Na^+/Li^+ Exchange in One-Dimensional Tunnels of the Framework Structure

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Metastable Li-titanogallate has been obtained by substituting Li^+ ions for Na^+ ions of $Na_xTi_{2-x}Ga_{4+x}O_{10}$ (x=0.85) in molten $LiNO_3$ at 450 °C. Na^+ ions in one-dimensional tunnels of the framework structure have been practically exchanged by Li^+ ions. Rietveld fitting of X-ray diffraction profile has clarified that the framework structure has been retained but reasonably deformed by the ion exchange reaction.

Ion exchange reactions can be observed for many compounds whose structures are characterized by layers or three-dimensionally interconnected tunnels. In contrast, little attention has been paid for exchange of ions in one-dimensional (1-D) tunnels. It is probably because 1-D pathways are disadvantageous for ion exchange. Two ions are almost unable to exchange their positions in a tunnel unless the tunnel has a sufficiently large cross section. It has been, however, reported that Li^+ ions in the 1-D tunnels of the ramsdellite-type are replaced by protons in HNO_3 aqueous solution.[1] England *et al.*[2] found the structure of $Na_2Ti_6O_{13}$ containing 1-D tunnels was considerably deformed by the treatment in molten $LiNO_3$ at 280 °C. This would be due to the Na^+/Li^+ exchange, although they gave no additional evidence for ion exchange and described that the removal of Na^+ ions might be imperfect. A few of other examples[3,4] also suggested that heat treatment in a molten salt can be an effective technique for ion exchange even in 1-D tunnels. In this report, the substitution of Li^+ for Na^+ in the 1-D Na^+ ion conductor $Na_xTi_{2-x}Ga_{4+x}O_{10}$ (x~0.85) has been confirmed by chemical composition analysis, TG-DTA and the Rietveld fitting of powder X-ray diffraction profile. The framework structure of this sodiumtitanogallate consisting of GaO_4 tetrahedra and GaO_6, TiO_6 octahedra contains 1-D tunnels of a large octagonal cross section where Na^+ ions are resided.[5] It should be noted that the derived Li^+-titanogallate is unable to be synthesized by conventional methods based on thermal equilibrium at high temperature. The Li-derivative is in particular promising for applications to electrochemical devices such as Li^+ ion conductors.

The parent compound $Na_xTi_{2-x}Ga_{4+x}O_{10}$ (x=0.85) was prepared by heating a mixture of Na_2CO_3, TiO_2 and Ga_2O_3 with a molar ratio of 0.85:2.30:4.85 at 900 °C for 1 h. The sample was ground and reheated at 1250 °C for 20 h. The products were identified by X-ray diffraction patterns, which had not changed after further reheating at 1250 °C for 20 h. Li^+ ion-exchange has been performed by reacting 1.0 g of the parent sample with an excess (*ca.* 10 g) of molten $LiNO_3$ at 450 °C for 20 h. The product was cooled and separated from the frozen nitrate by washing with water. This procedure was repeated three times. At every stage completion of ion-exchange can be qualitatively checked by the X-ray measurement of samples used for TG-DTA. The metastable Li-salt decomposes to give X-ray diffraction peaks indexed by lattice parameters of spinel type $LiGa_5O_8$,[6] while Na^+ ions remained lead to the formation of sodiumtitanogallte $Na_xTi_{1-x}Ga_{4+x}O_8$ (x~0.7)[7] which is stable up to more than 1300 °C. The contents of Ti and Ga in a product were determined by EDTA titration and those of Li and Na were by ICP-AES. The framework structure after the ion-exchange reaction has been refined by the Rietveld profile fitting of powder X-ray diffraction patterns. The diffraction data were collected on the *Rigaku RAD-2B* diffractometer with graphite-monochromatized Cu Kα radiation in a scan range of 20 ~ 80° at a step interval of 0.02° in 2θ. Initial atomic positions were taken from the data obtained for a single crystal of the Na-salt.[5] The program *RIETAN94*[8] was used for the refinement.

The product showed a strong exothermic peak around 715 °C on the DTA curve. The peak was based on a decomposition of the product, but the TG curve gave no indication for dehydration. Chemical analysis resulted in a chemical formula of $Li_{0.98}Na_{0.03}Ti_{1.16}Ga_{4.78}O_{10}$, which means that Na^+ ions in the tunnels were almost exchanged by Li^+. A total content of the alkali metal ions is, however, more than that in the parent compound or $Na_{0.85}Ti_{1.15}Ga_{4.84}O_{10}$. A significant decrease of Ga content by the ion exchange reaction suggests a small proportion of Ga^{3+} ions in the framework structure may be exchanged by Li^+ or expelled to form vacancies. General chemical formula $Li_{x+3y}Na_{0.85-x}Ti_{1.15}Ga_{4.85-y}O_{10}$ is consistent with the above composition by estimating x (the number of Na^+ ions exchanged) and y (the number of Ga^{3+} ions removed) at 0.82 and 0.06, respectively.

The results from the Rietveld analysis, of which the fitted profile is displayed in Figure 1, are listed in Table 1. Because of

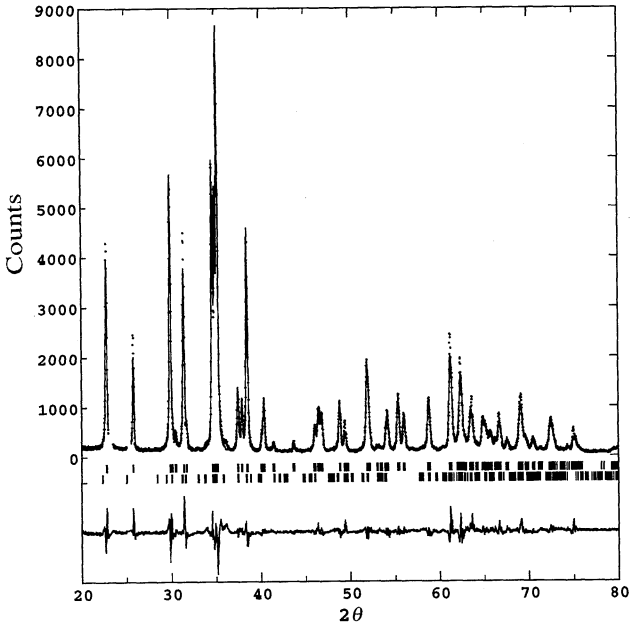

Figure 1. Final Rietveld fit for $Li_{0.98}Na_{0.03}Ti_{1.16}Ga_{4.78}O_{10}$. Dotted and solid lines are observed and calculated profiles, respectively. The differece plot is at the bottom.

Table 1. Atomic coordinates and isotropic temperature factors for $Li_{0.98}Na_{0.03}Ti_{1.16}Ga_{4.78}O_{10}$

Atom	x	z	B_{iso}(Å^2)
Ga1	0.0600(7)	0.1717(7)	1.5(3)
Ga2	0.3223(8)	0.1040(8)	0.6(2)
M(Ga/Ti)	0.2683(7)	0.626(1)	1.0(2)
O1	0.166(4)	0.018(3)	0.1(3)
O2	0.107(3)	0.337(3)	0.1
O3	0.217(2)	0.787(3)	0.1
O4	0.327(3)	0.438(2)	0.1
O5	0.487(3)	0.155(3)	0.1

Space group: *C2/m*.
y = 0 for all atoms. Ga:Ti=0.42:0.58 at the M site.
Positions of alkali cations are unable to be determined.
R_{wp}=0.116, R_p=0.088, R_I=0.023, R_F=0.014

a weak scattering ability and probably a broad distribution of Li^+, the positions of Li^+ ions could not be determined. The framework structure has been confirmed to be retained after the ion-exchange reaction as shown in Figure 2. Lattice parameters and interatomic distances between oxygens across the tunnel are compared with those of the Na-salt in Table 2. A significant decrease of O2-O2 could be attributed to the relaxation of a strain in the framework structure by the removal of Na^+ ions at (0, 0, 1/2). This six-coordination site, at 0.211(3) nm from two O2 and 0.263(3) nm from four O4, is one of the possible positions for location of a Li^+ ion judging from the ionic radius of Li^+, 0.074 nm, in six-coordination.[9] More unambiguous information about Li^+ ion distribution may be given by further experiments such as a neutron diffraction. The unit cell is remarkably contracted in the direction along the a-axis. An opposite result was reported for Li^+ ion-exchange of sodiumtitanate $Na_2Ti_6O_{13}$[2], in which the unit cell was unexpectedly elongated along the a-axis. The reason seems to be due to a coordination change for the Li^+ ion[2].

It is of interest in the future to confirm the anisotropic property

Table 2. Variation of lattice parameters and O-O distances across the tunnel section according to Li^+ ion exchange

	Na-salt [a]	Li-salt
lattice parameter		
a (nm)	1.2093(2)	1.18532(6)
b	0.30117(5)	0.30257(1)
c	1.04134(9)	1.03702(5)
β (°)	92.29(1)	90.069(3)
interatomic distance		
O2-O2 (nm)	0.4923(6)	0.423(6)
O4-O4	0.4352(6)	0.430(7)

[a] Michiue *et al.* [5]

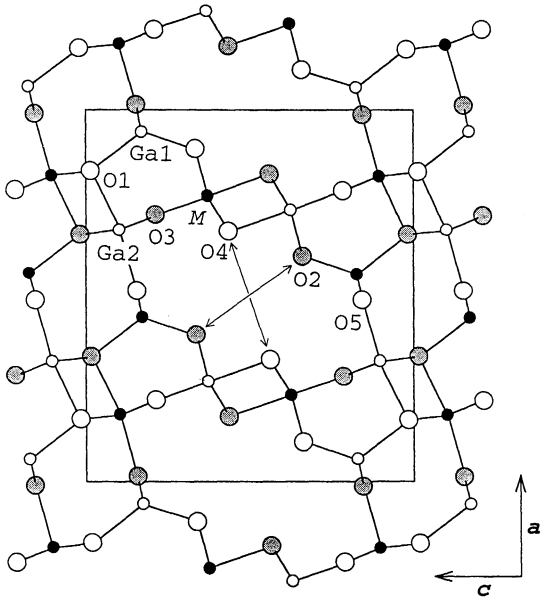

Figure 2. Projection along [0 1 0] for the framework structure of $Li_{0.98}Na_{0.03}Ti_{1.16}Ga_{4.78}O_{10}$. Atoms at y=0 and 1/2 are represented by open and filled circles, respectively.

in diffusion coefficients, ion conductivities, *etc.* for the present titanogallate in which fast ion transport seems to be restricted by utilizing 1-D tunnels. These data would also provide useful information about the exchanging process of the two ion species. The geometry of the tunnel with a large cross section may allow for the two ions to exchange their positions in a tunnel, while there is a possibility that the Li^+ ion transport by the 3-D pathway may be enhanced at 450 °C; Li^+ ions would migrate through the tunnel wall.

References and Notes

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