Japan Geoscience Union Meeting 2011
(May 22-27 2011 at Makuhari, Chiba, Japan)
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SMP044-P03 Room:Convention Hall Time:May 25 14:00-16:30

High-pressure X-ray diffraction and Raman spectroscopic studies of magnetite, ulvospinel, and chromite

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Magnetite Fe_3O_4, ulvospinel Fe_2TiO_4, and chromite $FeCr_2O_4$ have been investigated by high-pressure x-ray diffraction and Raman spectroscopy with diamond anvil cell techniques. The crystals used as starting materials were synthesized in a 1-atm furnace at 1100 ^{o}C for 48 hours with a CO/CO_2 gas flow from dried powdered oxides of Fe, Ti and Cr. A powder x-ray diffraction study of magnetite was performed up to 154 GPa with and without laser heating. The x-ray diffraction profiles showed changes at 28 GPa. With further compression up to 154 GPa, a phase change occurred above 80 GPa. Powder x-ray diffraction measurements of ulvospinel were carried out up to 60 GPa at ambient temperature. Phase transitions in ulvospinel were found near 9 GPa, 12 GPa, and 50 GPa, respectively where the crystal structure transforms from cubic to orthorhombic through a tetragonal phase. The phase observed above 50 GPa was reversibly changed to the lower-pressure phase with decompression. The x-ray diffraction profile above 50 GPa can be explained by the high pressure phase of the $CaTi_2O_4$?type structure (space group *Cmcm*) with lattice parameters a = 2.65, b = 9.25, c = 9.30 A, and V = 228 A^3. Structural refinements of chromite were obtained from single-crystal x-ray diffraction measurements collected at several pressures up to 15 GPa. A phase transition in chromite was found at 12 GPa. The crystal structure of chromite transforms from cubic to tetragonal in a manner similar to the pressure induced phase transitions in ulvospinel. Fitting of the P-V data to a Birch-Murnaghan equation of state (EoS) results in K_0 = 196(5) GPa, K' = 4.0 (fixed), and V_0 = 589.2(1) A^3. The K_0 value for chromite is in fair agreement with the experimental results of spinels and theoretical predictions of chromium spinels. From the structural refinements the tetrahedral site (T) is occupied by Fe^{2+} cation with a greater compressibility than the octahedral site (M) occupied by the Cr^{4+} cation owing to the Jahn-Teller effect at Fe^{2+}. The resulting EoS parameters for the T-site and M-site are K_0 = 141(3) GPa, K' = 4.0 (fixed), V_0 = 4.1(1) A^3 and K_0 = 256(9) GPa, K' = 4.0 (fixed), V_0 = 10.4(1) A^3, respectively.

The three spinels were studied by laser Raman spectroscopy using a laser power of the 532 nm laser line of 1-2 mW on the sample. There are five Raman-active modes ($A_{1g} + E_g + 3F_{2g}$) in the *Fd-3m* space group of the cubic spinel according. Two Raman active modes assigned to A_{1g} and F_{2g} are clearly observed around 500 and 700 cm^{-1} under ambient conditions. The A_{1g} mode in the cubic structure transforms to the A_g mode in the tetragonal and orthorhombic structures. In contrast, the F_{2g} mode in the cubic structure splits into $B_{1g} + E_g$ modes in the tetragonal structure, and then into $B_{1g} + B_{2g} + B_{3g}$ modes in the orthorhombic structure. With increasing pressure, in the Raman spectra of chromite, the A_{1g} and F_{2g} modes in chromite do not change up to 20 GPa except for a continuous shift to higher frequencies. The Raman spectra of ulvospinel and magnetite start to broaden gradually with increasing pressure. It seems reasonable to attribute the observed broadening to the peak splitting caused by the structural phase transitions. The most striking characteristic of the Raman spectrum of ulvospinel is that compression leads to the extinction of the Raman active mode derived from F_{2g} symmetry. The F_{2g} mode in ulvospinel disappears completely at 20 GPa, but its A_{1g} mode can be observed continuously up to 57 GPa. The Raman spectra of both A_{1g} and F_{2g} modes in magnetite disappear at 30 GPa.

Keywords: magnetite, ulvospinel, chromite, phase transition, high-pressure & high-temperature, diamond anvil cell