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Structural Change in Lithium Intercalation of Defect Perovskite $LiCuM_3O_9$ (M=Ta, Nb)

Mineo SATO,* Tetsuro JIN, Yoshiki HAMA, and Kazuyoshi UEMATSU
Department of Material and Chemical Engineering, Faculty of Engineering, Niigata University,
Ikarashi 2-nocho, Niigata 950-21

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The chemical lithium intercalation of defect perovskite $LiCuM_3O_9$ (M=Ta, Nb) compounds has been performed by using butyllithium. The content of the inserted lithium ions in the compounds was found to be ca. 1 mol per unit formula for M=Ta and ca. 4 mol per unit formula for M=Nb. The crystal structure of the intercalated compound was determined based on the powder X-ray diffraction pattern. The intercalated product was well crystallized for M=Ta, but almost amorphous for M=Nb. The Rietveld refinement confirmed that the intercalated tantalate, $Li_2CuTa_3O_9$, adopts a rhombohedrally distorted perovskite structure with $a=5.4896(8)$ Å, $\alpha=56.544(8)°$ and $Z=2$ for the $R\overline{3}c$ space group. The Li and Cu atoms are statistically distributed over an identical crystallographic site with an atomic ratio of Li : Cu = 2 : 1. The coordination of the nearest-neighbor oxygen atoms around the (Li,Cu) site was changed from square-planar four-fold to triangular three-fold, accompanied by an intercalation reaction. This structural change could be reasonably explained as being due to the occurrence of a reduction of strong Jahn-Teller Cu^{2+} ions to Cu^{+} ions as a result of the lithium insertion.

Transition metal oxides, into which mobile ions, such as Li^{+} and Na^{+}, can be reversibly inserted, are of particular interest for possible applications as active electrodes in batteries and electrochromic displays. The characteristics necessary for such electrode materials may be found in systems involving tunnel or framework structures available for the migration of mobile ions as well as easily reductive metal ions accompanying the intercalation reaction.$^{1)}$

Defect perovskite, $CuTa_2O_6$, seems to be favorable for such materials, owing to its framework of rigid TaO_6 octahedra and the existence of reductive Cu^{2+} ions. The crystal structure of $CuTa_2O_6$ is characterized by a defective perovskite-like structure, where the TaO_6 octahedra are tilted and linked to each other in such a manner so as to introduce a square-planar four-fold coordination around the Cu^{2+} (d^9) ions due to its Jahn-Teller distortion.$^{2)}$ As a result, there exist a large number of vacant sites in the A site of this compound. We recently reported on the synthesis and crystal structure of $LiCuM_3O_9$ (M=Ta, Nb) compounds which have essentially the same crystal structure as that of $CuTa_2O_6$.$^{3)}$ In this compound, although the sites for Cu^{2+} ions are diluted by 50% of Li^{+} ions with a total occupancy of 8/9, the square-planar coordination is still maintained. Another interesting feature of these compounds is the fact that the $LiCuNb_3O_9$ compound exists even though its mother compound of $CuNb_2O_6$ does not crystallize in any perovskite structures, but, rather, in a columbite structure.$^{4)}$ For an ideal perovskite structure of the ABO_3 type, the unit formula of these compounds can be expressed as $Li_{1/3}Cu_{1/3}MO_3$. This leads to the fact that one-third of the A sites per unit formula are vacant as interstitial spaces in a three-dimensional network of a rigid TaO_6 octahedron. An appreciable quantity of lithium is, therefore, expected to be inserted topochemically into the interstitial space with a possible simultaneous reduction of Cu^{2+} to Cu^{+}. Thereby, one can expect to render the $LiCuM_3O_9$ compounds as an attractive candidate for a suitable cathode material for a lithium battery.

We report here on a chemical lithium intercalation into $LiCuM_3O_9$ by using buthyllithium and the crystal structure of the intercalation product by a Rietveld method.

Experimental

Synthesis and Analysis. $LiCuM_3O_9$ (M=Ta, Nb) was prepared by the solid-state reaction in the same way as described previously.$^{3)}$ The lithium intercalation reaction of $LiCuM_3O_9$ was carried out by a chemical lithiation of $LiCuM_3O_9$ powder with an excess of butyllithium (1.49 mol dm^{-3} in hexane) in a water-free hexane solution at 25 °C for 5 days under a nitrogen atmosphere. After the reaction, the color of the product was changed from light green to black for M=Ta and from dark green to black for M=Nb. The product was thoroughly washed with hexane, dried at 100 °C under nitrogen, and stored in an ampule filled with nitrogen gas. Although both products were relatively stable in the ambient atmosphere, it was found that oxidation of the product proceeded gradually: The color changed from black to dark green for both products after exposure to moist air for a couple of days. A powder X-ray diffraction analysis showed a trace amount of $LiCuTa_3O_9$ compound still remaining in the tantalate product. The niobate product was found to be a considerably poorer crystalline than the tantalate product, probably becoming amorphous, as shown in the next section in detail. The lithium concentration in the intercalated product was analyzed by a conventional wet chemical analysis and secondary ion mass spectroscopy (SIMS). Since the intercalated products did not dissolve in any strong acid solutions, the lithium content was determined by a sort of back titration for the lithium remaining in the solution after the intercalation reaction. The samples were pressed into a disc for a SIMS measurement. A SIMS analyzer (HITACHI, IMA-2) was used. The amount of inter-

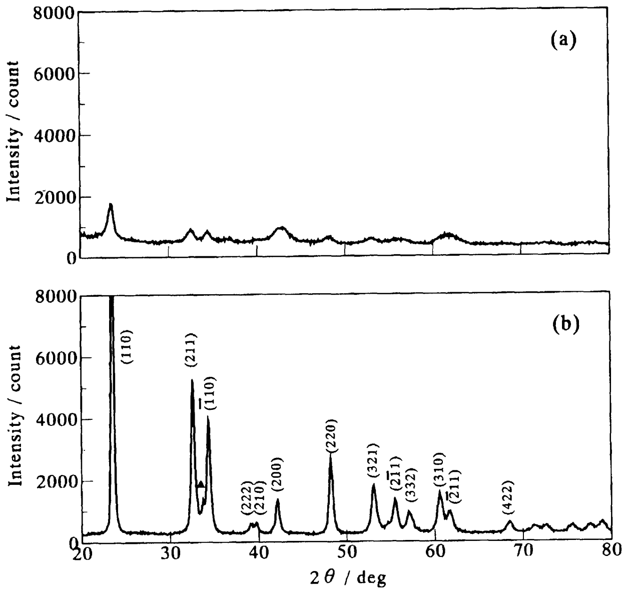


Fig. 1. Powder X-ray diffraction patterns for products of lithium intercalation into $LiCuM_3O_9$ where M=Nb (a) and M=Ta (b). The Miller indices given in the figure are based on the rhombohedral symmetry with the $R\bar{3}c$ space group. The reflection peak, indicated by a filled triangle, corresponds to that of the mother compound, $LiCuTa_3O_9$.

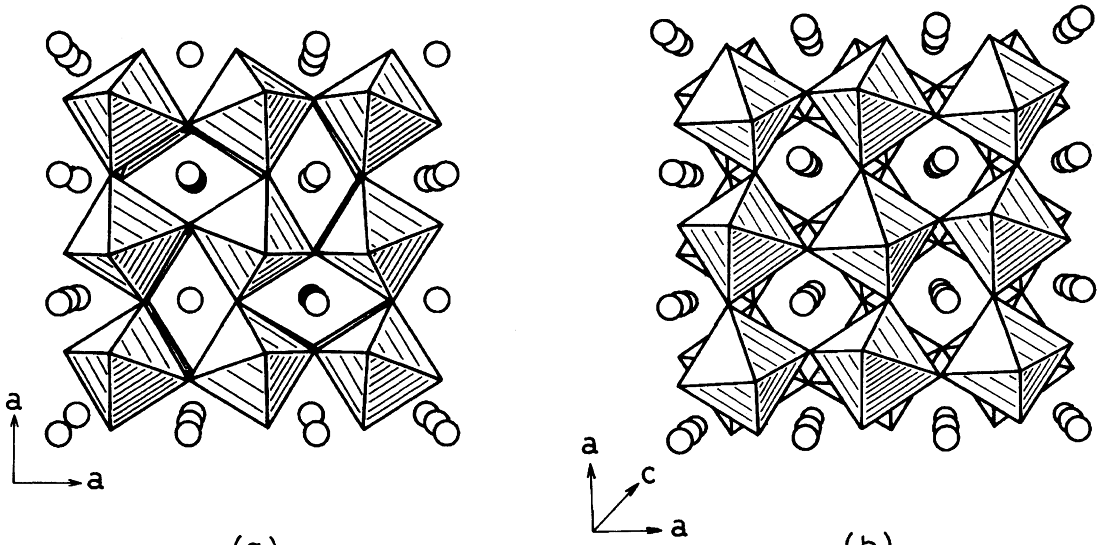
calated lithium ions determined by these method was found to be 0.9 mol per unit formula for the tantalate product and 4.2 mol for the niobate product. Considering the fact that the tantalate product contains a trace amount of the mother compound, $LiCuTa_3O_9$, the true composition of the intercalated tantalate may be regarded as being $Li_2CuM_3O_9$.

Data Collection of Powder X-Ray Diffraction. Powder X-ray diffraction data were collected using Cu$K\alpha$ radiation and a θ—2θ diffractometer (Rigaku Denki, Rotaflex RU-200BVS) with a curved-graphite monochrometer located on the diffracted beam side and with a high-temperature furnace attachment. Since the sample was slightly oxidized in the ambient atmosphere, the diffraction measurement was performed using a high-temperature furnace attachment at room temperature in a nitrogen atmosphere with a flow rate of 100 ml min^{-1}. The counting rate was 4 s at each step of 0.02° over the 2θ range of 20—120°. The structure refinement of the compound was performed using the total pattern fit program RIETAN$^{5)}$ based on the Rietveld method.$^{6)}$

Results and Discussion

Structural Analysis. Figure 1 shows the powder X-ray diffraction patterns of intercalated products for $LiCuNb_3O_9$ and $LiCuTa_3O_9$. The intercalated compound for the tantalate is well crystallized, while that for the niobate is a poorer crystalline, almost becoming amorphous. However, one can notice that each of the weak, broad reflections found in the niobate corresponds to that found in the tantalate. This means that the basic crystal lattice for the intercalated niobate is likely to be the same as that for the tantalate intercalated compound. Indexing of the reflection peaks was made by means of the program CELL.$^{7)}$ The reflection conditions found were $l=2n$ for hhl reflections and $h=2n$ for hhh reflections on the basis of a rhombohedral symmetry, leading to the Rxc-type space groups,$^{8)}$ i.e., $R3c$ and $R\bar{3}c$. Because of the poor crystallinity of the intercalated niobate, a Rietveld refinement was carried out for only the intercalated tantalate, the chemical formula of which was assumed to be $Li_2CuTa_3O_9$. An initial structural model for the Rietveld refinement was constructed for both space groups by assuming the formation of a TaO_6 octahedron. Based on these space groups, the approximate values of the cell parameters were obtained as being a=5.51 Å and α=56.5°, respectively, from the CELL. The O–Ta–O distance along the orthogonal direction of a TaO_6 octahedron is sometimes in the 3.85—3.95 Å range, as has been observed in many oxides systems involving corner-sharing TaO_6 octahedra.$^{9)}$ Considering these facts together with the results obtained from the CELL, it was found that two tantalum atoms should be involved in the unit cell of the intercalated compound. Therefore, an initial structural model for the Rietveld refinement was constructed by assuming that $Z=2$. Such a restriction condition for the molecular number of the unit cell should give a chemical formula, $Li_{2/3}Cu_{1/3}TaO_3$, per unit cell. No correction on the preferred orientation was made, since the intercalated sample comprised fine grains. Since a small amount of the mother phase remained in the sample, the recorded pattern was analyzed while assuming a two-phase mixture. In the two-phase refinement mode of RIETAN, a matrix refinement of the intercalated structure with the variables of the scale factor, lattice parameters, fractional coordinates and individual isotropic thermal parameters was undertaken, while the refinement of the mother phase as an impurity was made using only the scale factor and an overall isotropic thermal parameter as the variable parameters; the lattice parameters and fractional coordinates were fixed at the values reported in previous work.$^{3)}$

It was found that in the early refinement stage lithium and copper atoms cannot independently occupy respective crystallographic sites. This means that these atoms are statistically distributed over an identical site, such as that found in $LiCuTa_3O_9$. This site is thus expressed as (Li,Cu) in the following. Based on a chemical analysis of the lithium content, the mixed ratio of lithium and copper atoms at the site was fixed at 2 : 1. The R-factors could be reasonably reduced to less than 10% for both the $R3c$ and $R\bar{3}c$ space groups in the following refinement stage. However, since the isotropic thermal parameter for an oxygen site based on the $R3c$ space group converged to a large negative value (which has no physical meaning), this space group was eliminated from any further refinement stage. Table 1 gives the data-collection conditions, some crystallographic data and the final R-factors achieved. The positional pa-



(a) (b)

Fig. 2. Crystal structures projected along the [100] direction for $LiCuTa_3O_9$ (a) and along the [110] direction for $Li_2CuTa_3O_9$ (b), showing (Li,Cu) sites (open circles) and TaO_6 octahedra.

Table 1. Data-Collection Conditions, Crystallographic Data, and Reliable Factors for $Li_2CuTa_3O_9$

Radiation		Cu$K\alpha$
2θ range (°)		20—120
Step scan increment (2θ°)		0.04
Count time (s step^{-1})		4
Space group		$R\bar{3}c$ (No.167)
a (Å)		5.4896(8)
α (°)		56.544(8)
Volume (Å^3)		107.6
Z		2
Calculated density (g cm^{-3})		7.860
No. of parameters refined		24
No. of reflections		246
Reliable factors[a]	R_{wp}	0.0914
	R_p	0.0697
	R_I	0.0361
	R_F	0.0193

Defined as follows;

$$R_{wp}=\left[\frac{\Sigma w_i[Y_{\text{obs}}-Y_{\text{cal}}]^2}{\Sigma w_i[Y_{\text{obs}}]^2}\right]^{1/2},$$

$$R_p=\frac{\Sigma\mid Y_{\text{obs}}-Y_{\text{cal}}\mid}{\Sigma Y_{\text{obs}}},$$

$$R_I=\frac{\Sigma\mid I_{\text{obs}}-I_{\text{cal}}\mid}{\Sigma I_{\text{obs}}},$$

$$R_F=\frac{\Sigma\mid [I_{\text{obs}}]^{1/2}-[I_{\text{cal}}]^{1/2}\mid}{\Sigma[I_{\text{obs}}]^{1/2}}.$$

Table 2. Positional Parameters for $Li_2CuTa_3O_9$

Atom	Site[a]	g[b]	x	y	z	B/Å^2
(Li,Cu)	$2a$	1.0[c]	0.25	0.25	0.25	3.2(6)
Ta	$2b$	1.0	0.0	0.0	0.0	0.6(2)
O	$6e$	1.0	0.641(4)	−0.141(4)	0.25	0.2(6)

a) Multiplicity and Wyckoff notation. b) Site occupancy. c) Atomic ratio is assigned to be Li : Cu=2/3 : 1/3.

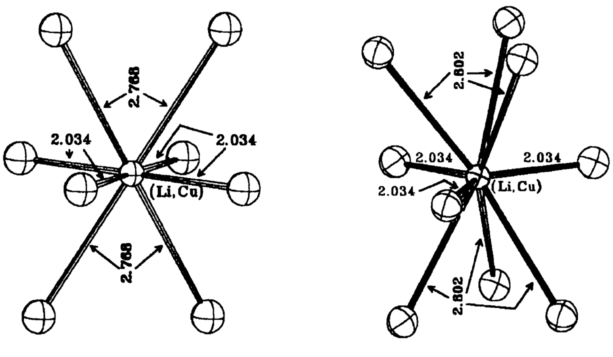
rameters and selected interatomic distances and angles are listed in Tables 2 and 3, respectively.

Description of the Structure. The crystal structure of $Li_2CuTa_3O_9$ built up from the obtained structural parameters is shown in Fig. 2 together with that of the mother material of $LiCuTa_3O_9$ (a=7.5178(1) Å, cubic with $Im\bar{3}$ space group and $Z=2$) as a reference. The difference found between the two structures is quite interesting. The TaO_6 octahedron in $LiCuTa_3O_9$ is tilted so as to produce an almost square-planar coordination around the (Li,Cu) sites due to the strong Jahn-Teller effect of the Cu^{2+} ion. In contrast to this structure, the TaO_6 octahedron in $Li_2CuTa_3O_9$ is twisted along the [1 1 0] direction. The O–Ta–O angles, comprising the nearest-neighbor oxygen within the TaO_6 octahedra for $Li_2CuTa_3O_9$, are quite close to 90° (Table 3), forming an almost perfect octahedron whose Ta–O bond distance and Ta–O–Ta angle between two TaO_6 octahedra (1.973 Å and 146.6°) are very compatible with those (1.980 Å and 143.2°) for $LiCuTa_3O_9$, respectively. Therefore, the intercalation of lithium causes no deformation of the TaO_6 octahedra, but a remarkable change in the twisting of the octahedron linkage so as to produce interstitial space for the accommodation of lithium ions. The environment around the (Li,Cu) site in the intercalated compound is shown in Fig. 3 together with that for the mother compound. The coordination number of the (Li,Cu) site by oxygen atoms including the second-neighbor oxygen atoms is ninefold, comprising three short (Li,Cu)–O bonds with 2.034 Å and six long (Li,Cu)–O bonds with

Table 3. Bond Distances (/Å) and Angles (/°) for $Li_2CuTa_3O_9$

Distance		
(Li,Cu)–O	2.034(21)×3	(nearest-neighbor)
(Li,Cu)–$O^{1)}$	2.802(4)×3	(second-neighbor)
Ta–$O^{2)}$	1.973(6)×4	(nearest-neighbor)
$O^{3)}$–$O^{4)}$	2.778(13)	(within TaO_6)
$O^{3)}$–$O^{5)}$	2.802(4)	(within TaO_6)
O–$O^{5)}$	3.524(36)	(within $(Li,Cu)O_3$)
Angle		
O–(Li,Cu)–$O^{5)}$	120.0	(within $(Li,Cu)O_3$)
$O^{6)}$–Ta–$O^{7)}$	180.0	(within TaO_6)
$O^{6)}$–Ta–$O^{8)}$	89.5(1)	(within TaO_6)
$O^{6)}$–Ta–$O^{2)}$	90.4(1)	(within TaO_6)
Ta–$O^{9)}$–$O^{10)}$	146.6(11)	(between two TaO_6)

Symmetry code: none x, y, z; 1) y, z, x; 2) $-y$, $-z$, $1-x$; 3) $-y$, $1-z$, $1-x$; 4) $1-x$, $-y$, $1-z$; 5) z, x, y; 6) $-1+x$, y, z; 7) $1-x$, $-y$, $-z$; 8) z, $1-x$, y; 9) $1-x$, $-y$, $-z$; 10) $1/2-y$, $1/2-x$, $-1/2-z$.



(a) (b)

Fig. 3. Environment around the (Li,Cu) site coordinated by oxygen atoms with nearest- and second-neighbors for $LiCuTa_3O_9$ (a) and $Li_2CuTa_3O_9$ (b).

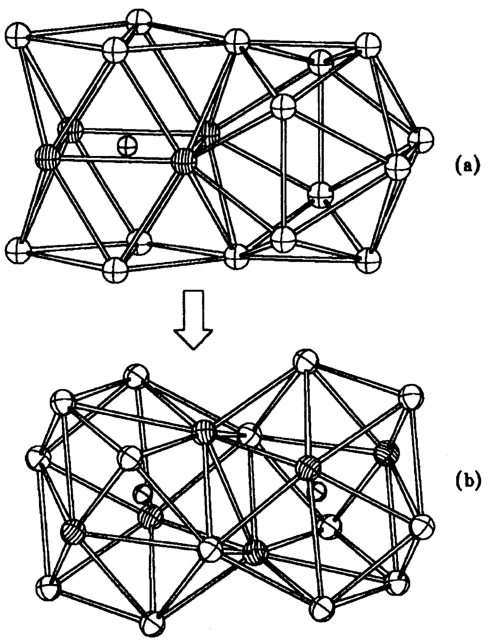


Fig. 4. Coordination polyhedra with (Li,Cu) site for $LiCuTa_3O_9$ (a) and $Li_2CuTa_3O_9$ (b). The shaded oxygen atoms are the nearest-neighbors to the (Li, Cu) site.

2.802 Å. These individual (Li,Cu)–O bond distances found in $Li_2CuTa_3O_9$ are quite compatible with those in $LiCuTa_3O_9$, i.e., the coordination number of the (Li, Cu) site including the second neighboring oxygen atoms is eightfold (four short square-planar bonds with 2.034 Å and four long bonds with 2.768 Å). However, a significant difference is found in the coordination around the (Li,Cu) site between these two compounds, i.e., the coordination number increases from eightfold to ninefold accompanied by lithium intercalation in the case within the second-neighbor oxygen atoms. When the third-neighbor oxygen atoms for the intercalated compound are included, the coordination number is twelvefold. Interestingly, this is also true for the mother compound. Such a situation is illustrated in Fig. 4. In the case of $LiCuTa_3O_9$, one of the cation sites corresponding to the A site in an ideal perovskite is vacant due to a distortion resulting from the square-planar coordination of the adjacent (Li,Cu) site with strong Jahn-Teller Cu^{2+} ions. On the other hand, two such adjacent sites become equivalent in an intercalated compound, in which a center of symmetry is located at the middle point between the two (Li,Cu) sites. These structural changes accompanied by the lithium intercalation reaction can be reasonably explained as follows. Lithium intercalation into $LiCuTa_3O_9$ results in a reduction of Cu^{2+} to Cu^{+}, thus relaxing the distortion at the A site due to the disappearance of Jahn-Teller Cu^{2+} ions. Consequently, the A sites can be fully occupied by (Li,Cu) species.

The structural change accompanied by the lithium intercalation reaction of $LiCuTa_3O_9$ is somewhat unique. Since the individual relative intensities of the X-ray diffraction peaks for the intercalated niobate is approximately compatible with the corresponding ones for the intercalated tantalate (Fig. 1), its structure is thought to be basically the same as that for the tantalate, although the crystallinity is considerably poor. Regarding the fact that the content of the intercalated lithium ions is about 4 mol per formula, the reduction of Nb^{5+} to Nb^{4+} could occur accompanied by the intercalation reaction. As long as the crystal structure shown in Fig. 1 does not change during the intercalation reaction of $LiCuNb_3O_9$, there is no crystallographic site available for accommodating beyond 1 mol of lithium ions. Therefore, such additional lithium ions intercalated in the niobate is thought to be located in the interstitial sites without any crystallographic symmetry, probably making the crystallinity so poor. In view of practical applications to lithium batteries, $LiCuNb_3O_9$ may have many more advantages than $LiCuTa_3O_9$ because of its intercalated product with a high accommodation of lithium ions as well as the poor crystallinity, which can provide smooth insertion and deinsertion of lithium ions during both charging and discharging processes of the battery, as observed in V_2O_5–P_2O_5 glass systems.$^{10)}$

The present Rietveld analysis using a powder X-ray diffraction method was capable of giving a structural model based on the site assignment of lithium and copper atoms to the same crystallographic site. Because of the considerably small X-ray scattering factor of lithium compared with other elements, another structural model based on individual site assignments for these atoms may be possible. The authors are planing to carry out neutron diffraction experiments of this compound in order to clarify this possibility.

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