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High-pressure Raman spectroscopic studies of ulvöspinel Fe_2TiO_4

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Abstract

We report in situ Raman spectroscopic studies of ulvöspinel in a diamond-anvil cell under hydrostatic conditions up to 57 GPa at room temperature. Two modes near 493 and 681 cm^{-1} are observed clearly at 1 GPa. In the cubic spinel structure, the lower frequency peak can be assigned to a mode of F_{2g} symmetry and the higher frequency peak can be assigned to a mode with A_{1g} symmetry. The remaining three modes could not be observed unambiguously in the measurements, although there are five Raman-active modes ($A_{1g}+E_g+3F_{2g}$) in the $Fd\bar{3}m$ space group of the spinel structure according to factor group analysis. The peak positions and shapes in the Raman spectra agree well with those measured under ambient conditions. With increasing pressure, the frequencies of the A_{1g} and F_{2g} modes increase continuously up to 9 GPa with pressure derivatives of 2.5 and 2.1 cm^{-1}/GPa, respectively. There is no obvious degradation of crystal symmetry or structural change observed within this pressure range. Upon increasing pressure to ~20 GPa, the F_{2g} mode splits into $B_{1g}+E_g$ modes, and then into $B_{1g}+B_{2g}+B_{3g}$ modes. The intensities of the Raman bands gradually decrease due to the tetragonal-orthorhombic phase transition. This mode completely disappears at a pressure of 29 GPa. The most striking characteristic of the Raman spectrum of ulvöspinel is that compression leads to the extinction of the Raman-active mode derived from F_{2g} symmetry. Only one peak resulting from the A_{1g} mode can be observed continuously up to 57 GPa. The peak shift derived from the A_{1g} mode and its full-width at half maximum (FWHM) values suggests another phase transition occurring around 30 GPa. The Raman spectrum of ulvöspinel is in good agreement with the spectra of $ZnCr_2O_4$ and $ZnFe_2O_4$ spinels.

Keywords: Ulvöspinel, Raman spectroscopy, phase transformation, diamond-anvil cell