BRIEF COMMUNICATIONS

One-Dimensional Large Tunnels in the New Compound: $K_xGa_{16+x}Ti_{16-x}O_{56}$ ($x \leq 2$)

MAMORU WATANABE, TAKAYOSHI SASAKI, YOSHIZO KITAMI, AND YOSHINORI FUJIKI

National Institute for Research in Inorganic Materials, Namiki 1-1, Sakura-mura, Niihari-gun, Ibaraki 305, Japan

Some of potassium priderites (titania-based hollandites), which have tunnels for potassium ion conduction, have been well investigated as typical one-dimensional ionic conductors. The potassium conduction was not of Arrhenius type and was found to depend anomalously on frequency (*1*). Highly purified priderites $K_xAl_xTi_{8-x}O_{16}$ and $K_{2x}Mg_xTi_{8-x}O_{16}$ might have a large frequency-independent component of conductivity (*2*), whose value is comparable to that of dc-conductive $Na\beta-Al_2O_3$ at room temperature. A new compound $K_xGa_{16+x}Ti_{16-x}O_{56}$($x \leq 2$) which has one-dimensional tunnels with a very large diameter of 6.2 Å and a smooth inside wall, i.e., no virtual bottlenecks, was successfully prepared (*3*). These features are very attractive from the structural viewpoint of ionic conduction. In fact, ionic conductivity measurements revealed an extremely high value of about 10 S/cm even at room temperature in the microwave range where the intrinsic response of mobile ions to electric field dominates the ion conduction (*4*). We report here an outline of this new crystal structure and, in comparison with priderites, de-

scribe its structural features relateable to ion conduction.

Light greenish fibrous crystals of $K_xGa_{16+x}Ti_{16-x}O_{56}$($x \sim 1$) were grown from a flux melt of $K_2CO_3-MoO_3$ containing TiO_2 and Ga_2O_3. The crystal has a body-centered lattice with Laue symmetry $4/m$ and $a = 18.135(2)$ Å and $c = 2.9966(4)$ Å. The structure was determined for the space group $I4/m$ by a usual single crystal X-ray structure analysis, and a high-resolution lattice image taken along [001] was used effectively to extract metal–metal vectors from the Patterson maps. The structure was refined with 23 positional parameters and anisotropic thermal parameters using 726 unique reflections below ~ 0.9 in $\sin \theta/\lambda$, resulting in 4.36 and 2.87% for R and wR factors, respectively. The details of this analysis will be described elsewhere (*5*).

Atomic coordinates and equivalent isotropic temperature factors are listed in Table I. The crystal structure is illustrated by a sketch projected on (001) in Fig. 1. The network consists of the structure columns of rutile and β-gallia which are alternately arrayed in the (001) plane and joined at oc-

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TABLE I

ATOMIC COORDINATES AND EQUIVALENT ISOTROPIC
THERMAL PARAMETERS

	X	Y	Z	$B_{eq.}$ (Å^2)
K	0	0	0.242(9)	8.0(14)
Ga (M1)	0.16218(5)	0.11819(5)	$\frac{1}{2}$	0.36(4)
Ga and Ti (M2)	0.31089(6)	0.20322(6)	0	0.41(4)
Ti and Ga (M3)	0.03559(7)	0.22118(8)	0	0.57(5)
Ti (M4)	0.54276(9)	0.11930(9)	0	0.58(6)
O1	0.0201(3)	0.4102(3)	0	0.60(24)
O2	0.1507(3)	0.3950(3)	$\frac{1}{2}$	0.49(24)
O3	0.0019(3)	0.2803(3)	$\frac{1}{2}$	0.60(24)
O4	0.1314(3)	0.2645(3)	0	0.56(24)
O5	0.2369(3)	0.1892(3)	$\frac{1}{2}$	0.44(23)
O6	0.0673(3)	0.1558(3)	$\frac{1}{2}$	0.58(25)
O7	0.1689(3)	0.0613(3)	0	0.76(25)

$B_{eq.} = \frac{4}{3} \sum_i \sum_j \beta_{ij} a_i a_j.$

tahedral and tetrahedral apexes. Large tunnels surrounded by the columns occur in parallel to [001]. All atoms except for K are located on mirror symmetry planes with $z = 0$ and $\frac{1}{2}$. Tetrahedra in the gallia regions and central octahedra in the rutile regions are preferentially occupied by Ga and Ti atoms, respectively. In the remaining octahedra in both regions, Ga and Ti atoms are mixed to some degrees. Oxygen atoms make an anion packing close to *hcp* supposing additional oxygen atoms in the tunnels. Actually, K ions having the thermal ellipsoid unusually elongated along the channel axis are accommodated there and are placed at 0, 0, $\pm z$ and $\frac{1}{2}, \frac{1}{2}, \frac{1}{2} \pm z$, where $z = 0.242$, $\beta_{11} = 0.003$, and $\beta_{33} = 0.436$. The cations cannot stay at 0, 0, $\pm z$ or $\frac{1}{2}, \frac{1}{2}, \frac{1}{2} \pm z$ at the same time due to the steric hindrance between them. The "x," therefore, can change crystallographically in the range from 0 to 2. The present K content was about 1.0 per unit cell, which means that the cation is placed on average in every four equivalent sites each tunnel.

The large tunnels have an octagonal shape on the projected figure. The octagons really consist of two similar squares with different heights ($z = 0$ and $\frac{1}{2}$) and mutually twisted by ~45° around the channel axis as

schematically shown in Fig. 2b. These squares are stacked at a half period of the c-axis and are about 3.4 and 3.7 Å in free diameter assuming 1.40 Å for the oxygen radius. Even the smaller diameter is larger than the effective ionic sizes of K$^+$ ($r^{viii} \sim 3.0$ Å) and Rb$^+$ ($r^{viii} \sim 3.2$ Å) and comparable to that of Cs$^+$ ($r^{viii} \sim 3.5$ Å) (6).

Similarly to the other compounds like Ga$_4$Ti$_{21}$O$_{48}$ (7), the new network can be related to the rutile structure by crystallographic shear operations. The required operations are (210) $[\frac{1}{4} \frac{1}{2} \frac{1}{2}]$ and ($\bar{1}$20) $[\frac{1}{2} \frac{\bar{1}}{4} \frac{1}{2}]$ in the rutile structure, and they take place every two and a half rutile units for either of (210) and ($\bar{1}$20). The octagonal tunnels are formed at all crosspoints of both operations.

The tunnels in priderites are of a straight linkage of cuboctahedra joined mutually with their basal planes normal to the channel axis as schematically compared with the new type in Fig. 2, and are separated from
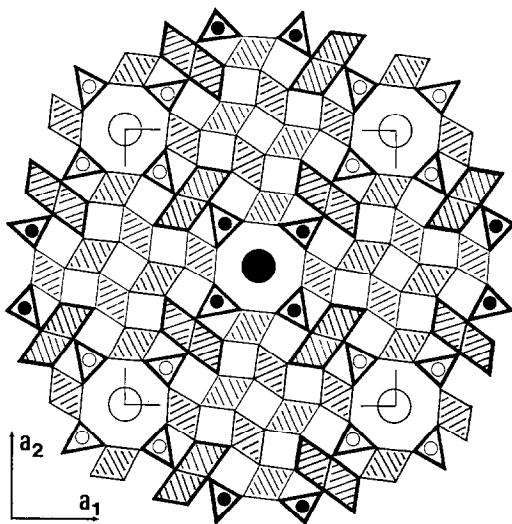

FIG. 1. (001) projection of the crystal structure. Tetrahedra are represented by triangles and octahedra by diamonds. Central cations in the tetrahedra are located at $z = 0$ for dark circles and at $z = \frac{1}{2}$ for open ones. Large open and dark circles represent K ions placed at $z = \pm 0.242$ and $\frac{1}{2} \pm 0.242$, respectively. β-gallia parts are heavily outlined.
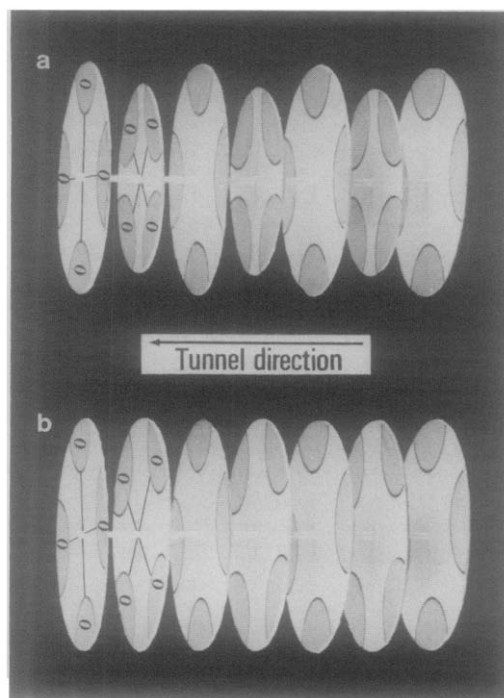
FIG. 2. Comparison of the new type and the priderite type tunnels. Six oxygen layers normal to the c-axes, or three times the c-axial periods, are schematically shown. Only oxygen atoms forming the inside wall of each tunnel are illustrated as semicircles. In (b), similar squares with 3.7- and 3.4-Å diagonal lengths are stacked at the intervals of 1.49 Å while twisted by ~45° about the column axis. In (a), the squares with 3.8- and 2.5-Å diagonal lengths are alternately stacked at the intervals of 1.49 Å with a twisting angle of ~45°. Smaller disks at the second, fourth, and sixth layers correspond to bottlenecks.

the nearest by one octahedral layer. A free diameter of the priderite tunnels is only 2.5 Å at the bottlenecks. It is considerably smaller than the effective size of K^+ in spite of the good conductivities (2). Among one-dimensional ion conductors, the priderite tunnels are notable owing to better one-dimensionality, that is, the shielding octahedral layers are unlikely to allow K ions to move from one channel to another and those in different channels to make interactions. However, the detailed measurement of X-ray diffuse scattering from K_xAl_x $Ti_{8-x}O_{16}$ showed that there still exists such an interchannel correlation between K ions (8). In comparison with these priderites, the new compound has the following advantages: (1) a large tunnel separation of three layers, and (2) a large effective tunnel diameter of 3.4 Å and no virtual bottlenecks for K and Rb ions. These are closely related to the property of the intrinsic barrier for ion diffusion. The large tunnel separation would probably make the interchannel correlation of K ions weaker and the barrier simpler in nature than in priderites. The disappearance of bottlenecks should lower the height of the intrinsic barrier through a decrease in the rigid body repulsion term between K ions and bottleneck oxygen atoms. This would result in an increasing number of energetically quasi-equivalent sites available for K ions as compared with the priderite cases, which suggests a more distinct delocalization of the ions in the tunnels.
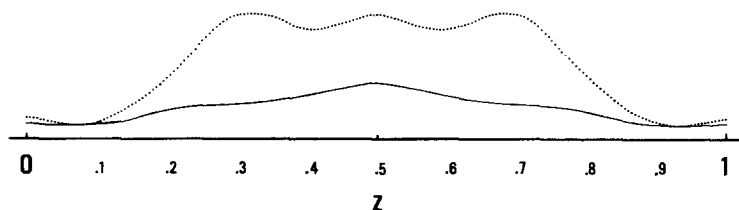

FIG. 3. Electron densities on $\frac{1}{2}, \frac{1}{2}, z$ in $K_xGa_{16+x}Ti_{16-x}O_{56}$ and $K_xAl_xTi_{8-x}O_{16}$. Minimum densities on the lines are set to each other and the unit of density is arbitrary. Solid and dotted lines show the densities in the present compound and the (K,Al)-priderite, respectively.

The electron density curve on $(\frac{1}{2}, \frac{1}{2}, z)$ in this compound is in fact much flatter than that in the high ac-ion conductive priderites, e.g., $K_xAl_xTi_{8-x}O_{16}$ (9), as shown in Fig. 3. In addition, it is inferred that the effects of extrinsic barriers and Coulomb repulsive interactions between K ions in the same tunnel are emphasized. From these things, we expect that this compound could present a more basic and useful system for theoretical and experimental studies on ion conduction phenomena.

Acknowledgments

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