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Crystal structure of a new high-pressure phase, $K_{0.82}Mg_{1.68}(Cr_{2.84}Fe_{0.84}Ti_{2.11}Zr_{0.08})O_{12}$, with one-dimensional tunnels

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Abstract

The crystal structure of a new complex Ti–Cr oxide phase, $K_{0.82}Mg_{1.68}(Cr_{2.84}Fe_{0.84}Ti_{2.11}Zr_{0.08})O_{12}$, synthesized at 13 GPa and 1400 °C, has been determined with single-crystal X-ray diffraction. It has a hexagonal symmetry with the space group $P6_3/m$ and unit-cell parameters $a = 9.1763(13)$ and $c = 2.8790(6)$ Å, $V = 209.89(8)$ Å^3, $Z = 1$. The structure is characterized by the hollandite-type double chains of edge-shared $M2$ octahedra occupied by trivalent and tetravalent cations (Ti + Cr + Fe + Zr); these double chains are linked to one another through shared octahedral apexes to form a framework structure containing two types of tunnels running parallel to the c-axis. One type of tunnels has a hexagonal cross-section and is occupied by large K^+, whereas the other has a triangular cross-section and is occupied by Mg^{2+}. The K^+ cation is disordered between two crystallographically equivalent (2a) sites in the tunnels and displays a U_{33} displacement parameter that is significantly greater than U_{11}. The new high-pressure phase reported in this study possesses many structural features similar to those for the hollandite compounds, making it a candidate for the 1-D fast ionic conductors.

Keywords: High-pressure synthesis; Complex Ti–Cr oxide; Crystal structure of a Ti–Cr oxide

1. Introduction

Complex Ti–Cr oxides that can accommodate large cations have been a subject of a variety of studies because of their importance in industrial applications and the Earth sciences. Of particular interest are compounds with hollandite ($A_{0–2}M_8O_{16}$), crichtonite ($AM_{21}O_{38}$), and magnetoplumbite ($AM_{12}O_{19}$) structures, where A represents mostly large alkaline and/or earth alkaline ions (e.g., K, Ba, Sr) and M relatively small ions, such as Ti, Cr, Zr, Fe, Mg. It has been proposed that synthetic rocks (SYNROC) containing a hollandite- or crichtonite-type compound as a major component may be used as storage media for high-level radioactive waste, especially radio-nuclides with large ionic radii [1,2]. On the other hand, hollandite-type compounds are one of the most typical one-dimensional (1-D) fast ionic conductors, in which the 1-D tunnels are available for transport of cations (tunnel ions). Extensive research has been conducted to understand the behavior of the tunnel ions in response to cation vacancies in the tunnels [3–5], atomic substitutions [6,7], and variation of temperature [8,9]. Complex Ti–Cr oxides with hollandite-, crichtonite-, and magnetoplumbite-type structures are known from natural rocks originating in the Earth's upper mantle [10–15], which makes these phases potentially important non-silicate reservoirs for a large number of incompatible trace elements in the source regions of deep-seated alkaline magmas, such as kimberlites and lamproites [16–18].

In this paper, we report the crystal structure of a new complex Ti–Cr oxide, $K_{0.82}Mg_{1.68}(Cr_{2.84}Fe_{0.84}Ti_{2.11}Zr_{0.08})O_{12}$, which was synthesized at 13 GPa and

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1400 °C as a breakdown product of a crichtonite-type compound $KTi_{13}Cr_4FeZrMg_2O_{38}$ (mathiasite) [19]. The new Ti–Cr oxide phase possesses many structural features comparable to those of hollandite compounds, especially the large 1-D tunnels, and thus may become a potential ionic conductor, as well as a storage material for large elements at high temperatures and pressures.

2. Experimental procedures

The Ti–Cr oxide crystal used in this study was synthesized from high-purity (>99.9%) TiO_2, ZrO_2 Cr_2O_3, Fe_2O_3, and MgO with K added as $K_2Ti_2O_5$. The latter was pre-synthesized from a stoichiometric mixture of TiO_2 and K_2CO_3 that was fired at 910 °C for 24 h [12]. The starting material was pre-dried at 150 °C and welded into a 1.7 mm outer diameter platinum capsule fitted with an inner graphite liner to suppress Fe-loss to the sample container. The platinum capsule was then placed in a 10/5 assembly (10 mm edge length of octahedron, 5 mm truncations of WC-cubes) using an MgO octahedron and pre-fabricated pyrophyllite gaskets. The high-pressure synthesis was carried out at a pressure of 13 GPa and a temperature of 1400 °C using a 600 t hydraulic press fitted with a Walker-type multi-anvil module at the Geophysical Lab, Carnegie Institution of Washington. The temperature was measured with a W3%Re–W25%Re thermocouple without pressure correction for the emf and both pressure and temperature were computer-controlled during the entire run duration of 72 h. Details of the experimental and calibration procedures were described by Bertka and Fei [20]. The synthesis conditions were chosen based on results of experiments on the stability of mathiasite [19]. In the system K_2O–TiO_2–ZrO_2–Cr_2O_3–MgO–Fe_2O_3, the new Ti–Cr-oxide appears as small crystals together with a number of additional breakdown products [19]. Unfortunately, these crystals were too small for structure analysis. Therefore, we used the averaged composition of the new Ti–Cr-oxide synthesized at 13 GPa and 1400 °C to make a new starting material and ran it under the identical *P–T* conditions. The run that produced large crystals for the present study contained primarily the new Ti–Cr-oxide (~95% in the modal proportion) with some additional TiO_2 and ZrO_2 (~5%) (Fig. 1).

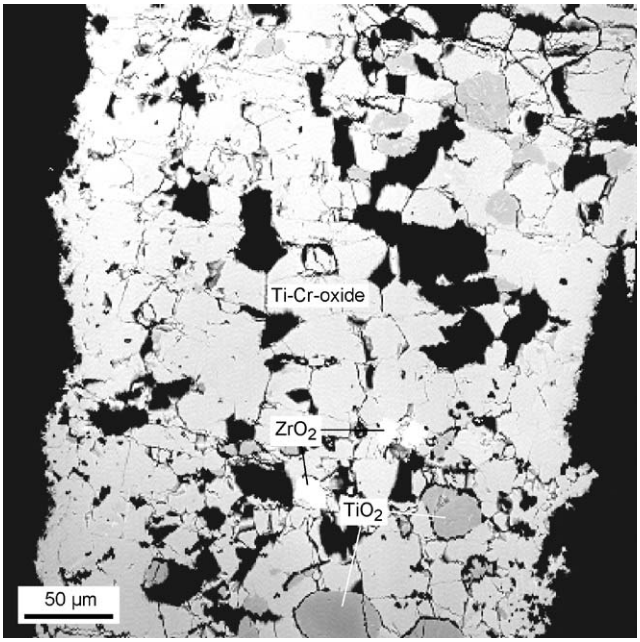

Fig. 1. Photomicrograph of the experimental products (13 GPa and 1400 °C).

Table 1
Averaged composition ($n = 9$) of $K_{0.82}(Cr_{2.84}Fe_{0.84}Ti_{2.11}Zr_{0.08})Mg_{1.68}O_{12}$

Oxide	wt%	Cation	Cation numbers[a]
TiO_2	30.13(76)	Ti	2.11(5)
ZrO_2	1.75(19)	Zr	0.08(1)
Cr_2O_3	38.58(57)	Cr	2.84(5)
Fe_2O_3[b]	12.00(57)	Fe	0.84(4)
MgO	12.09(21)	Mg	1.68(3)
K_2O	6.91(08)	K	0.82(1)
Total	101.46(36)		8.37(3)

[a] Cation numbers were calculated based on 12 O^{2-}.
[b] Total Fe was assumed to be Fe^{3+}.

After the experiment, the platinum capsule was recovered from the 10/5 assembly, embedded in epoxy resin, and ground to expose the center of the capsule. This central section was polished for microprobe analysis, which was carried out with a JEOL microprobe at the Geophysical Lab. Analytical conditions were 15 kV/50 nA with 20 s on peaks and 10 s on backgrounds of the X-ray lines. The following standards were used: ilmenite for Ti, magnesiochromite for Cr and Mg, baddeleyite for Zr, magnetite for Fe, and orthoclase for K. Raw counts were corrected on-line with the ZAF correction procedure and all Fe was assumed to be Fe^{3+}. The averaged composition of the crystal based on the analysis of 18 grains is listed in Table 1.

Based on optical examination, a nearly cube-shaped crystal was selected and mounted on a Bruker Smart CCD X-ray diffractometer equipped with graphite-monochromatized Mo*K*α radiation. A hemisphere of three-dimensional X-ray diffraction data was collected with frame widths of 0.3° in ω and 30 s counting time per frame (see Table 2 for the experimental details). The data were analyzed to locate peaks for the determination of the unit-cell parameters. All reflections were indexed based on a hexagonal unit cell:

$a = 9.1763(13)$ and $c = 2.8790(6)$ Å, with possible space group $P6_3$ or $P6_3/m$. An empirical correction for X-ray absorption was made using the program SADABS (part of the Bruker program SAINT). Equivalent reflections were merged into a set of 243 independent reflections ($R_{\text{int}} = 0.051$), out of which 217 ones had $I_{\text{obs}} > 2\sigma(I_{\text{obs}})$ and were used for the structure analysis and refinements.

Because the *E*-value statistics of the X-ray intensity data showed that the structure of $K_{0.82}Mg_{1.68}(Cr_{2.84}Fe_{0.84}Ti_{2.11}Zr_{0.08})O_{12}$ is probably centric, we began solution of the structure with space group $P6_3/m$. The crystal structure was solved and refined with the program SHELX97. All atoms were refined with anisotropic thermal displacement parameters, by assuming K^+, Mg^{2+}, and ($Cr^{3+} + Fe^{3+} + Ti^{4+} + Zr^{4+}$) at the *A*, *M*1, and *M*2 sites, respectively. The cation occupancies at the *A* and *M*1 sites were also refined, yielding K = 0.431(1) and Mg = 0.845(2). However, owing to the difficulty of refining occupancies for more than two atoms in one site simultaneously, the cation occupancies at the *M*2 site were fixed to the values determined from microprobe analysis. The resultant R_1 factor is 0.023 for the observed reflections and 0.028 for all independent reflections. Final atomic coordinates and anisotropic thermal displacement parameters are presented in Table 3 and selected bond distances in Table 4.

Table 2
Summary of crystal data and refinement results

Structural formula	$K_{0.82}(Cr_{2.84}Fe_{0.84}Ti_{2.11}Zr_{0.08})Mg_{1.68}O_{12}$
Formula weight	567.86
Crystal size (mm^3)	0.05 × 0.05 × 0.06
Space group	$P6_3/m$ (No. 176)
a (Å)	9.1763(13)
c (Å)	2.8790(6)
V (Å^3)	209.89
Z	1
ρ_{calc} (g/cm^3)	4.493
λ (Å)	0.71069
μ (mm^{-1})	7.58
θ range for data collection	0–29
No. of reflections collected	1684
No. of independent reflections	243
No. of reflections with $I > 2\sigma(I)$	217
No. of parameters refined	27
R_{int}	0.051
Final *R* factors [$I > 2\sigma(I)$]	$R_I = 0.023$
Final *R* factors (all data)	$R_1 = 0.028$, w$R_2 = 0.050$
Goodness-of-fit	0.937

3. Results and discussion

Intriguingly, the crystal structure of $K_{0.82}Mg_{1.68}(Cr_{2.84}Fe_{0.84}Ti_{2.11}Zr_{0.08})O_{12}$ (abbreviated as KMCT hereafter for the simplicity of discussion) has many features similar to those of the hollandite structure (Fig. 2). They both are characterized by a very short *c* dimension (~2.9 A) and the same type of double chains of edge-shared octahedra occupied by trivalent and tetravalent cations (Fig. 3); these double chains are linked to one another through sharing octahedral apexes to form a framework containing two types of tunnels running parallel to the *c*-axis. The major difference between the hollandite and KMCT structures lies in the configurations of tunnels and cations therein. In the hollandite structure, one kind of tunnel is comprised of eight octahedra and occupied by large K^+, whereas the other is an empty rutile-type tunnel formed by four octahedra. In contrast, the two kinds of tunnels in the KMCT structure are both made up of six *M*2 octahedra: one has a hexagonal cross-section and is occupied by large K^+, whereas the other has a triangular cross-section and is occupied by Mg^{2+}.

The most interesting aspect of the KMCT structure pertains to the position and occupancy of K^+ in the hexagonal tunnels. Compared to the hollandite structure in which the K–K separation is approximately one *c* dimension (~2.9 Å), the K^+ cation in KMCT is distributed over two crystallographically equivalent (2*a*) sites in the tunnels and has a site occupancy of 0.43. The separation of the two sites is only half the *c* dimension (1.44 Å). The atomic displacement parameter U_{33} of K is significantly greater than U_{11} (Table 3), suggesting a strong positional disordering of K along the tunnels. It should be pointed out that in most

Table 3
Atomic coordinates and anisotropic displacement parameters for $K_{0.82}(Cr_{2.84}Fe_{0.84}Ti_{2.11}Zr_{0.08})Mg_{1.68}O_{12}$

Atom	*x*	*y*	z	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}	U_{eq}
A	0	0	1/4	0.0104(10)	0.0104(10)	0.2581(131)	0	0	0.0052(5)	0.0930(44)
*M*1	2/3	1/3	1/4	0.0109(5)	0.0109(5)	0.0114(8)	0	0	0.0055(3)	0.0111(5)
*M*2	0.6549(1)	0.6413(1)	1/4	0.0071(3)	0.0078(3)	0.0048(3)	0	0	0.0035(2)	0.0067(2)
O1	0.8882(3)	0.6844(2)	1/4	0.0109(9)	0.0154(10)	0.0107(11)	0	0	0.0072(8)	0.0121(5)
O2	0.4022(2)	0.5357(2)	1/4	0.0097(9)	0.0123(9)	0.0093(10)	0	0	0.0060(8)	0.0102(5)

Table 4
Selected interatomic bond distances (Å) in $K_{0.82}Mg_{1.68}(Cr_{2.84}Fe_{0.84}Ti_{2.11}Zr_{0.08})O_{12}$

A–O1 (×3)	2.543(2)	*M*2–O1	1.973(2)
A–O1 (×6)	2.922(2)	*M*2–O1 (×2)	1.945(1)
Avg.	2.796	*M*2–O2	2.017(2)
		*M*2–O2 (×2)	2.033(1)
		Avg.	1.991
*M*1–O1 (×6)	2.162(1)		
Avg.	2.162		

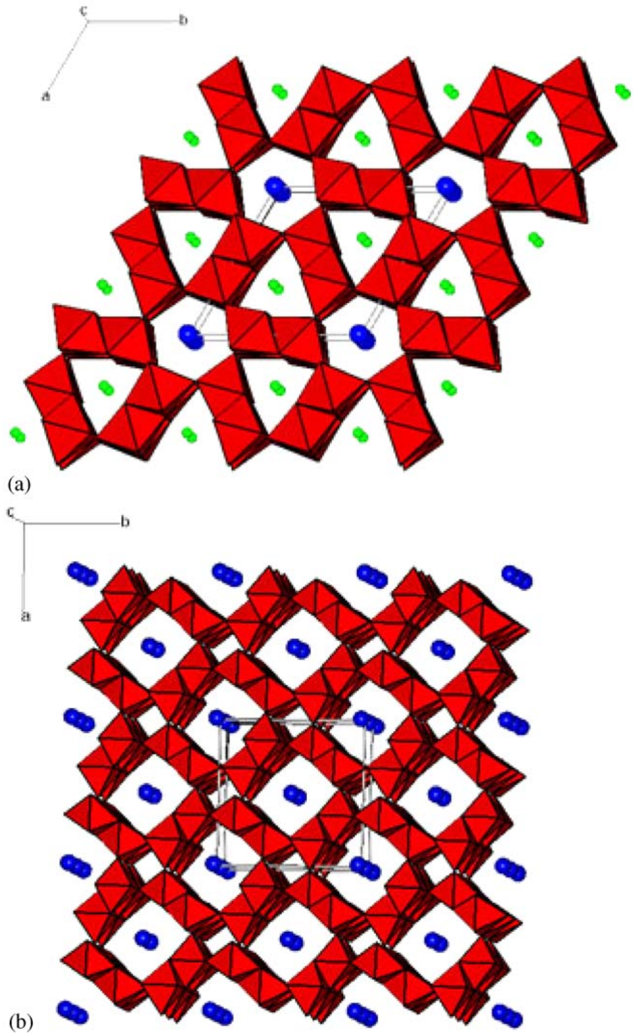

Fig. 2. Crystal structures of (a) $K_{0.82}Mg_{1.68}(Cr_{2.84}Fe_{0.84}Ti_{2.11}Zr_{0.08})O_{12}$ and (b) hollandite. In both structures, the octahedra are occupied by trivalent or tetravalent cations and the large blue spheres represent the K^+ cations. The small green spheres in the $K_{0.82}Mg_{1.68}(Cr_{2.84}Fe_{0.84}Ti_{2.11}Zr_{0.08})O_{12}$ structure are Mg^{2+}.

hollandite-structure compounds, some of large tunnel ions are displaced from their sites along the tunnel axis to minimize the coulombic repulsive forces between tunnel cations (e.g., [4,6,7,24,25]). However, such an off-centered phenomenon was not detected for K^+ in the KMCT structure.

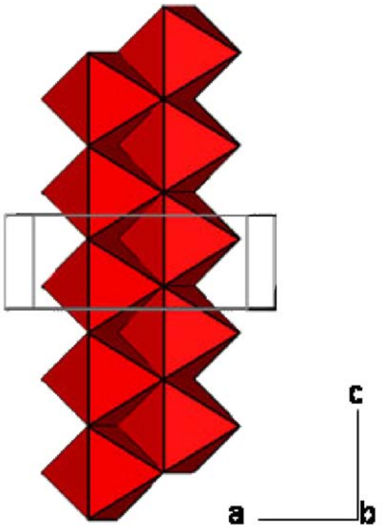

Fig. 3. Double chains of hollandite-type edge-shared octahedra in $K_{0.82}Mg_{1.68}(Cr_{2.84}Fe_{0.84}Ti_{2.11}Zr_{0.08})O_{12}$.

Abriel et al. [21] studied crystal structures of three new hollandite-type compounds, $K_2V_8O_{16}$, $K_{1.8}V_8O_{16}$, and $Tl_{1.74}V_8O_{16}$, and noted that $K_{1.8}V_8O_{16}$ and $Tl_{1.74}V_8O_{16}$ displayed appreciably greater U_{33} values, 0.26 and 0.25, respectively, than that (0.12) for $K_2V_8O_{16}$. They attributed their observation to the existence of vacant tunnel sites in the two former compounds, as more vacant sites give more room for tunnel cations to displace along the tunnels. A similar conclusion was also drawn by Tamada et al. [3], who found that the K^+ tunnel cation exhibits an insignificant displacement along the tunnels in a fully occupied site in the hollandite compound $K_2Cr_8O_{16}$, which has a U_{11} value of 0.0200 and U_{33} of 0.0104. Accordingly, it is not surprising to see a large U_{33} parameter for K^+ in KMCT, since about half of the tunnel sites for this cation are vacant. This result further suggests that, like hollandite-type compounds, the new high-pressure phase we report here may also serve as a potential candidate for the 1-D fast ionic conductors.

In the KMCT structure, each K^+ is bonded to nine oxygen atoms (Fig. 4a), with three at a distance of 2.543 Å and six at 2.922 Å. This configuration is significantly different from that of the K^+ cation in hollandite compounds (Fig. 4b), which has an 8+4 coordination, with eight oxygen atoms at a distance of ~2.90 Å and four at ~3.40 Å. It should be noted that even though the 9-oxygen coordinated K^+ cation in KMCT has an average K–O bond length of 2.80 Å, which is noticeably shorter than 2.90–3.02 Å for the 8-oxygen coordinated K^+ in

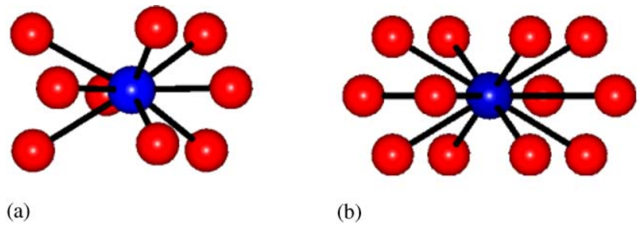

Fig. 4. Configurations of tunnel ions of K^+ in (a) $K_{0.82}Mg_{1.68}(Cr_{2.84}Fe_{0.84}Ti_{2.11}Zr_{0.08})O_{12}$ and (b) hollandite. Large blue spheres represent K^+ and small red ones O^{2-}.

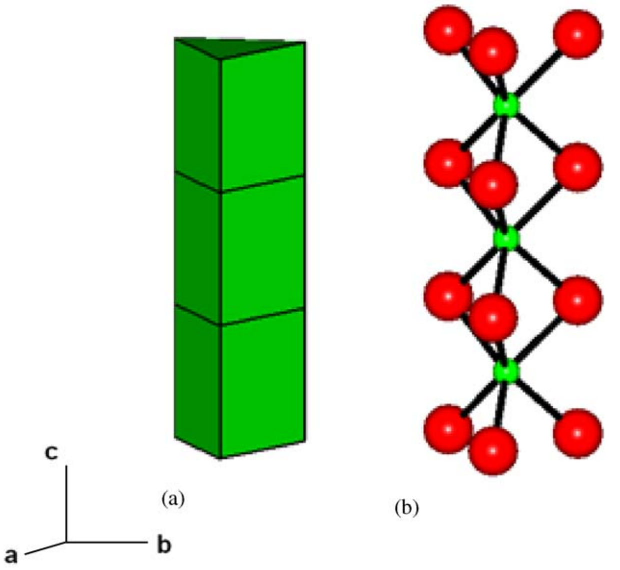

Fig. 5. Configuration of Mg^{2+} in $K_{0.82}Mg_{1.68}(Cr_{2.84}Fe_{0.84}Ti_{2.11}Zr_{0.08})O_{12}$. (a) The polyhedral view and (b) the ball-stick view.

hollandite compounds, the K^+ polyhedral volumes in the two types of structures are similar (~40 Å^3). Nonetheless, due to the lack of a bottleneck-like configuration for the large ions, as observed in hollandite compounds, the KMCT structure may not be a good storage candidate for radioactive elements with large ionic radii.

The Mg^{2+} cation in KMCT is in a trigonal-prism coordination formed by six oxygen atoms (Fig. 5) and has an average Mg–O bond distance of 2.162 Å. Unlike K^+, Mg^{2+} in the triangular tunnels appears to be fully ordered at the (2*d*) sites and shows little displacement along the tunnel, as indicated by its similar U_{11} (0.0109) and U_{33} (0.0114) parameters.

Based on structural studies of a number of hollandite compounds synthesized at various pressures, including $K_2Mo_8O_{16}$ at 0.3 GPa [22], $K_2V_8O_{16}$, $K_{1.8}V_8O_{16}$, and $Tl_{1.74}V_8O_{16}$ at 2.5–3.5 GPa [21], $K_2Cr_8O_{16}$ at 5.5–6.5 GPa [3], $Rb_2Cr_8O_{16}$ at 7 GPa, $K_2Cr_2V_6O_{16}$ and $K_2V_8O_{16}$ at 3 GPa [23], Tamada et al. [3] concluded that high pressure tends to induce a high tunnel-cation occupancy in these compounds, which may lead to a way to control the occupancy and, hence, physical properties related to the tunnel cations, such as the 1-D ionic conductivity and immobilization of tunnel cations. They further suggested that the tunnels would collapse at high pressures if they had vacant sites. There are many structural similarities between KMCT and hollandite-type compounds. However, despite the fact that KMCT was synthesized at much higher pressure (13 GPa) than any of the samples listed above, it still shows a significant amount of unoccupied tunnel sites. As both occupancy and configuration of tunnel cations have a profound influence on the physical properties of hollandite compounds, our results on KMCT evidently point to the necessity of further investigations into the pressure effects on the crystal chemistry of hollandite compounds.

Acknowledgments

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