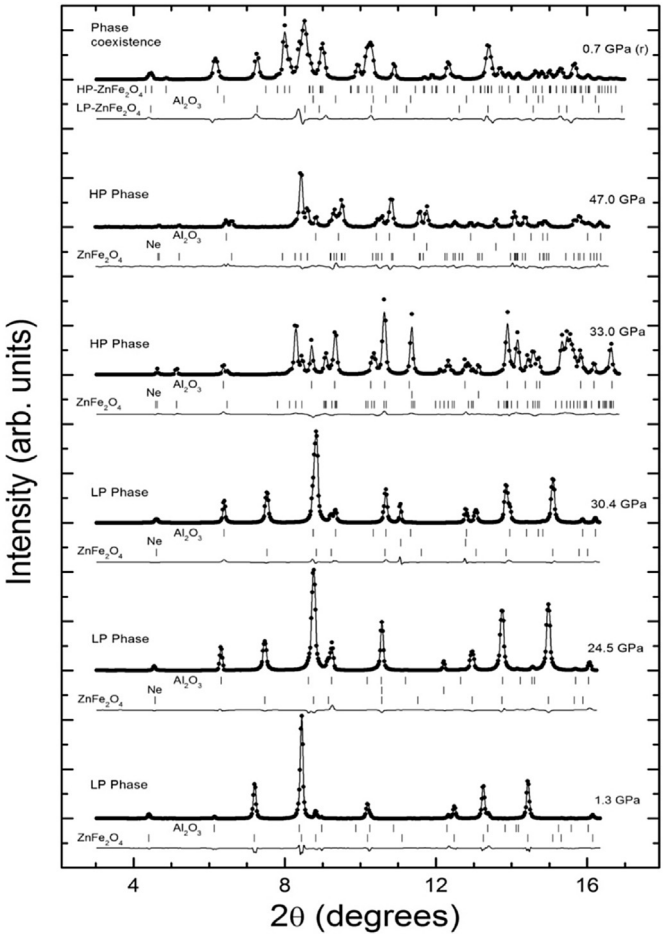

Fig. 2. Experimental X-ray diffraction patterns of $ZnFe_2O_4$ nanoparticle for different pressures (dots) superimposed with calculated profiles (solid lines). Below each pattern the ticks represent the peaks of each crystalline phase found and the solid line represents the difference between experimental and calculated profiles.

3. Results and discussion

3.1. Zinc ferrite nanoparticles ($P < 33$ GPa)

Fig. 2 shows a selection of XRD patterns measured for $ZnFe_2O_4$ nanoparticles up to 47 GPa. The patterns indicate that the nanoparticles remain in spinel structure up to 30.4 GPa. At 33 GPa and above, changes in the diffraction patterns showed a phase transition to a HP phase. The crystal-structure identification of such