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Structural Characterization of $LiMnVO_4$ with a Spinel-Related Structure

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A new compound of $LiMnVO_4$ has been synthesized. The crystal structure was determined by the Rietveld analysis. The framework structure is comprised of nearly regular octahedra of MnO_6 with edge-sharing. The lithium and vanadium ions occupy alternatively the tetrahedral interstitial sites constructed by close-packing arrays of oxide ions. The structure is discussed in relation to a normal spinel structure.

The lithium oxide spinels, $Li_xMn_2O_4$ ($0<x<2$), have been widely investigated for cathode materials in rechargeable lithium batteries because of their high cell voltage, a long self life and a wide operating temperature.1) In a spinel of general formula $A[B_2]X_4$ with prototypic symmetry $Fd\bar{3}m$, the structure is characterized by the $[B_2]X_4$ framework, of which the anion arrays are stacked with cubic close-packing.2) This framework which provides a three-dimensional interstitial space for lithium ion transport, remains intact over the lithiation process.3–6) Vanadium oxides, such as V_2O_5,7) V_6O_{13},8) and LiV_3O_8,9) are also attractive cathode materials for the lithium batteries because of their high valence state of the vanadium ions. The crystal structures of them are not spinel type but a sort of bronze-like structure where a nearly two-dimensional framework responsible for lithium insertion is realized. Therefore, if possible for synthesis, the oxide systems consisting of manganese and vanadium ions in a rigid framework may be an interesting candidate for cathode material of lithium batteries.

During investigations of the pseudo-binary system of $LiMn_2O_4$ and LiV_2O_4, we have found a new compound formulated by $LiMnVO_4$ with a spinel-related structure. We report here the crystal structure of this compound determined by the Rietveld analysis.

$LiMnVO_4$ was prepared by a conventional solid-state reaction of the stoichiometric mixture of Li_2CO_3, $Mn(CH_3COO)_24H_2O$ and V_2O_5 powders. The reactants were ground, pelletized under a pressure of 300 MPa and fired in an alumina crucible at 600 °C for 24 h in air. The phase purity, the composition and the valence state for metallic ions of the product was confirmed by powder X-ray diffraction, X-ray fluorescence and magnetic susceptibility measurements, respectively. The powder X-ray diffraction analysis showed a trace amount of a cubic spinel phase remaining in the product in addition to a new $LiMnVO_4$ compound. The product was found to be paramagnetic down to 77 K with a Weiss constant equal to about −80 K. The valence state for manganese and vanadium ions were found to be 2+ and 5+, respectively, from the estimation of the effective magnetic moment. The details of the magnetic property of this compound will be reported elsewhere. Powder X-ray diffraction pattern for the Rietveld analysis were recorded using a Rigaku RAD-rA diffractometer. The CuKα radiation used was monochromated by a curved-crystal graphite. The data were collected on thoroughly ground powders by a step scanning mode in a 2θ range from 10 to 100° with a step width of 0.02° and a step time of 4s. The powder pattern obtained was analyzed by the Rietveld method, using a RIETAN[10] profile refinement program. The indexing of the reflection peaks was made by means of the program CELL.[11] In the early stage of the indexing, the peaks observed at 2θ=18.6° and 36.2° were found to correspond to a cubic spinel phase. Considering from the cell constants for spinel compounds of $LiMn_2O_4$ (a=8.247 Å)[12] and LiV_2O_4 (a=8.241 Å),[13] these peaks may be attributable to the 1 1 1 and 3 1 1 reflections, respectively, of the spinel compounds, probably forming a solid solution such as $Li[Mn,V]_2O_4$. The remaining peaks were easily indexed on the basis of an orthorhombic system with approximate cell parameters of a=5.75 Å, b=8.70 Å, and c=6.35 Å. The reflection conditions found were h+k=2n for $h\,k\,l$ reflections and h, l=2n for $h\,0\,l$ reflections, leading to the C*c*-type space groups, *i.e.*, Cmcm, $Cmc2_1$, and C2cm (standard expression; Ama2). An initial structural model for the Rietveld refinement was constructed as follows. Assuming the formation of MnO_6 octahedron in this compound, the edge length of the octahedron (O–O distance) can be roughly estimated as a value equal to 3.08 Å by using the sum of the effective ionic radii[14] of Mn^{2+} (VI fold) and O^{2-} (II fold). This value is approximately equal to the half length of the c axis obtained from the CELL results. Similarly, the length of the orthogonal distance (O–Mn–O distance) can be estimated as a value of 4.36 Å, nearly equal to the half length of the b axis. These results means four MnO_6 octahedra involved in the unit cell when assuming a chemical formula of $LiMnVO_4$, leading to Z=4. The site for manganese ions was assigned to be at the origin in the unit cell, while that for vanadium ions was determined by some trials and errors in the early refinement stages. The assignment for lithium ions was not included in this refinement stage because of its considerably low atomic scattering factor. After several refinement stages, the location of the lithium ions could be found by means of the difference Fourier maps. Since a small amount of the spinel phase remains in the sample, the recorded pattern was analyzed by assuming a two-phase mixture. In the two-phase refinement mode of

Table 1. Positional parameters for $LiMnVO_4$. The cell parameters are a=5.7474(1) Å, b=8.7009(2) Å, c=6.3494(1) Å and Z=4 for Cmcm space group. The reliable factors[a] are R_{wp}=9.54%, R_p =6.97%, R_I =4.63%,[b] and R_F =3.80% [b]

Atom	Site	x	y	z	B/Å^2
Li	4c	0.0	−0.332(3)	0.25	1.1(8)
Mn	4a	0.0	0.0	0.0	1.0(1)
V	4c	0.0	0.3566(4)	0.25	0.3(1)
O(1)	8f	0.0	0.2480(1)	0.037(1)	0.8(1)
O(2)	8g	0.2636(9)	−0.0253(7)	0.25	1.1(1)

a) Defined in Ref.10. b) Those for impurity spinel phase are R_I =6.65% and R_F =3.80%.

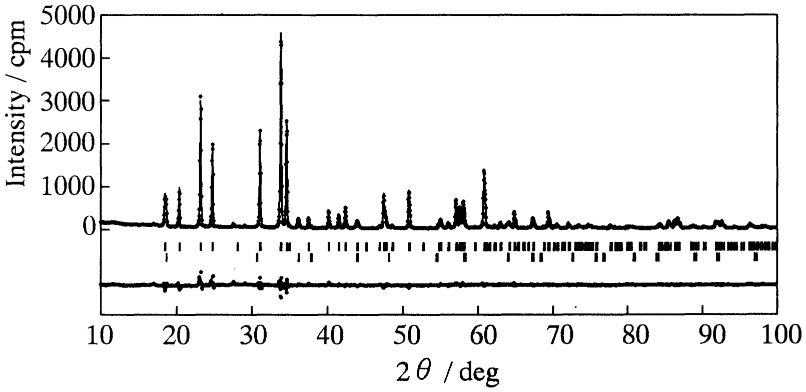

Fig.1. Powder X–ray diffraction pattern for $LiMnVO_4$. The calculated and observed data are shown as solid line and dots, respectively. The upper and lower bars are diffraction positions for $LiMnVO_4$ and impurity phase, respectively. The trace is a plot of the difference between calculated and observed data.

RIETAN, an isotropic thermal parameter for each of component elements was undertaken for the $LiMnVO_4$ phase, while an overall isotropic thermal parameter was adopted for the spinel phase. The site assignment for the spinel phase was based on the cubic space group $Fd\bar{3}m$. Finally, the Rietveld refinements were performed for the three space groups suggested from the CELL results. The *R*–factor for the weighted pattern fitting, R_{wp}, was reasonably reduced to around 9% for all space groups. However, the isotropic thermal parameters for the lithium site and for one of the oxygen sites were converged to relatively large negative values in the cases of $Cmc2_1$ and Ama2 space groups. These facts may result from an uncertainty for the lithium site because of its low contribution to the X–ray diffraction intensity. Although it can not be concluded at present which space groups are true, the Cmcm space group is adopted as the most probable one for the $LiMnVO_4$ compound in this study. In Table 1 are given the positional parameters finally obtained. Figure 1 shows the results of the pattern fitting of $LiMnVO_4$, where the reflection peaks corresponding to the impurity spinel phase are shown as bars at the lower side in the middle of the figure.

The weight ratio of the impurity phase was determined on the basis of the scale factors finally obtained for $LiMnVO_4$ and the impurity. From the method proposed by Hill *et. al.*,15) the ratio was found to be 6.08%. At present, it is unknown whether the mixture of $LiMn_2O_4$ and LiV_2O_4 or the solid solution of $Li[Mn,V]_2O_4$ is the true composition for the spinel phase because of their quite nearly equal lattice parameters and of the fairly low concentration in the product. The crystal structure of $LiMnVO_4$ is illustrated in Fig.2. The edge–sharing MnO_6 octahedra with almost regular run along the *c* axis. There are two kinds of Mn–O bond distances in the MnO_6 octahedron, *i.e.*, one is the bond of Mn–O(1) (2.171 Å) and the other the bond of Mn–O(2) (2.205 Å), the average distance of which is 2.188 Å, almost equal to the distance (2.192 Å) estimated from the effective ionic radii14) of Mn^{2+}(VI fold) and O^{2-}(II fold). The three oxygen atoms of the octahedron form close–packing arrays running in the direction parallel to the (110) plane. Lithium and vanadium ions occupy alternatively the sites located in the interstitial space constructed by the close–packing arrays of oxide ions. Figure 3 shows the environment around the lithium and vanadium ions. LiO_4 and VO_4 tetrahedra are linked each other with sharing two O(2) ions. Both of the two tetrahedra are fairly distorted from an ideal tetrahedron. The position of the lithium and vanadium ions is shifted toward the opposite direction each other from the center of the tetrahedron. Since the distortion of the LiO_4 tetrahedron with a less positive charge of central cation is larger than that of the VO_4

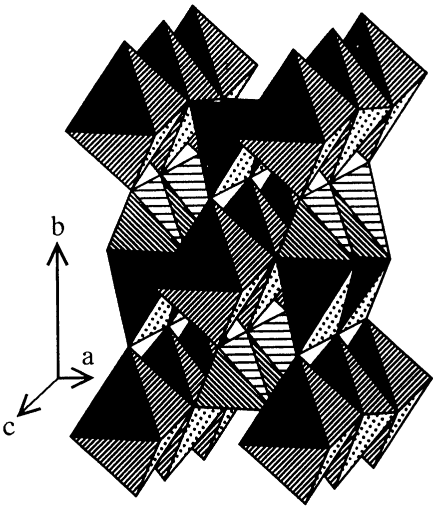

Fig.2. Crystal structure of $LiMnVO_4$. Small tetrahedra, large tetrahedra, and octahedra are VO_4, LiO_4, and MnO_6, respectively.

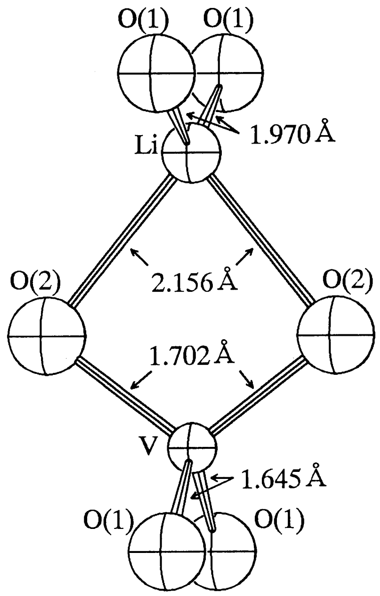

Fig. 3. Environment around Li and V ions. The size of the spheres for atoms is drawn with the ratios of their ionic radii.

tetrahedron, such distortion seems to be due to a coulomb repulsion between the two cations. There exists an interesting structural similarity in comparison between a normal spinel and $LiMnVO_4$. Both structures have cubic close-packing arrays of oxide ions, running along the direction parallel to the (111) plane for the spinel and the (110) plane for $LiMnVO_4$. The cations are distributed in the interstitial sites produced between the two neighboring arrays. Such situations for the two structures are schematically illustrated in Fig.4 in the view from the direction perpendicular to the arrays. In the spinel structure there is a set of layers where tetrahedra and octahedra coexist in the same layer, while the layers involving only tetrahedra or only octahedra are alternatively stacked between the oxygen arrays in $LiMnVO_4$. A similar example of such a spinel-related structure has been reported for $LiCuVO_4$,$^{16)}$ the structure of which is somewhat different from that of $LiMnVO_4$ because of high concentrations of Jahn–Teller Cu^{2+} ions in $LiCuVO_4$. In this compound, the lithium and the copper ions are situated on the octahedral sites and the vanadium ions on the tetrahedral sites.

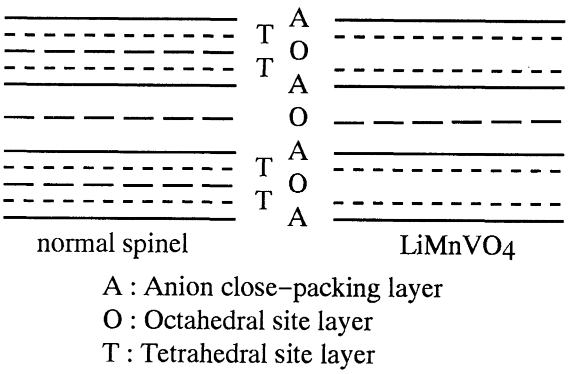

Fig.4. Structural comparison between normal spinel and $LiMnVO_4$. The stacking structure is projected along the directions parallel to (111) plane for normal spinel and (110) plane for $LiMnVO_4$.

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