High pressure synthesis and properties of ternary titanium (III) fluorides in the system KF–TiF$_3$ containing regular pentagonal bipyramids [TiF$_7$]

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ABSTRACT

Titanium trifluoride TiF$_3$ has the distorted ReO$_3$ structure composed of corner sharing TiF$_6$ octahedra linked with Ti–F–Ti bridges. Potassium fluoride KF was inserted into the bridges using high-pressure and high-temperature conditions (5 GPa, 1000–1200 °C). When the molar ratio KF/TiF$_3 \geq 1$, a few low dimensional compounds were obtained forming non-bridged F ions. At the composition KF/TiF$_3$=1/2, a new compound KTi$_2$F$_7$ was formed, which crystallizes with the space group $Cmmm$ and the lattice parameters of a=6.371(3), b=10.448(6), c=3.958(2) Å, consisting of edge-sharing pentagonal bipyramids [TiF$_7$] forming ribbons running along the a axis. The ribbons are linked by corners to construct a three-dimensional framework without forming non-bridged F ions. The compound is antiferromagnetic with the Néel temperature T_N=75 K, and the optical band gap was 6.4 eV. A new fluoride K$_2$TiF$_5$ (KF/TiF$_3$=2) with the space group $Pbcn$ and the lattice parameters of a=7.4626(2), b=12.9544(4) and c=20.6906(7) Å was also obtained by the high pressure and high temperature treatment (5 GPa at 1000 °C) of a molar mixture of 2 KF+TiF$_3$. The compound contains one-dimensional chains of corner-sharing TiF$_6$ octahedra.

1. Introduction

The application of high-temperature and high-pressure conditions has often generated unexpected effects with a strong surprise in the preparation of new compounds. The main effect of high pressure is due to the total decrease in the volume of the system. Structural phase transitions to induce dense forms, and the formation of compounds with higher coordination numbers and higher oxidation states are favorable under pressure [1,2]. The high pressure transformation of silicon with the diamond structure having four-fold bonded Si atoms to the β-tin structure with six-fold bonded Si atoms [3], and the transformation of quartz with four coordinated Si to stishovite of the rutile structure with six coordinated Si are well known [4]. Recently silicon nitride Si$_3$N$_4$ has been changed into the spinel structure with six coordinated Si with nitrogen under high pressure [5]. In the preparation of high-T_c cuprate superconductors, application of high-pressure with strongly oxidizing conditions stabilizes the homologous multi-layered copper oxide series [6–8]. The recent developments in group 14 elements are the formation of expanded framework allotropes of C and Si. The fullerene C$_{60}$ was polymerized under high pressure to form 2D and 3D covalent networks [9–13]; a variety of silicon clathrate compounds isomorphous with gas hydrates have been prepared. The Ba containing clathrate compounds Ba$_8$Si$_{46}$ and Ba$_{24}$Si$_{100}$ have been prepared only under high pressure [14,15], both of which show superconductivity with T_cs=1.4 and 8.0 K, respectively. Note that the formations of these expanded frameworks are also accompanied by a large decrease in the molecular volumes of the systems under pressure.

The high pressure reaction cells can realize the reactions which will not be possible by using normal sealed quartz glass tubes; much higher pressures of reactants can be confined up to several GPa in a sealed metal capsule, the inner pressure being balanced by the pressure applied from the outside through anvils. In the synthesis of single crystals of layer structured metal nitride halides MNX (M=Zr, Hf; X=Cl, Br, I), ammonium halide (NH$_4X$) was sealed with MNX as flux in Au or Pt capsules, and heated under pressure at temperatures up to 1000–1200 °C [16,17].

In this study, insertion reaction of metal fluoride into three dimensional TiF$_3$ with the distorted ReO$_3$ structure is examined under pressure. In ambient condition, the insertion of alkali metal fluoride (AF) into the fluorine bridging bonds generates new non-bridging fluorine atoms;

$$\text{Ti–F–Ti} + \text{AF} \rightarrow \text{Ti–F} \cdots \text{A} \cdots \text{F–Ti} \tag{1}$$

A similar reaction is used to modify silicate glass network with alkali or alkaline earth metal (R) oxides, forming non-bridging oxygen;

$$\text{Si–O–Si} + \text{RO} \rightarrow \text{Si–O} \cdots \text{R} \cdots \text{O–Si} \tag{1}$$

The ternary TiF$_3$ compounds are known for a long time, such as A_3TiF$_6$ and ATiF$_4$ (A=Na, K, Rb, Cs), containing [TiF$_6$]$^{3-}$ octahedra

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[18–23]. In A_3TiF_6, all of the fluorine ions are non-bridging, and the octahedra are isolated. In $ATiF_4$ the octahedra are linked two-dimensionally, and the sheets are separated by alkali metal ions through non-bridging fluorine ions. It was reported that $CsTiF_4$ containing the $3d^1$ Ti^{3+} ion has a two-dimensional antiferromagnetic character [20]. The ternary TiF_4 compounds such as A_2TiF_6 and A_3TiF_7 also consist of $[TiF_6]^{2-}$ octahedra. In the present ternary system KF–TiF_3 under high-pressure and high-temperature conditions, a couple of new ternary fluorides have been obtained. The compound with a composition KTi_2F_5 ($KF+2TiF_3$) has been found to be composed of edge and corner shared 7 coordinated polyhedra $[TiF_7]$ without containing non-bridging fluorine atoms.

2. Experimental

2.1. High pressure synthesis

KF (Katayama Chemical, 99.99%) and TiF_3 (Aldrich) were dried by evacuation at $110\,°C$ over night, were mixed in various ratios, and sealed in a Pt capsule (4 mm in diameter, 5 mm in length, and 0.1 mm in thickness). The capsule was electrically isolated by a hexagonal BN (h-BN) tube from a tubular graphite heater, which was thermally insulated by a surrounding zirconia tube with a thickness of 1 mm. The whole assembly was placed in a pierced MgO octahedron as pressure medium, which was compressed in Kawai-type multi-anvil [24] with a truncation edge length of 12 mm. More detailed procedure was described elsewhere [25]. The reaction was kept at the preset temperature for 1 h, and the temperature was slowly cooled down to room temperature in 2 h under pressure. The pressure was released after the cooling.

2.2. Characterization

Single crystal X-ray structural analysis was performed on a Rigaku AFC7R Mercury CCD diffractometer with $MoK\alpha$ radiation (λ=0.71073 Å). The single crystal structure was refined with the program SHELX97 [26] and the WinGX software package [27]. The composition of the crystals were determined by an electron probe microanalyzer (JEOL JCMA-733II), and Hitachi S3400 with an energy dispersive X-ray analyzer (EDX, EDAX Genesis XM2) using the standards of CaF_2 for F, TiO_2 for Ti, and $KTiOPO_4$ for K. The magnetic susceptibility was measured using a SQUID magnetometer (Quantum Design MPMS-5) under a field of 1000 Oe. The UV/VIS absorption of the crystal was measured using a Perkin–Elmer Spectrometer (lambda 900), where a single crystal ($0.1 \times 0.2 \times 0.05\,mm^3$) was mounted on a pin-holed Al foil for the optical transmittance measurement. The ab initio calculation of the band structure was preformed by the program CASTEP in Accelrys software suit [28,29]. The calculation was carried out using GGA-PBE (general gradient approximation, Perdew–Burke–Ernzehof) functional with a Hubbard U value of 2.5 eV for Ti d orbitals. Ultrasoft pseudopotentials were used within a plane wave basis with a cut off energy 370 eV. A $4 \times 3 \times 3$ Monckhorst–Pack mesh was used for k-point sampling within the Brillouin zone.

3. Results

Mixtures of KF and TiF_3 in various ratios were treated under high-temperature and high-pressure conditions. New crystals were obtained with compositions of KTi_2F_7 and K_2TiF_5.
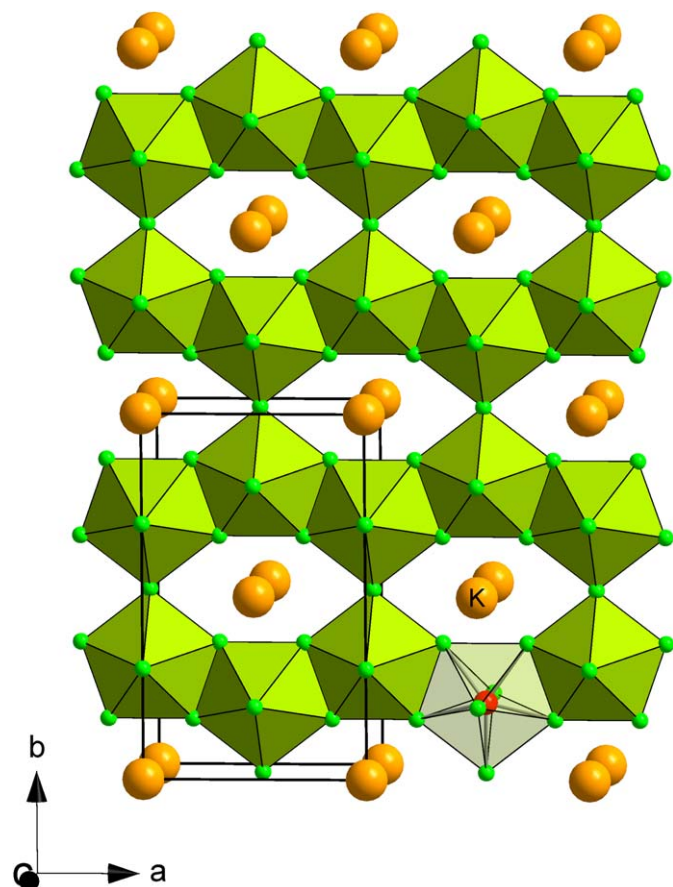
3.1. KTi_2F_7

When KF and TiF_3 are mixed in a molar ratio KF/TiF_3=1/2 and compressed at 5 GPa at $1200\,°C$, a new crystal was obtained, which crystallized with the space group $Cmmm$ and the lattice parameters of a=6.371(3), b=10.448(6), and c=3.958(2) Å. The crystallographic data and structural parameters are given in Tables 1 and 2. The electron probe microanalysis showed the composition of $K_{1.03}Ti_2F_{7.03}$, in good agreement with that suggested by the X-ray structural analysis. A schematic illustration of the structure is shown in Fig. 1. Note that the

Table 1
Details of the crystal structure investigations for KTi_2F_7 and K_2TiF_5.

	KTi_2F_7	K_2TiF_5
Formula weight	267.9	221.1
Crystal size (mm)	$0.15 \times 0.12 \times 0.09$	$0.08 \times 0.08 \times 0.07$
Space group	Cmmm (no. 65)	Pbcn (no. 60)
R_{int}	0.028	0.030
a (Å)	6.371(3)	7.4626(2)
b (Å)	10.448(6)	12.9544(4)
c (Å)	3.958(2)	20.6906(7)
V (Å^3), Z	263.4(2), 2	1998.9(1), 16
d_{calc} (g/cm^3)	3.377	2.939
Temperature, K	293	293
λ Mo$K\alpha$ (Å)	0.71073	0.71073
μ mm^{-1}	3.895	3.376
Absorption correction	Numerical	Numerical
F(000)	252	1680
θ_{max} (°)	27.4	27.48
Index ranges	$-7 \leqslant h \leqslant 8$, $-13 \leqslant k \leqslant 10$, $-5 \leqslant l \leqslant 3$	$-9 \leqslant h \leqslant 6$, $15 \leqslant k \leqslant 16$, $-26 \leqslant l \leqslant 26$
Reflection numbers	1019	14931
Total reflections	194	2284
Observed [$I \geqslant 2\sigma(I)$]	178	2104
No. of variables	22	149
GOF on Fo^2	1.055	1.123
$R1/wR2$ [$I \geqslant 2\sigma(I)$]	0.021/0.0561	0.0241/0.0623
$R1/wR2$ (all data)	0.022/0/0559	0.0268/0.0638
Largest diff. peak and hole, e$^-$/Å^3	0.571, -0.482	0.43, -0.416

Table 2
Atomic coordinates, anisotropic and equivalent displacement parameters (Å^2) for KTi_2F_7 and K_2TiF_5.

Atom	Position	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}	U_{eq}
KTi_2F_7											
Ti1	4j	1/2	0.19206(5)	1/2	0.0084(4)	0.0095(4)	0.0119(4)	0	0	0	0.0099(3)
K1	2a	0	0	0	0.0414(8)	0.0199(7)	0.0173(6)	0	0	0	0.0261(4)
F1	2c	1/2	0	1/2	0.015(2)	0.015(2)	0.046(2)	0	0	0	0.0253(8)
F2	4i	1/2	0.1980(2)	0	0.026(1)	0.036(2)	0.009(1)	0	0	0	0.0235(7)
F3	8q	0.1900(2)	0.1457(2)	1/2	0.0125(8)	0.0121(9)	0.0266(8)	−0.0013(6)	0	0	0.0170(4)
K_2TiF_5											
Ti1	8d	0.66052(4)	0.30146(2)	0.17152(1)	0.0200(2)	0.0154(2)	0.0156(2)	−0.0014(1)	−0.0001(1)	−0.0008(1)	0.01700(1)
Ti2	8d	0.33535(4)	0.49938(2)	0.07766(1)	0.0214(2)	0.0144(2)	0.0180(2)	−0.0016(1)	−0.0009(1)	−0.0013(1)	0.0179(1)
K1	4c	1/2	0.06879(4)	1/4	0.0235(2)	0.0201(3)	0.0194(3)	0	−0.0001(2)	0	0.0210(1)
K2	8d	0.51110(5)	0.26560(3)	0.00591(2)	0.0254(2)	0.0222(2)	0.0243(2)	0.0041(1)	0.00062(14)	−0.0030(2)	0.0240(1)
K3	4c	1/2	0.53660(5)	1/4	0.0309(3)	0.0193(3)	0.0388(4)	0	0.0092(2)	0	0.0297(2)
K4	8d	0.84591(6)	0.51723(4)	0.08317(2)	0.0362(2)	0.0353(3)	0.0244(2)	−0.0088(2)	−0.0031(2)	0.0045(2)	0.03200(1)
K5	8d	0.14520(6)	0.28592(4)	0.16471(2)	0.0381(2)	0.0288(2)	0.0286(2)	−0.0055(2)	−0.0039(2)	0.0074(2)	0.0318(1)
F1	8d	0.2237(1)	0.37801(8)	0.04025(5)	0.0270(5)	0.0240(6)	0.0334(6)	−0.0068(4)	−0.0026(4)	−0.0075(5)	0.0281(2)
F2	8d	0.7936(2)	0.41701(9)	0.20371(6)	0.0352(6)	0.0334(6)	0.0309(6)	−0.0167(5)	−0.0012(5)	−0.0061(5)	0.0331(3)
F3	8d	0.1748(2)	0.58807(9)	0.03068(5)	0.0413(6)	0.0356(7)	0.0244(6)	0.0176(5)	0.0021(5)	0.0061(5)	0.0338(4)
F4	8d	0.7998(2)	0.20126(9)	0.22107(5)	0.0378(6)	0.0329(6)	0.0249(6)	0.0150(5)	−0.0008(5)	0.0046(5)	0.0319(3)
F5	8d	0.8143(2)	0.29689(9)	0.09651(5)	0.0403(6)	0.0424(7)	0.0221(6)	0.0147(5)	0.0112(5)	0.0054(5)	0.0349(3)
F6	8d	0.5098(2)	0.19552(9)	0.14040(6)	0.0481(7)	0.0253(6)	0.0313(6)	−0.0135(5)	−0.0086(5)	−0.0028(5)	0.0349(3)
F7	8d	0.4685(2)	0.60927(9)	0.11217(6)	0.0473(7)	0.0263(6)	0.0462(7)	−0.0121(5)	−0.0062(6)	−0.0110(5)	0.0400(3)
F8	8d	0.1790(2)	0.48972(9)	0.15135(6)	0.0443(7)	0.0317(7)	0.0267(6)	0.0096(5)	0.0160(5)	0.0051(5)	0.0342(3)
F9	4c	1/2	0.31683(13)	1/4	0.0323(8)	0.0346(9)	0.0273(8)	0	0.0129(6)	0	0.0314(4)
F10	4a	1/2	1/2	0	0.0352(8)	0.0403(9)	0.0321(9)	0.0033(7)	0.0151(7)	0.0046(7)	0.0359(4)
F11	8d	0.5059(1)	0.40259(9)	0.12293(6)	0.0350(6)	0.0361(7)	0.0358(7)	0.0134(5)	−0.0049(5)	0.0079(6)	0.0356(3)

Fig. 1. Schematic structural model of KTi_2F_7 composed of edge and corner shared pentagonal bipyramid polyhedra TiF_7.

compound is composed of only one kind of regular pentagonal bipyramids TiF_7. The structure is isotropic with KSc_2F_7 [30]. As for the titanium fluoride, this is the first compound composed of pentagonal bipyramid polyhedra. The selected bond distances and an angle of the coordination of the pentagonal bipyramid are shown in Fig. 2 and Table 3. The coordination of Ti is a regular pentagonal bipyramid with the bond distances Ti–F in a range of 2.007–2.082 Å in the pentagonal plane, and 1.980 Å along the five fold axis. The F3–F3 distance (2.310 Å) of the pentagonal edges sharing with the neighbors is slightly shorter than the distances of unshared edges (2.420 and 2.494 Å). This is probably due to the effect of the electrostatic repulsion between Ti^{3+} ions across the shared edge. As the result, the Ti atom is very slightly shifted toward F1, off the center in the pentagonal plane, and the bond angle F2–Ti–F1 (91.80(6)°) becomes slightly larger than 90°. The short Ti–F1 distance (2.007 Å) is also attributable to the result of the Ti–Ti repulsion effect. In this view point, this is a typical ionic crystal adhering to the Pauling's third rule on polyhedral linkages in ionic crystals [31]. It is noteworthy that the high-pressure and high-temperature condition can introduce KF without forming non-bridged fluorine atoms. The bond valence sum (bvs) calculation on the Ti atom gives bvs=3.08, in good agreement with the oxidation number of the Ti atom [32].

Fig. 3 shows the magnetic susceptibility (χ) as a function of temperature (T). This compound has a Néel transition at 75 K. In the paramagnetic temperature range, the inversed susceptibility fits well on the Currie–Weiss plot $\chi^{-1} = C/(T-\theta)$; the effective magnetic moment was determined to be 1.71 μ_B from the Currie constant C, in good agreement with the calculated spin-only value 1.72 μ_B for Ti^{3+} ($3d^1$). The Weiss temperature θ was determined to be −18 K, showing an antiferromagnetic spin structure. The reason of the large Curie-like tail of the susceptibility at the low temperature range and a small bump observed around 50 K is not known. It is probably due to paramagnetic impurity. The optical transmittance spectrum of the single crystal is shown in Fig. 4. The crystal is transparent and has a pale blue green color. The
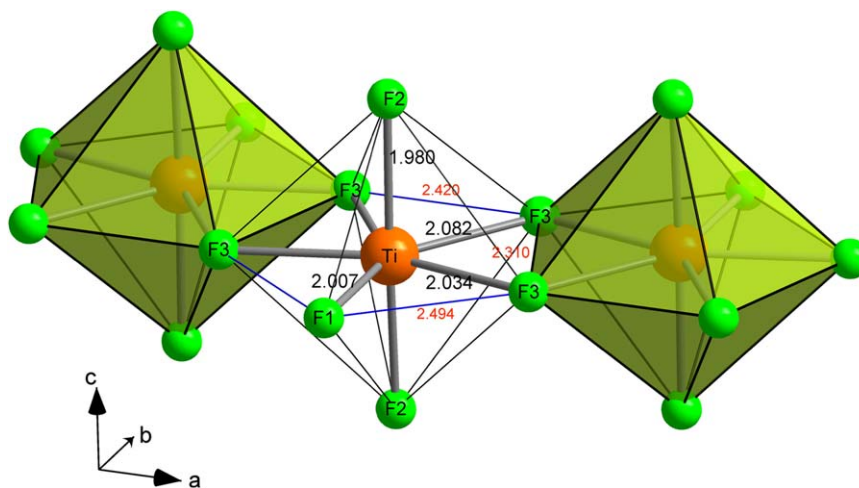
Fig. 2. Bond distances of the coordination of the pentagonal bipyramid polyhedra in KTi_2F_7.

Table 3
Selected bond distances (Å) and an angle (°) of KTi_2F_7 and K_2TiF_5.

KTi_2F_7					
Ti–F1	2.007(1)	Ti–F2 × 2	1.980(1)	Ti–F3 × 2	2.082(2)
Ti–F3 × 2	2.034(2)	F1–F3 × 2	2.494(2)	F2–F2 × 2	2.310(3)
F3–F3	2.420(2)	∠ F1–Ti–F2	91.80(6)°		
K_2TiF_7					
Ti1–F2	1.915(1)	Ti1–F4	1.953(1)	Ti1–F5	1.931(1)
Ti1–F6	1.887(1)	Ti1–F9	2.0287(3)	Ti1–F11	2.014(1)
Ti2–F1	1.940(1)	Ti2–F3	1.923(1)	Ti2–F7	1.876(1)
Ti2–F8	1.924(1)	Ti2–F10	2.0229(3)	Ti2–F11	2.017(1)
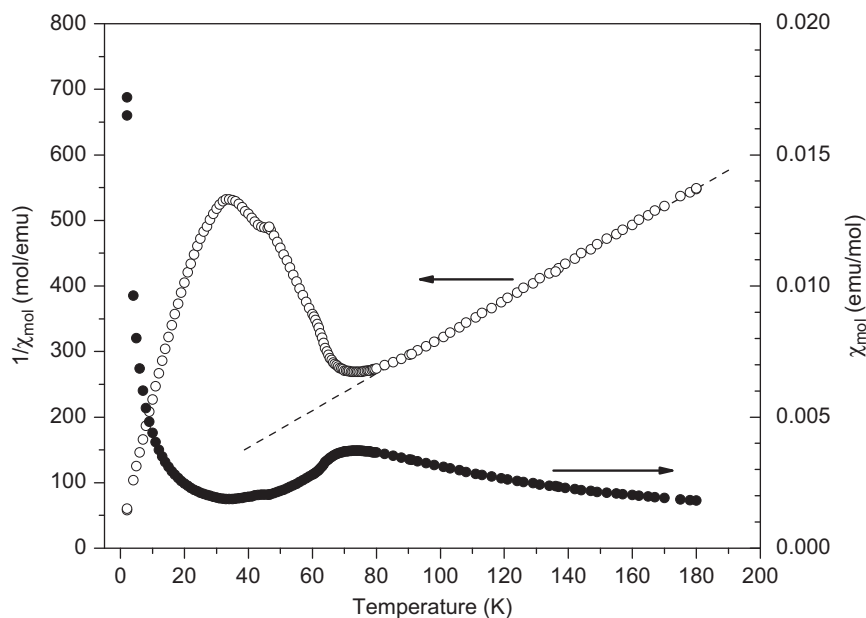
Fig. 3. Magnetic susceptibility and the inverse magnetic susceptibility of KTi_2F_7 as a function of temperature.

optical band gap was determined to be as large as 6.5 eV. The electrical band structure was calculated with LDF-U function. The Hubard U was tentatively assigned to be 2.5 eV, a default value of CASTEP. The calculated band structure and the electron density of states (DOS) are shown in Fig. 5. The calculation results also support that the Ti^{3+} ($3d^1$) ions are antiferromagnetically coupled along the all directions. The crystal has a large band gap with a localized d-orbital between the band gap of 5 eV. The density functional theory (DFT) calculation usually underestimates the gap value. The real gap can be estimated to be 6–6.5 eV, which is in good agreement with the optical gap observed experimentally.

3.2. K_2TiF_5

With a molar mixture $KF/TiF_3 = 2/1$ at 5 GPa and 1000 °C, we had another new crystal with a composition of K_2TiF_5 of purple color. The compound was not obtained as single phase, but always accompanied by K_2TiF_6 of black color. The X-ray single crystal analysis was made on the crystal. The crystallographic parameters are presented in Tables 1 and 2, together with the data of KTi_2F_7. The composition was determined to be $K_{2.11}TiF_{5.05}$ by EDX analysis, in good agreement with the X-ray data. The compound has a large unit cell with $Z=16$, isotypic with K_2FeF_5 (Space group, Pbcn) [33]. As shown in Fig. 6, the structure is composed of TiF_6 octahedra, which are cis-corner-connected along the c-axis to form one-dimensional chains. The selected bond distances are given in Table 3. Another type of one-dimensional chains of TiF_6 octahedra is found in $(NH_4)_2TiF_5$, where the octahedra are trans-corner-connected to infinite chains [34].
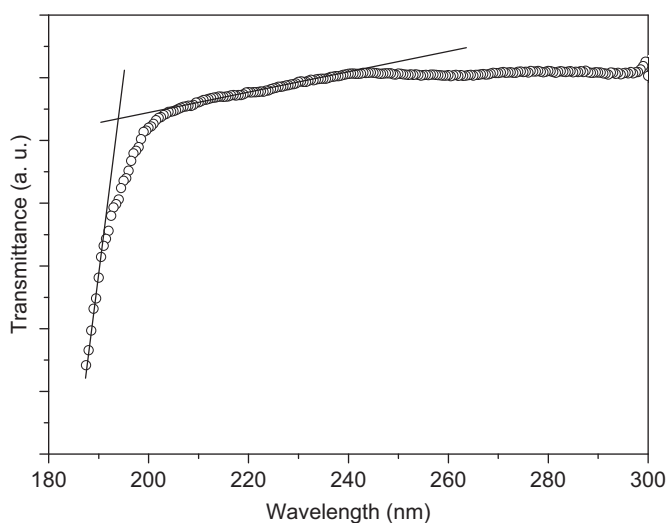

Fig. 4. Optical transmittance spectrum of KTi_2F_7 in the band gap range. The band gap was estimated to be 194 nm in wavelength.
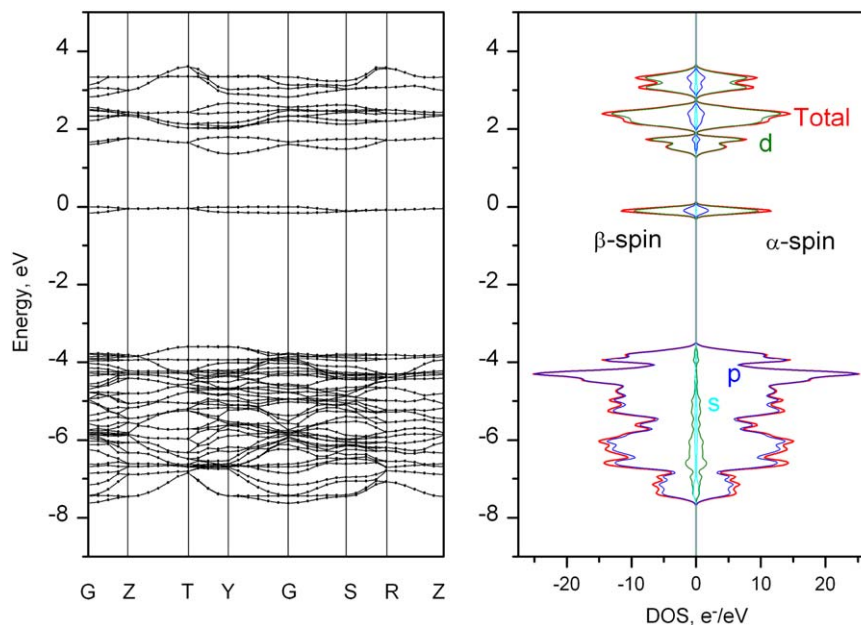
4. Discussion

In the ternary system $KF–TiF_3$ under pressure, we have found two new crystal structures KTi_2F_7 and K_2TiF_5, which are isotropic with KSc_2F_7 and K_2FeF_5, respectively. The compounds so far reported in this system are $KTiF_4$ ($KF/TiF_3 = 1$) [21], K_3TiF_6 ($KF/TiF_3 = 3$) [35] and $K_5Ti_3F_{14}$ ($KF/TiF_3 = 5/3$) [36]. The molar ratio $m = KF/TiF_3$ and the dimensionality, n of the crystal structure has the following relation;

$$m + n = 3.$$

When $m < 1$, the crystal has a 3D structure, containing no non-bridging fluorine atoms in the structure. The compound $K_5Ti_3F_{14}$ ($m=5/3$) has a value $n=4/3$ between $n=1$ and 2, and has a dimension between 1D and 2D. In $K_5Ti_3F_{14}$ two types of TiF_6 octahedra are included. One type of the octahedra share two trans-corners, i.e., 1D linking, leaving four non-bridging fluorine ions. The other type of the octahedra share four corners in equatorial plane (2D linking), leaving two non-bridging fluorine ions. The compound $KTiF_4$ with $n=2$ has a 2D layered structure. In the compound K_3TiF_6 with $n=0$, the TiF_6 octahedra are isolated without sharing the corners. The high-pressure and high-temperature condition should be favorable for the formation of bipyramidal coordination with Ti^{3+} ions, which have smaller ionic radius than that of the Sc^{3+} ion in the isotypic KSc_2F_7. In the formation of K_2TiF_5, the structure is composed of normal $[TiF_6]^{3-}$ octahedra, and the pressure appears to be not necessary. However, without pressure, more stable $KTiF_4$ was formed even from a mixture with the molar ratio $KF/TiF_3 = 2/1$.

5. Conclusions

The new compound KTi_2F_7 composed of pentagonal bipyramids TiF_7 was prepared using high-pressure and high-temperature conditions. The compound is a typical ionic crystal adhering to the Pauling's third rule. The high-pressure and high-temperature conditions are favorable for the synthesis of the high coordination number structure without containing non-bridging fluorine ions.
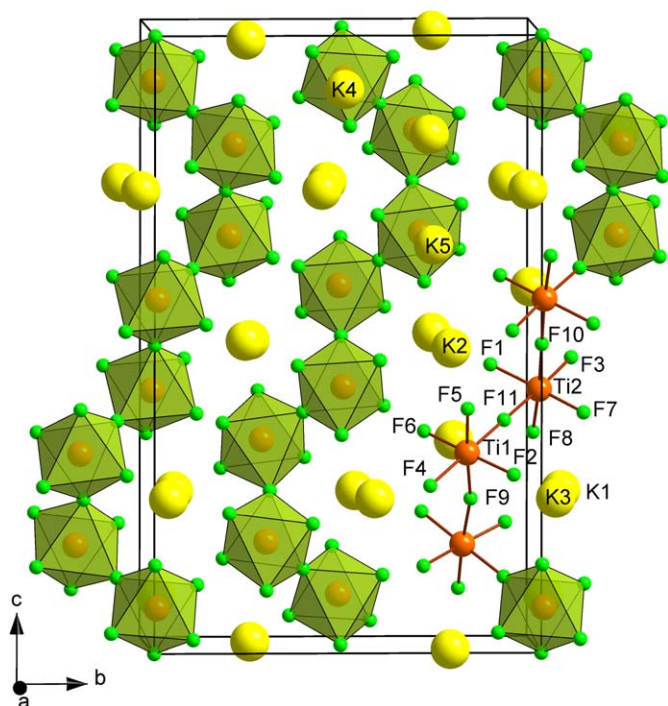

Fig. 5. Calculated band structure and the density of states (DOS) of KTi_2F_7.

Fig. 6. Schematic structural model of K_2TiF_5 containing one dimensional TiF_6 octahedral chains.

Acknowledgments

Appendix A. Supplementary material

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.jssc.2009.11.012.

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