Pressure effect of electron density distribution of FeTiO3 ilmenite by Maximum Entropy Method

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Much attention has been given to the structure transformations of spinel and perovskite bearing transition elements from earth interiors and industrial uses. $Fe^{2+}Ti^{4+}O_3$ ilmenite (R-3, Z = 6) is one of the significant materials for geophysical interests. In the present study, the electron density distribution has been investigated as a function of pressure by X-ray single-crystal diffraction study at high pressures up to 8.2 GPa using MEM. Fe^{2+} (3d6) and Ti^{4+} (3d0) cations across the shared face are alternatively located along the c axis. FeO_6 and TiO_6 octahedra are respectively located in a plane parallel to (001) and linked with adjacent octahedra with shared edge.

The diffraction intensity measurements at high pressures of 3.6, 5.3 and 8.2 GPa were made using wavelength l= 0.61907 of SR at BL-10A, KEK with DAC. The cation positions move in the direction of the c axis and approach the center of FeO_6 and TiO_6 with increasing pressure. The regularity of TiO_6 octahedra is enhanced at higher pressure. The longer M-O (sh face) bonds are more shortened under pressure than shorter M-O (unsh face). Therefore, the cation shifts toward the center of the octahedron. The compressions of Ti-O bond lengths are smaller than those of Fe-O. The shared edge of the octahedron, O-O (sh edge) is less influenced by compression than the O-O (unsh edge). With increasing pressure the M-O (sh face) of both the octahedra is more compressed than M-O (unsh face).

In comparison with the difference Fourier synthesis, MEM calculation using Fmem(hkl)-Fcal(hkl) brings a much more precise electron distribution that indicates the deformation electron density. We tested the accuracy of the electron density analysis corresponding to the number of Fobs(hkl) related with the observed reciprocal space in sinq/l, because the diffraction angle using DAC is limited up to 70 in 2q. The test proves that the electron density distributions using Fobs(hkl) within 2q=60, 80, 100 and 120 are not so greatly different, but the localization of the electron distribution is more clearly indicated by the data sets from a larger region of reciprocal space.

The MEM analysis reveals the electron density distributions around Fe^{2+} (3d6) and Ti^{4+} (3d0) cations are not spherical, but elongated along the direction of the c-axis due to the d-electron orbital. The compression affects the Coulomb potential in M-O (M = Fe, Ti) bonds and the repulsive force is enhanced under high-pressure conditions. The electron densities on the Fe-O (sh) and Ti-O (sh) bonds are more increased with pressure than those on the Fe-O (unsh) and Ti-O (unsh) bonds, respectively. The former two densities indicate a greater increase in the bonding electron on their bonds with compression than the latter two. On the other hand, the compression reduces the bonding electron on the both Fe-O (unsh) and Ti-O (unsh) bonds. The electron density between Fe^{2+} (3d6) and Ti^{4+} (3d0) cations across the shared face becomes smaller with increasing pressure.

The localization of the valence electron around the cation is enhanced under higher pressure. The pressure dependence of the electron radial distribution obviously shows the more localization of electrons around cations with increasing pressure. The electron density between Fe^{2+} and Ti^{4+} cations across the shared face becomes smaller with increasing pressure. This is because the repulsion of d-electrons between two cations is enlarged with the external compression. However, the electron conductivity measurement using a polycrystalline sample, which will be reported elsewhere, reveals increasing conductivity at higher pressure. The electron distribution between Fe and Ti along 001 direction becomes lower with pressure. Hence neither charge transfer nor electron hopping in FeTO3 is possible under pressure.