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$Na_xCr_xTi_{8-x}O_{16}$, Priderite with Sodium Ions in the Tunnel—Structural Study for Stability and Na Ion Transport

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Single crystals of Na priderite $Na_xCr_xTi_{8-x}O_{16}$ ($x \sim 1.7$) with the hollandite-type tunnel structure have been grown by a flux method; tetragonal, $I4/m$ with $a = 10.058(1)$, $c = 2.957(1)$ Å, and $Z = 1$. Formation of Na priderite has been unexpected due to the size fitness between the framework structure and the tunnel ion because the cavity in the hollandite-type tunnel appears too large to stabilize Na ions. Single-crystals X ray diffraction analysis has revealed that the Na ion distribution in the tunnel is essentially different from that of large ions such as K, Rb, and Cs. In contrast with the usual case of K priderite, a part of the Na ions are located in particular around the center of the square plane of oxygens connecting adjacent cavities. This fact suggests this oxygen square would no longer act as a bottleneck for transport of the tunnel ion as in K priderite. Other Na ions are distributed at four equivalent positions around the tunnel axis in the cavity. Such a unique situation of the Na ions never seen in K priderite will give rise to characteristic behavior in Na ion conduction.

INTRODUCTION

Priderite generally represented by $A_xM_yTi_{8-y}O_{16}$ (A, alkali or alkaline earth ions; M, di- or trivalent cations) has the one-dimensional (1-D) tunnel structure isotypic to hollandite (1). The A ions reside in the tunnels and are called the tunnel ion. Usual priderites contain K, Rb, Cs, Ca, and Ba for the tunnel ion. Ba and Cs priderites have been well investigated in order to use their hollandite-type tunnels as a microcontainer for immobilization of radioactive cations (2). K priderites such as $K_xMg_{x/2}Ti_{8-x/2}O_{16}$ ($x \sim 1.5$) have been also studied in detail about 1-D ionic conduction of K ions, of which the ionic conductivity analyzed by the complex impedance method reached so much as 10^{-2} (S/cm) at 300 K (3). In contrast with these priderites containing large alkaline ions, a Na derivative of priderite has been hardly paid attention thus far. $Na_xCr_xTi_{8-x}O_{16}$ reported by Bayer and Hoffmann (4) may be the only example of Na priderite.

In the chemical formula $Na_xM^{3+}_xTi_{8-x}O_{16}$ (M = Al, Cr, Fe, Ga, Ti, etc.) or $Na_xM^{2+}_{x/2}Ti_{8-x/2}O_{16}$ (M = Mg, Ni, Fe, etc.) with $x \leq 2$, freudenbergite-type compounds are usually obtained at high temperature around 1000 ~ 1250°C (4). Na ions are contained in the 1-D tunnel of this structure of which the cavity is smaller than that of priderite. These facts lead us to the presumption that large cations such as K, Rb, and Cs may be stabilized in the large tunnels of priderite and the small cation (i.e., Na) is also in the small cavities of the freudenbergite structure. However, when Cr was used for the M ion, the priderite phase could be obtained as well as the freudenbergite phase (4). This behavior of chromia, especially the formation of Na priderite $Na_xCr_xTi_{8-x}O_{16}$ (hereafter NCTO), is very interesting from the viewpoint of crystal chemistry.

As for 1-D tunnel structures, the ion conduction behavior is primarily affected by geometrical factors such as the sizes of tunnels and tunnel ions. The size effect of tunnel cations on the priderite structure was studied by comparing K, Rb, and Ba priderite (5). Substitution of Na ions for these cations seems to be so drastic as to much reduce or thoroughly eliminate the bottleneck effect on transport of the mobile species along the tunnel. It is, therefore, informative to compare structural properties between NCTO and K priderite in order to understand a conduction mechanism of ions in the 1-D pathways.

Thus, NCTO is mainly of interest from two points of view: as a unique compound in crystal chemistry and as a promising 1-D Na ion conductor. In order to clarify the relationship, single crystals of NCTO have been grown by a flux method and the structure has been refined by a single-crystal X ray diffraction technique.

EXPERIMENTAL

Single Crystal Growth

Single crystals of NCTO were grown by a flux method. A typical condition is as follows. The mixture of 0.56 g of Na_2CO_3, 0.82 g of Cr_2O_3, 0.64 g of TiO_2 (molar ratio of $Na_2CO_3 : Cr_2O_3 : TiO_2 = 2 : 2 : 3$) in a platinum crucible was heated at 1300°C for 10 hr with the flux consisting

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TABLE 1
Crystallographic Data for $Na_xCr_xTi_{8-x}O_{16}$ ($x \sim 1.7$)

Crystal system	tetragonal
Space group	$I4/m$
a (Å)	10.058(1)
c	2.957(1)
V (Å^3)	299.1(1)
Z	1
Dx (g/cm^3)	3.8
μ(Mo$K\alpha$) (cm^{-1})	55.6

of 3.40 g of Na_2CO_3 and 4.60 g of MoO_3 (molar ratio $Na_2CO_3 : MoO_3 = 1 : 1$). The melt was cooled down to 1200°C at a rate of 4°C/hr and then taken out of the furnace. Needle-shaped deep-blue crystals of $Na_xCr_xTi_{8-x}O_{16}$ remained in the crucible after the flux was dissolved in water. The EPMA (electron probe microanalysis) measurement of the crystals gave the composition parameter x of ca. 1.6 ~ 1.7.

Structure Refinement

A single crystal was mounted on an automated four-circle diffractometer (Rigaku AFC-5) for intensity data collection.[2] Crystallographic data of NCTO ($Na_xCr_xTi_{8-x}O_{16}$, $x \sim 1.7$) are shown in Table 1. Full-matrix least-squares calculations were adopted for the refinement of parameters. Conditions for the data collection and the refinement are summarized in Table 2. Initial values for the positional parameters of Ti(Cr) and oxygens were taken from the literature (5). Na ions were found by Fourier syntheses and difference Fourier syntheses. Na occupanies and the occupation ratio of Ti to Cr at the metal position were refined under the constraint of keeping charge neutrality of the chemical formula and full occupation at the metal site: [Ti] + [Cr] = 1, 8 × [Na1] + 4 × [Na2] + 2 × [Na3] = 8 × [Cr], where [X] is the occupancy of X, and [Ti], [Na1], and [Na2] were refined independently. Atomic scattering factors were taken from "International Tables for X-ray Crystallography, Vol. IV" (6). Programs ACACA (7), RSSFR-5 (8), RADY (9), and BADTEA (10) were used for the calculations.

TABLE 2
Conditions for Data Collection and Parameters of Refinement

Crystal size	0.05 × 0.05 × 0.1 mm
Radiation	Mo$K\alpha$ (0.71069 Å) (graphite-monochromatized)
Refinement of cell parameters	16 reflections ($48° < 2\theta < 64°$)
Scan mode	$\omega - 2\theta$
Scan speed	2°/min
$2\theta_{max.}$	100° ($-21 \le h \le 21$, $0 \le k \le 21$, $0 \le l \le 6$)
Standard reflections	3 out of every 100 (variation within 1.0%)
Reflections measured	1884
Reflections used for calculation	785 ($F_0 > 3\sigma(F_0)$, $R_{int} = 0.03$)
Transmission factor	0.585 ~ 0.611
Extinction factor (iso)	4.71×10^{-6}
Final R, wR	0.0375, 0.0275 (weight factor: $1/\sigma(F_0)^2$)
Residuals	$-1.7 \sim 1.6$ eÅ^{-3}

[2] Structure factor tables and anisotropic temperature factors are available on request from the authors.

RESULTS

Final atomic coordinates, occupancies, and equivalent isotropic temperature factors are listed in Table 3. The crystal structure of $Na_xCr_xTi_{8-x}O_{16}$ ($x \sim 1.7$) projected along the c axis is shown in Fig. 1. Interatomic distances are listed for metal–oxygen coordination polyhedra in Table 4.

The framework is of a typical hollandite-type construction. The tunnel wall is made up of alternate stacking of two kinds of square planes of oxygen along the c axis at $c/2$ intervals as shown in Fig. 2. One consists of four O1 oxygens (O1-square, hereafter) and the other of four O2 oxygens (O2-square). Na ions are located at three positions Na1, Na2, and Na3 in the tunnel. A total amount of Na is about 1.71 (= 0.11 × 8 + 0.16 × 4 + 0.10 × 2) per unit cell, that is $x = 1.71$ in the formula $Na_xCr_xTi_{8-x}O_{16}$. This value obtained by the structure analysis is in good agreement with the result from EPMA. The Na3 site is positioned in the center of a square-planar coordination of four O1 atoms. The Na3–O1 distance, 2.565(2) Å, is an average value for the Na–O bond length. The Na1 site is off the tunnel center toward the O2 atom on a square plane and, as shown in Table 4, reasonably away from the four O1 and one O2 atoms.

DISCUSSION

Factors Affecting the Tunnel Size in Priderite

The geometry of conduction paths is one of the important factors for ionic conduction behavior. The size of tunnel cross-section in priderite is generally affected by three factors (5, 11), that is, (i) size of framework cations, (ii) size of tunnel ions, and (iii) concentration of tunnel ions. The diagonal O1–O1 distance in NCTO (5.130(4) Å) is significantly smaller than those in K priderites $K_xAl_xTi_{8-x}O_{16}$ (KATO) (5.18 Å) or $K_xGa_xTi_{8-x}O_{16}$ (KGTO) (5.21 Å) (5), although the composition-weighted mean radius of framework cations in NCTO (0.607 Å) is similar to that in KGTO (0.608 Å) and larger than that in

TABLE 3
Occupancies, Atomic Coordinates, and Equivalent Isotropic Temperature Factors

Atom	Position	Occupancy	x	y	z	B_{eq} (Å^2)
Na1	8(h)	0.110(5)	0.072(2)	0.014(3)	0.5	4.3(10)
Na2	4(e)	0.16(4)	0	0	0.203(10)	7.0(14)
Na3	2(a)	0.10(8)	0	0	0	5.3(53)
M (Ti/Cr)	8(h)	0.786(3)/0.214	0.35161(4)	0.16876(5)	0	0.64(1)
O1	8(h)	1	0.1545(2)	0.2029(2)	0	0.59(5)
O2	8(h)	1	0.5429(2)	0.1643(2)	0	0.67(5)

Note. $B_{eq} = (4/3)\Sigma_i\Sigma_j \beta_{ij}\mathbf{a}_i\mathbf{a}_j$.

KATO (0.591 Å). This can be mainly attributed to the second factor, the size difference between Na and K ions, and partly due to the third factor, the concentration of tunnel ions in NCTO, 1.7 per unit cell, higher than that in the two K priderites, ca. 1.5 per unit cell. The latter factor has been pointed out for the priderite-type titanium dioxide bronze with various contents of K ions (11). The more tunnel ions are contained, the more the O1 oxygens deviate toward the tunnel center by an increasing attractive force from the tunnel ions, which causes a decrease of the diagonal O1–O1 distance.

Structural Features Related to Na Ion Transport

Structural features important for 1-D ionic conduction in NCTO, not found for other priderites, are as follows.

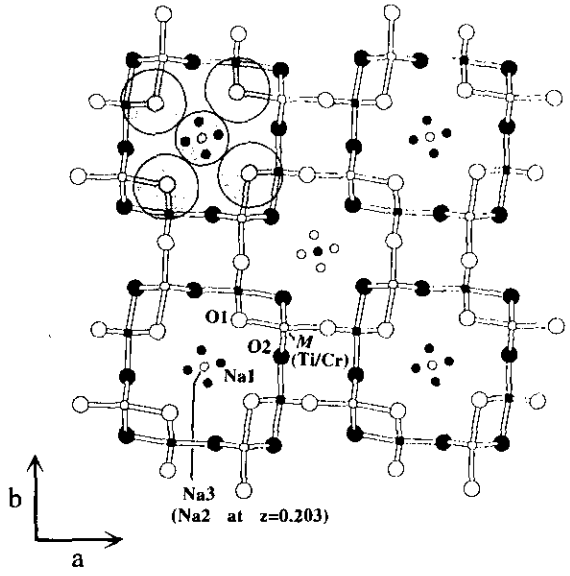

FIG. 1. Structure of $Na_xCr_xTi_{8-x}O_{16}$ ($x \sim 1.7$) projected along the c axis. The large and small circles constituting the framework are oxygen and Ti (partly substituted by Cr), respectively. The small circles in tunnels are Na ions. All atoms except for the Na2 at $z = 0.203$ are located at $z = 0$ or $\frac{1}{2}$ which are represented by open and filled circles, respectively. Shaded circles in one tunnel represent the effective size of the O1 and Na3.

The first is disappearance of bottleneck effects for transport of the tunnel ions and the second is the splitting of the conduction path. The effective size of oxygen squares can be approximately estimated by subtracting 2.80 Å, the ionic diameter of O^{2-}, from the diagonal O–O distance. Those of O1 squares in K priderites are estimated to be 2.38 and 2.41 Å for KATO and KGTO, respectively, which are considerably smaller than the size of K^+ (3.02 Å) (12). In general, it is well known for K priderites that O1 squares play a bottlenecking role for the ionic conduction at which the probability density of K ions is significantly lowered (13). The O1 square of NCTO is smaller than that of K priderites, but keeps an effective size of 2.33 Å as large as the size of Na^+ (2.32 Å) (12). This suggests that Na ions could easily move in the tunnel across the O1 square because the square would no longer act as a bottleneck for transport of the tunnel ions.

The effective size of the O2 square, 4.01 Å, is far larger than that of Na^+. If a Na ion resided at the center of the O2 square, (0, 0, $\frac{1}{2}$), it would be 3.405 Å away from four O2 oxygens and also 2.961 Å from eight O1 oxygens. Accordingly, the Na ion is inferred to be drawn toward the tunnel wall so that bond distances from itself to O1 and O2 become appropriate values as shown in Table 4. Such interaction results in the observation that Na ions at ca. $z = \frac{1}{2}$ are concentrated at four equivalent sites separated around the tunnel axis, that is, the conduction path is splintered in the vicinity of the O2 square.

Formation and Stability of the NCTO Structure

Na ions are also contained in some hollandite-type compounds such as $NaAlGe_3O_8$ (14) and $NaRu_4O_8$ (15). It is

TABLE 4
Interatomic Distances (Å)

M–O1	2.012(2)	Na1–O1 × 2	2.54(2)
–O1 × 2	1.964(1)	–O1 × 2	2.60(2)
–O2	1.925(2)	–O2	2.66(2)
–O2 × 2	1.953(1)	Na2–O1 × 4	2.634(7)
Average	1.962(1)	Na3–O1 × 4	2.565(2)

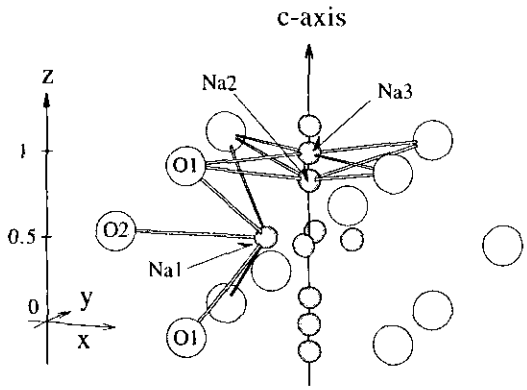

FIG. 2. Coordination between the Na and O atoms.

noted that their *a* axes are significantly short, 9.648 Å for $NaAlGe_3O_8$ and 9.872 Å for $NaRu_4O_8$. Tunnels in these compunds are, therefore, expected to be considerably smaller than that of NCTO despite their structural data being unavailable. In general, formation of Na priderite has been unlikely because the TiO_6 octahedra framework appears too large to stabilize Na ions. Kesson and White (16) proposed the radius-ratio tolerance factor for the hollandite-type structure and predicted that priderite cavities were unfavorable to Na ions. For example, the tolerance factor for hypothetical Na priderite $Na_2Al_2Ti_6O_{16}$, 0.88, is far less than the ideal value, i.e., the unity. Based on this factor, NCTO gives nearly the same value as the above hypothetical priderite. The stabilizing mechanism for NCTO can be insufficiently explained by a conventional estimation such as the radius-ratio tolerance factor, and it may be more intricate.

Despite that it appears unstable, NCTO can be actually obtained by heating at 1300°C. The present structural data gives some basis for stabilization of NCTO. The existence of Na ions at the Na3 site is very striking because this site is positioned at the bottleneck of the tunnel in usual priderites and unfit for stay of tunnel ions. The reason is because the O1 square in NCTO is just fit for a square-planar coordination with the Na ion. It may be speculated that the formation of a square-planar coordination makes a certain contribution for stabilization of Na ions and, as a result, of the whole structure of NCTO. It should be noted that Kesson and White's estimation is based on the ideal condition that all tunnel ions are situated at (0, 0, $\frac{1}{2}$), the center of the O2 square.

The size fitness of the Na ion in the O1 square may be also satisfied when Cr is replaced by other metals similar in size. We are now trying to synthesize new Na priderite containing various metals instead of Cr at higher temperatures than that in Bayer and Hoffmann's investigation.

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