Investigation of the High-Pressure Phase of Fe_2O_3

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ntroduction

The structural, electronic, and magnetic properties of Fe_2O_3 at high pressure have received a great deal of attention during the past year as a result of the work of Pasternak et al.[1] who reported that the corundum structure of hematite transforms to the Rh_2O_3-II arrangement[2] at approximately 60 GPa. Previously, Staun Olsen et al.[3] proposed that Fe_2O_3 transforms to a perovskite structure, with a Fe^{2+} state and a low-spin state in the A and B sites, respectively, on the basis of synchrotron powder diffraction results. Thus, although the work of Pasternak et. al would appear to settle the structural question, several issues associated with this problem remain unsolved. First and foremost, while the Mössbauer data appear to confirm that only one crystallographically equivalent metal site exists in the high-pressure phase, the powder diffraction work is far from definitive. Calculated patterns for Fe_2O_3 in the Rh_2O_3-II (*Pbam*) and perovskite (*Pbnm*) structures are nearly identical (Fig. 1), and apart from the intensities of two of the diffraction peaks at low angle, it is virtually impossible to differentiate one from the other. The structures used in calculating the patterns were determined by constant-pressure lattice enthalpy minimization using the volume calculated for Fe_2O_3 at 70 GPa. These are compared with the observed data of Pasternak et al., which are replotted here with peak widths comparable to the calculated patterns. While it is clear that there are definite similarities between the experimental pattern and the two calculated ones, an unambiguous assignment of the high-pressure phase to either structure is not possible.

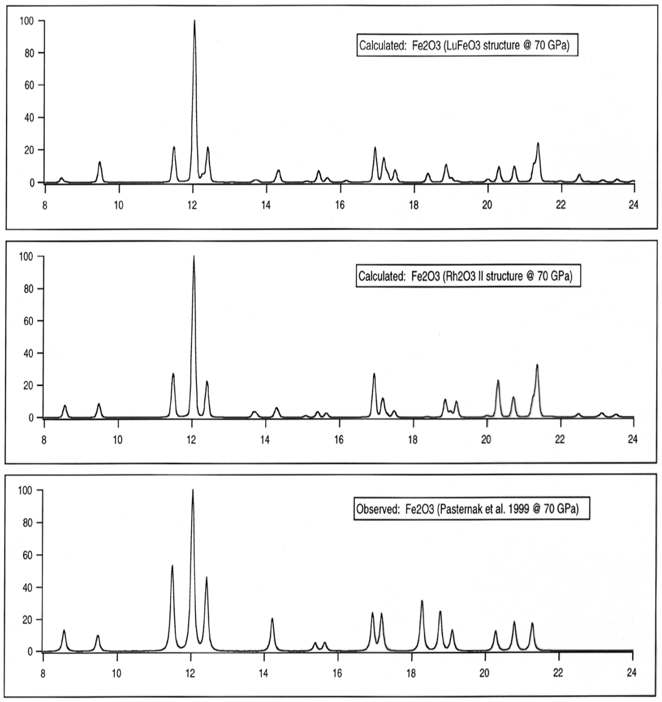

FIG. 1. Top, calculated powder pattern of Fe_2O_3 in the perovskite structure; middle, calculated pattern of Fe_2O_3 in the Rh_2O_3-II structure; bottom, observed pattern of Fe_2O_3 at 70 GPa from Ref. 1.

In this experiment, we attempted to resolve this problem by collecting high-resolution synchrotron powder diffraction data and refining it by the Rietveld method in both crystal structures. Our results illustrate some of the challenges encountered in the investigation of high-pressure phase transitions in minerals.

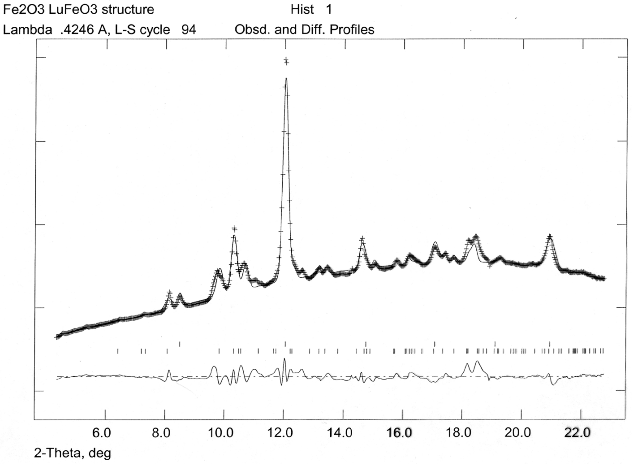

FIG. 2. Rietveld refinement of Fe_2O_3 in the perovskite structure. The solid line is the observed pattern, and the (+) mark the calculated pattern; the difference shown at the bottom. The top set of tick marks shows the positions of the NaCl peaks, and the bottom set the calculated positions of the sample peaks.

Experiment

Our high-pressure cell was a Mao-Bell diamond anvil cell that contained diamonds with 250 μm culets. A 100-μm hole was drilled in the center of a preindented Re gasket, and a grain of polycrystalline Fe_2O_3 was loaded into the sample chamber along with two thin flakes of NaCl, which served as both a pressure medium and a pressure calibrant. To sharpen the diffraction peaks as much as possible and thereby collect diffraction data that could be refined with Rietveld techniques, we attempted to laser-heat the sample very gently at selected pressures during the compression cycle, without heating the sample enough to create unwanted grain growth. As expected, we noted that increasing pressure resulted in significantly broadened diffraction peaks, but with subsequent laser heating for approximately one minute at the lowest possible power, the diffraction lines sharpened significantly. Some grain growth was observed as a result of the heating, but with subsequent compression, we found that grain growth was actually reversed. On the basis of intensities of the hematite patterns obtained in this way, it appears that with a judicious use of laser heating and careful increases in pressure, it is possible to minimize the effects of preferred orientation at high pressure.

Results and Discussion

At approximately 35 GPa and after laser-heating the sample, we noticed that a phase change had taken place. The diffraction

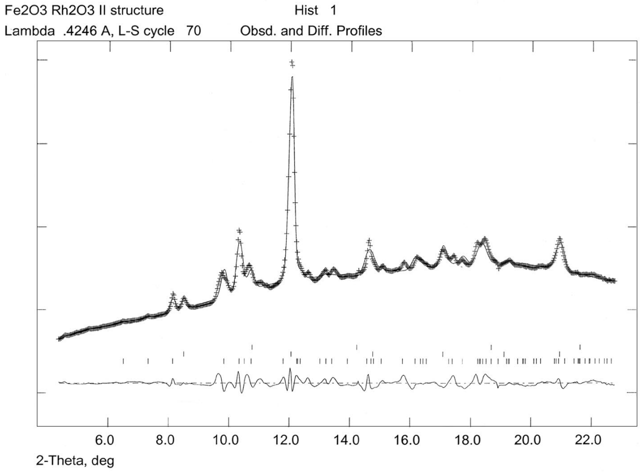

FIG. 3. Rietveld refinement of Fe_2O_3 in the Rh_2O_3-II structure. Description as in Fig. 2.

pattern remained essentially unchanged up to the highest pressure reached in the experiment, 65 GPa. Figures 1 and 2 show the Rietveld refinements attempted with both the Rh_2O_3-II (*Pbam*) and perovskite (*Pbnm*) structures. In this particular case, the diffraction from the NaCl pressure medium completely overwhelms the diffraction from the sample in crucial 2θ regions, making the refinement difficult. Based on the calculated patterns, however, our results in the low-angle region appear to suggest the presence of the perovskite-structured Fe_2O_3 rather than the Rh_2O_3-II alternative.

Figures 2 and 3 show the progress of Rietveld refinements of the synchrotron powder diffraction data in the *Pbnm* and *Pbam* space groups, respectively. While the NaCl pressure medium was very effective in absorbing the laser beam and producing even heating in the sample, its presence causes major problems in the refinement of the data. In principle, the Rietveld method should allow simultaneous refinement of both phases, but the intensity of the NaCl peaks so dominates the diffraction pattern that a clean refinement in either crystal structure is not possible. In addition, the low-angle peaks that would differentiate one structure from the other are nearly lost in the noise of the background. At this point, we are investigating alternative pressure media in an attempt to limit this type of interference.

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