

Mn₄O₄ heterocubane cluster in LiMn₂O₄Kenji TATEISHI¹, Hironaga IGUCHI², Minami KAMOSITA², Nobuo ISHIZAWA*²¹Gifu Prefectural Ceramics Research Institute, Tajimi, Gifu, 507-0811, Japan²Nagoya Institute of Technology, Asahigaoka, Tajimi, Gifu 507-0071, Japan**Introduction**

Crystals of LiMn₂O₄ as used for the positive electrode in Li-ion battery undergo a structural phase transition near the room temperature. Structural information about these two phases is essential for understanding of the dynamics of Li-diffusion. Powder X-ray and neutron diffraction experiments have been reported previously by other authors but high precision single-crystal X-ray diffraction experiments can provide more accurate three-dimensional information about the electron density. This is especially important in the characterization of the electron density distribution of Mn₄O₄ heterocubane cluster in a very complicated structure like the low temperature modification of LiMn₂O₄ with unit cell volume of more than 5000Å³.

Experimental

Single crystals of LiMn₂O₄ were synthesized using a Li₂MoO₄ flux. Transition temperature was investigated through the examination of superlattice reflections. The compound showed a first order phase transition at 294 (1) K on cooling and at 310 (1) K on heating.

Single-crystal diffraction data were measured using a horizontal type four-circle diffractometer at beamline 14A of the Photon Factory, Tsukuba, Japan [1]. An eight-channel avalanche photodiode detector was used for photon counting [2]. The 0.75044 (5) Å wavelength used was calibrated using a spherically ground Si standard reference crystal.

Crystals of LiMn₂O₄ were mounted on tapered glass capillaries and preprocessed at low temperatures before the synchrotron diffraction experiment. Cell dimensions were determined using 24 reflections from 2θ≈86°. A half sphere of diffraction data to 2θ≤73° was measured at 297 (1) K, using an octahedrally shaped crystal of size 0.05 mm along the edge. Because no reflections violating the F lattice-centering conditions were observed in the sphere of 2θ ≤ 15°, only the F-centred reflections were measured up to 2θ = 73°. The measured reflections also satisfied the conditions *h*00: *h* = 4*n*, 0*k*0: *k* = 4*n* and 00*l*: *l* = 4*n*, which are conditions of *Fddd* symmetry.

The structure was essentially the same as that given by the neutron diffraction study [3]. The structural parameters were then refined using Xtal3.7. The merging R factor reduced from 2.7 to 2.5% after applying an analytical absorption correction. Dispersion and absorption coefficients were determined from the tables of Sasaki [4] and the final least-squares R factor reduced to 0.038. The populations of individual chemical elements

were refined with all other parameters fixed at values obtained in the final cycle. They ranged from 1.12 (3) to 1.13 (4) for independent four Li atoms, from 0.991 (3) to 0.996 (3) for five Mn atoms, and from 0.992 (6) to 1.002 (7) for nine O atoms. Thus, a stoichiometric composition was assumed for the present crystal. The maximum positive residual density of 3.0 e/Å³ was found at 0.71 Å from Mn3 and the minimum negative residual density of -0.7 e/Å³ at 1.65 Å from Li2.

The high temperature (HT) form adopts a normal spinel-type structure (cubic, *Fd-3m*) with the octahedral sites populated statistically with heterovalent Mn(III) and Mn(IV) in the equal ratio. The low temperature (LT) form adopts a 3x3x1 superstructure (orthorhombic, *Fddd*) with respect to the HT form, containing Mn(III), Mn(IV), and the intervalent Mn atoms.

The synchrotron X-ray single-crystal electron-density analysis revealed a large anisotropy of the atomic displacement parameters for part of O atoms, suggesting a possible occurrence of the bond-length fluctuation along the pseudo-tetragonal Jahn-Teller distortion parallel to the *a*-axis in the heterocubane Mn₂O₉ cluster. The cluster presumably shares three electrons among four *e*-parentage orbitals of Mn2 and behaves as a core of Zener-type polaron. The heterocubane Mn₂O₉ clusters are isolated from each other and embedded in an orbitally-ordered way in the charge-ordered matrix containing Mn(III) and Mn(IV). The transition between the LT and HT forms of LiMn₂O₄ can be regarded as an order-disorder transition of the Zener-type heterocubane polarons. It is notable that the heterocubane cluster in LiMn₂O₄ has a geometrical resemblance to oxygen-evolving complex composed of Mn-O-Ca in the enzyme photosystem II which enables water-splitting under light and release dioxygen in air.

References

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* ishizawa@nitech.ac.jp