High-pressure phase transition and properties of spinel ZnMn2O4

X-ray photoelectron spectroscopy, magnetic measurements, and a single-crystal x-ray structure determination at normal pressure have shown that Jahn-Teller active manganese ions in ZnMn2O4 are present in one valence state (III) on the octahedral sites of the spinel structure. The high-pressure behavior of ZnMn2O4 was investigated up to 52 GPa using the energy-dispersive x-ray diffraction technique and synchrotron radiation. The structural first-order phase transition from the body-centered to primitive-tetragonal cell takes place at P-c = 23 GPa. The high-pressure phase is metastable down to normal pressure. The c/a ratio reduces from 1.62 to 1.10 above P-c and remains nearly pressure independent in the high-pressure phase. The transition is attributed to the changes in electron configuration of the Mn3+ ions. According to the crystal field theory, the e(g) electron of octahedrally coordinated Mn3+ is either in the d(z)(2) orbital or in the d(x2-y2). In the first configuration the MnO6 octahedron will be elongated and this is the case at normal pressure, while the second configuration gives the flattened octahedron. In the high-pressure phase some proportion of the e(g) electrons of the Mn3+ ions is moved to the d(x2-y2) level, which is revealed as an abrupt fall of observed magnitude of the distortion of the bulk crystal above P-c. [S0163-1829(99)08341-1].