

Electron density distribution of LiMn_2O_4 by the single-crystal diffraction study

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Introduction

Lithium manganese spinels are attractive candidates for cathode materials of rechargeable lithium ion batteries. Stoichiometric LiMn_2O_4 is a mixed valence compound comprised of distinct Mn(III) and Mn(IV) ions in equal proportions. Above the transition temperature T_c , Mn(III) and Mn(IV) ions are randomly distributed amongst the 16d sites of Fd-3m symmetry, while they are localized on five independent sites in Fddd symmetry below T_c . The lithium ion dynamics, which is very important from a viewpoint of practical applications, is also different in the high (HT) and low temperature (LT) phases. Structural information about these two phases is therefore essential for understanding of the processes involved. Powder X-ray and neutron diffraction experiments have been reported previously by other authors but high precision single crystal X-ray diffraction experiments in principle can provide more accurate three dimensional information about the electron density. Here we report on the LT structure determined via single-crystal synchrotron X-ray diffraction.

Experimental

Single crystals of LiMn_2O_4 were synthesized using a Li_2MoO_4 flux. Reagent grade Li_2CO_3 and MnCO_3 were weighed and combined together to form a nominal 7 mol% LiMn_2O_4 mixture. Approximately 31.7 g of the mixture was placed in a platinum crucible and heated to 1373 K at the rate of 45 K h^{-1} in an air atmosphere. The peak temperature was maintained for 10 h, and then reduced to 723 K at 5 K h^{-1} before discharge. The flux was rinsed out with warm water. The crystals were black and octahedrally shaped with a maximum size of about 0.1x0.1x0.1 mm³ along the edge. Transition temperatures were revealed by the existence of superlattice reflections using a Rigaku RAPID imaging plate diffractometer with a cryostat using nitrogen gas flow. This compound presented 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. An eight-channel avalanche photodiode detector was used for photon counting (Kishimoto et al. 1998). The 0.75044(5) Å wavelength was calibrated using a spherically ground Si standard reference crystal. Crystals of LiMn_2O_4 were mounted on tapered glass capillaries and preprocessed at low temperatures before the synchrotron diffraction

experiment. Cell dimensions were determined using 24 reflections. The crystal has a 3x3x1 superstructure of the spinel-type, with unit cell volume exceeding 5000 Å³. A half sphere of diffraction data up to $2\theta=73^\circ$ 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 $2\theta<15^\circ$, only the F-centred reflections were measured up to $2\theta=73^\circ$. Moreover the measured reflections also satisfied the conditions $h00: h=4n, 0k0: k=4n$ and $00l: l=4n$ which are the conditions for the Fddd symmetry. The merging R factor reduced from 2.7 to 2.5 % after applying an analytical absorption correction.

The populations of individual chemical elements are 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. Given that the excess values at Li sites was only 0.39(12) electrons at the most, the degree of contamination of Mn atoms at Li sites seemed marginal. Thus a stoichiometric composition was assumed for the present crystal. The checkCIF software suggested the possibility of pseudosymmetry $I4_1/amd$ for the final positional parameters. However the merge R factor was 0.107 after transforming the unit cell from orthorhombic to tetragonal. In addition the difference between the a and b cell dimensions was 0.028(2)Å, being 14 times larger than the esu. The tetragonality of the crystal was thus discarded in the present study. The final least-squares R factor reduced to $R(F)=0.038$. 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.

Part of the initial results have been published in our paper (Tateishi et al., 2004). A full discussion, including new findings about the ordered arrangement of Zenner polarons in the structure, will be given in our next paper which is being in progress.

References

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