

High-pressure behavior of cuprospinel CuFe_2O_4 : the Jahn-Teller effect of Cu^{2+} on the spinel structure

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The Jahn-Teller-effect at Cu^{2+} in cuprospinel CuFe_2O_4 was investigated using high-pressure single-crystal synchrotron x-ray diffraction (XRD) techniques at beamline BL10A at the Photon Factory, KEK, Japan. Six data sets were collected in the pressure range from ambient to 5.9 GPa at room temperature. Structural refinements based on the data were performed at 0.0, 1.8, 2.7, and 4.6 GPa. The unit cell volume of cuprospinel decreases continuously from 590.8 (6) \AA^3 to 579.5 (8) \AA^3 up to 3.8 GPa. Least-squares fitting to a third-order Birch-Murnaghan equation of state yields zero-pressure volume $V_0 = 590.7$ (1) \AA^3 and bulk modulus $K_0 = 188.1$ (4.4) GPa with K' fixed at 4.0. The crystal chemical composition determined by electron-probe analysis and site-occupancy refinement is represented as $^{[4]}[\text{Fe}_{0.901}\text{Cu}_{0.099}]^{[6]}[\text{Fe}_{1.500}\text{Cu}_{0.500}]\text{O}_4$. Most of the Cu^{2+} are preferentially distributed onto the octahedral (M) site of the spinel structure. At 4.6 GPa, a cubic-tetragonal phase transition is indicated by a splitting of the a axis of the cubic structure into a smaller a axis and a longer c axis, with unit cell parameters $a = 5.882$ (1) \AA and $c = 8.337$ (1) \AA . The tetragonal crystal structure with space group $I4_1/amd$ was refined to $R1 = 0.0332$ and $wR2 = 0.0703$ using observed 39 x-ray reflections. The M -O bond distances along the c -axis direction of the unit cell are elongated, whereas those parallel to the a - b plane are compressed. At the T site, on the other hand, the tetrahedral O- T -O bond angles along the c -axis direction of the unit cell increases from 109.47° to 111.7 (6)°, which generates a compressed tetrahedral geometry along the c -axis. The cubic-to-tetragonal transition induced by the Jahn-Teller effect at Cu^{2+} is attributable to the elongation at the M site. The Jahn-Teller distortion by the Cu 3d orbital at the M site is confirmed by *ab-initio* quantum chemical calculations. With the competing distortions between the elongated octahedron and the compressed tetrahedron along the c -axis, the a unit cell parameter is shortened with respect to the c unit cell parameter, giving a c/a ratio slightly greater than unity as referred to cubic lattice ($c/a = 1.002$). The c/a value increases to 1.007 with pressure, suggesting a further variation of the elongated octahedron and the compressed tetrahedron. The variation of c/a ratio of the cuprospinel is similar to that observed in the tetragonally distorted cuprospinel with Cu^{2+} fully occupying the octahedral site of the structure.

Keywords: cuprospinel CuFe_2O_4 , high-pressure, single-crystal synchrotron x-ray diffraction method, Jahn-Teller effect