Kudryavtsevaite, $Na_3MgFe^{3+}Ti_4O_{12}$, a new kimberlitic mineral

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ABSTRACT

Kudryavtsevaite, ideally $Na_3MgFe^{3+}Ti_4O_{12}$, is a new mineral from kimberlitic rocks of the Orapa area, Botswana. It occurs as rare prismatic crystals, up to 100 μm across, associated with Mg-rich ilmenite, freudenbergite and ulvöspinel. Kudryavtsevaite is opaque with a vitreous lustre and shows a black streak. It is brittle; the Vickers hardness (VHN_{100}) is 901 kg mm^{-2} (range: 876−925) (Mohs hardness ~6). In reflected light, kudryavtsevaite is moderately bireflectant and very weakly pleochroic from dark grey to a slightly bluish grey. Under crossed polars, it is very weakly anisotropic with greyish-bluish rotation tints. Internal reflections are absent. Reflectance values (%), R_{min} and R_{max}, are: 21.3, 25.4 (471.1 nm), 20.6, 24.1 (548.3 nm), 20.0, 23.5 (586.6 nm) and 19.1, 22.4 (652.3 nm).

Kudryavtsevaite is orthorhombic, space group *Pnma*, with $a = 27.714(1)$, $b = 2.9881(3)$, $c = 11.3564(6)$ Å, $V = 940.5(1)$ Å^3, and $Z = 4$. The crystal structure [$R1 = 0.0168$ for 819 reflections with $I > 2\sigma(I)$] consists of edge-sharing and corner-sharing chains composed of Mg, Fe^{3+} and Ti atoms coordinated by six atoms of oxygen and running along the *b* axis, with Na filling the tunnels formed by the chains. The eight strongest powder-diffraction lines [*d* in Å (I/I_0) (*hkl*)] are: 7.17 (100) (301), 4.84 (70) (302), 2.973 (35) (901), 2.841 (50) (004), 2.706 (50) (902), 2.541 (50) (312), 2.450 (70) (611), and 2.296 (45) (612). The average results of 12 electron microprobe analyses gave (wt.%): Na_2O 16.46(15), CaO 1.01(3), MgO 5.31(5), Fe_2O_3 22.24(32), Cr_2O_3 1.05(6), Al_2O_3 0.03(2), TiO_2 53.81(50), total 99.91, corresponding to the empirical formula $(Na_{2.89}Ca_{0.10})_{\Sigma2.99}(Ti_{3.67}Fe^{3+}_{1.52}Mg_{0.72}Cr_{0.08})_{\Sigma5.99}O_{12}$, or ideally $Na_3MgFe^{3+}Ti_4O_{12}$.

The new mineral has been approved by the IMA-CNMNC and named for Galina Kudryavtseva (1947−2006), a well known Russian mineralogist and founder of the Diamond Mineralogy Laboratory and scientific school for investigation of diamond mineralogy and geochemistry at the Lomonosov State University in Moscow, Russia.

Introduction

Kimberlite represents a hybrid ultrabasic rock that is composed of mineral assemblages of different provenance. These rocks usually contain Ti oxides, such as Ti-rich spinel (Dawson and Hawthorne, 1973), Mg-rich ilmenite (Fe,Mg)TiO_3, perovskite $CaTiO_3$ and, more sporadically, freudenbergite $Na_2Fe^{3+}_2Ti_6O_{16}$. The latter was reported in xenoliths of the lower crust and upper mantle from Liberia (Haggerty, 1983*a*)

and South Africa (Haggerty, 1983*b*, 1991; Haggerty and Gurney, 1984). Freudenbergite was also found as inclusions in Mg-rich ilmenite megacrysts from the kimberlite pipe Dalnaya, Yakutia (Patchen *et al.*, 1997).

Here we report the occurrence and description of kudryavtsevaite, ideally $Na_3MgFe^{3+}Ti_4O_{12}$, a new kimberlitic Ti-rich oxide. It was discovered in a kimberlite-hosted xenolith recovered from a drill-core sample from a depth of 138 m in the pipe AK-8 in the Orapa kimberlite cluster,

Botswana (21º18′S 25º24′E) (e.g. Gernon *et al.*, 2009, and references therein). The host kimberlite consists of serpentinized forsterite and less common phlogopite and Mg-rich ilmenite, as well as Cr-rich diopside and pyrope, cemented by fine-grained carbonate-serpentine aggregates containing minute grains of unidentified opaque minerals. In fractures within the Mg-rich ilmenite, a secondary mineralization is found, including freudenbergite, kudryavtsevaite and ulvöspinel (Fig. 1).
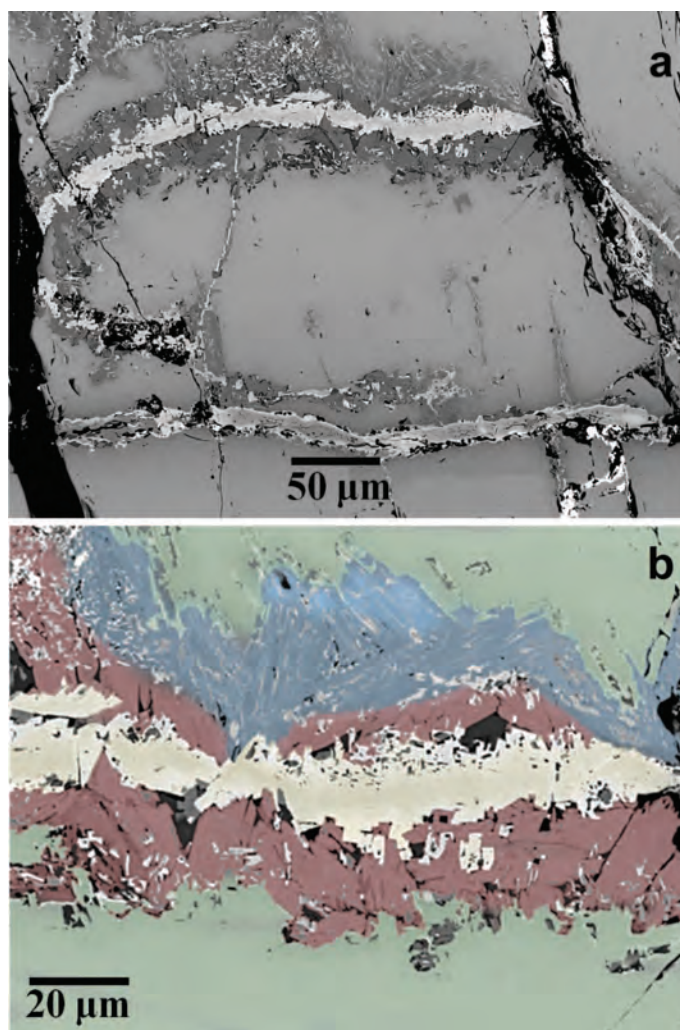

FIG. 1. Back-scattered-electron (BSE) image of a fracture in Mg-rich ilmenite containing the new mineral kudryavtsevaite (*a*). The false-colour BSE image in (*b*) is an enlargement of the upper region shown in (*a*). False colours indicate ilmenite (light green), kudryavtsevaite (light blue), freudenbergite (rosy brown) and ulvöspinel (greyish white).

The new mineral (IMA 2012−078) has been approved by the IMA-Commission of New Minerals, Nomenclature and Classification and named for Galina Kudryavtseva (1947−2006), a well known Russian mineralogist and founder of the Diamond Mineralogy Laboratory and scientific school for investigation of diamond mineralogy and geochemistry at the Lomonosov State University in Moscow. Galina Kudryavtseva together with her collaborators carried out pioneering studies of diamond kimberlite deposits in Yakutia and the Arkhangelsk region.

The holotype material is deposited in the mineralogical collections of the Museo di Storia Naturale, Università degli Studi di Firenze, Italy, under catalogue number 3115/I.

Physical and optical properties

Kudryavtsevaite exhibits a prismatic habit elongated along [010], and shows no inclusions of, or intergrowths with, other minerals. The maximum grain size of kudryavtsevaite is ~100 μm. It is greyish black in colour and shows a black streak. The mineral is opaque in transmitted light and exhibits a vitreous lustre. No cleavage is observed and the fracture is uneven. The density calculated on the basis of the empirical formula (see below) is 3.845 g cm^{-3}. Micro-indentation hardness measurements carried out with a VHN load of 100 g give a mean value of 901 kg mm^{-2} (range: 876−925) corresponding to a Mohs hardness of ~6.

In plane-polarized incident light, kudryavtsevaite is dark grey in colour, moderately bireflectant and very weakly pleochroic from dark grey to slightly bluish grey. In cross-polarized light, kudryavtsevaite is anisotropic with greyish-bluish rotation tints. Internal reflections are absent and there is no optical evidence of zonation.

Reflectance measurements were performed in air using an MPM-200 Zeiss microphotometer equipped with an MSP-20 system processor and coupled to a Zeiss Axioplan ore microscope. The filament temperature was approximately 3350 K. An interference filter was adjusted to select four reference wavelengths for the measurement (471.1, 548.3, 586.6 and 652.3 nm). Readings were taken for both specimen and standard (synthetic SiC) maintained under the same focus conditions. The diameter of the circular measuring area was 0.1 mm. Reflectance values (R_{min} and R_{max}, %) are 21.3, 25.4 (471.1 nm),

20.6, 24.1 (548.3 nm), 20.0, 23.5 (586.6 nm), and 19.1, 22.4 (652.3 nm).

X-ray crystallography and crystal-structure determination

A crystal ($70 \times 80 \times 95$ μm) was chosen for the collection of X-ray diffraction (XRD) data, which was done with an Oxford Diffraction Xcalibur 3 diffractometer (Mo$K\alpha$ radiation) equipped with a Sapphire 2 CCD detector (see Table 1 for details). Intensity integration and standard Lorentz-polarization corrections were done with the *CrysAlis* RED (Oxford Diffraction, 2006) software package. In this package, the program *ABSPACK* was used for the absorption correction. The R_{int} (Laue group *mmm*) decreased from 0.1024 to 0.0577 after the absorption correction.

Reflection conditions (0*kl*: $k + l = 2n$; *hk*0: $h = 2n$; *h*00: $h = 2n$; 0*k*0: $k = 2n$; 00*l*: $l = 2n$) were consistent with the space group *Pnma*. The positions of most of the atoms were determined by direct methods (Sheldrick, 2008). A least-squares refinement on F^2 using these heavy-atom positions and isotropic temperature factors gave an *R* factor of 0.1243. Three-dimensional difference Fourier synthesis yielded the position of the remaining atoms. The full-matrix least-squares program SHELXL-97 (Sheldrick, 2008) was used for the refinement of the structure. Site-scattering values were refined using scattering curves for neutral species (Ibers and Hamilton, 1974), including: Na *vs.* Ca in the *A* sites, Mg *vs.* Fe and Ti *vs.* Fe in the *M* sites, and O *vs.* □ (vacancy) in the anion sites. All oxygen sites were found fully occupied, and their occupancy then fixed to 1.00. The refined site-populations at the *A* and *M* sites are given in Table 2. The introduction of anisotropic temperature factors for all of the atoms led to $R = 0.0168$ for 819 observed reflections [$F_o > 4\sigma(F_o)$] and $R = 0.0183$ for all 1334 independent reflections. Fractional atomic coordinates and isotropic-displacement parameters are listed in Table 2 together with the bond-valence sums calculated according to Brese and O'Keeffe (1991). Anisotropic displacement parameters are given in Table 3. Structure factors (Table 4) are deposited with the Principal Editor of *Mineralogical Magazine* at http://www.minersoc.org/pages/e_journals/dep_mat.html. Bond distances are given in Table 5.

Powder XRD data (Table 6) were collected with an automated CCD-equipped Oxford Diffraction PX Ultra diffractometer with Cu$K\alpha$

TABLE 1. Data and experimental details for the selected kudryavtsevaite crystal.

Crystal data

Formula	$Na_3MgFe^{3+}Ti_4O_{12}$
Crystal size (mm)	$0.070 \times 0.080 \times 0.095$
Form	block
Colour	black
Crystal system	orthorhombic
Space group	*Pnma* (#62)
a (Å)	27.714(1)
b (Å)	2.9881(3)
c (Å)	11.3564(6)
V (Å^3)	940.5(1)
Z	4

Data collection

Instrument	Oxford Diffraction Excalibur 3
Radiation type	Mo$K\alpha$ ($\lambda = 0.71073$)
Temperature (K)	298(3)
Detector to sample distance (cm)	4.5
Number of frames	2312
Measuring time (s)	80
Maximum covered 2θ (º)	56.06
Absorption correction	multi-scan (*ABSPACK*; Oxford Diffraction 2006)
Collected reflections	8975
Unique reflections	1334
Reflections with $F_o > 4\sigma(F_o)$	819
R_{int}	0.0577
R_σ	0.0307
Range of h, k, l	$-36 \leqslant h \leqslant 36, -3 \leqslant k \leqslant 3, -15 \leqslant l \leqslant 15$

Refinement

Refinement	Full-matrix least squares on F^2
Final $R_{(obs)}$ [$F_o > 4 \sigma (F_o)$]	0.0168
Final R (all data)	0.0183
Number of least squares parameters	132
$\Delta\rho_{max}$ (e Å^{-3})	0.26
$\Delta\rho_{min}$ (e Å^{-3})	-0.61

radiation. The unit-cell parameters refined from the powder data [$a = 27.701(1)$, $b = 2.9879(1)$, $c = 11.3562(4)$ Å, and $V = 939.92(4)$ Å^3] are in excellent agreement with those determined by single-crystal methods.

Electron microprobe analysis and Raman spectroscopy

A preliminary chemical analysis using energy dispersive spectrometry, performed on the crystal fragment used for the structural study indicated the presence of Na, Mg, Ti, Fe and minor Al, Ca and Cr. The chemical composition was then determined using wavelength dispersive X-ray spectrometry (WDS) using a Jeol JXA-8600 electron microprobe. We used 30 s as counting time. The matrix correction was performed with the Bence and Albee (1968) program as modified by Albee and Ray (1970). The standards employed were: albite (Na), diopside (Mg and Ca), synthetic Fe_2O_3 (Fe), synthetic Cr_2O_3 (Cr), orthoclase (Al) and ilmenite (Ti). Mn, V and Zn were sought but were below the detection limit. The crystal was homogeneous (12 spot analyses) within the analytical uncertainty. The average chemical composition (in wt.%) is reported in Table 7. On the basis of 12 oxygen atoms and in accordance with the refinement results, the empirical formula can be written as $(Na_{2.89}Ca_{0.10})_{\Sigma2.99}$ $(Ti_{3.67}Fe^{3+}_{1.52}Mg_{0.72}Cr_{0.08})_{\Sigma5.99}O_{12}$, or ideally $Na_3MgFe^{3+}Ti_4O_{12}$.

TABLE 2. Bond valence sums, site populations, atom coordinates and equivalent isotropic-displacement parameters ($Å^2$) for the selected kudryavtsevaite crystal.

Atom	BV	Site population	x/a	y/b	z/c	U_{iso}
A1	0.96	$Na_{1.00}$	0.13084(2)	¾	0.10294(7)	0.0365(2)
A2	0.99	$Na_{1.00}$	0.46383(2)	¾	0.10029(7)	0.0322(2)
A3	1.03	$Na_{0.862(4)}Ca_{0.138}$	0.79699(2)	¾	0.10885(6)	0.0361(3)
M1	2.63	$Mg_{0.764(4)}Fe_{0.236}$	0.00631(1)	¼	0.12027(4)	0.0304(2)
M2	2.96	$Fe_{0.732(4)}Ti_{0.268}$	0.33943(2)	¼	0.11998(5)	0.0269(1)
M3	3.17	$Fe_{0.698(4)}Ti_{0.302}$	0.67279(2)	¼	0.12058(4)	0.0301(1)
M4	3.80	$Ti_{0.986(4)}Fe_{0.014}$	0.07668(1)	¾	0.33797(3)	0.0269(1)
M5	3.87	$Ti_{1.00}$	0.40996(1)	¾	0.33855(3)	0.0287(1)
M6	3.74	$Ti_{1.00}$	0.74352(1)	¾	0.33743(3)	0.0300(1)
O1	1.83		0.04152(3)	¾	0.1844(1)	0.0333(3)
O2	2.01		0.37527(4)	¾	0.1861(1)	0.0338(3)
O3	1.89		0.70814(4)	¾	0.1856(1)	0.0353(3)
O4	2.04		0.04332(3)	¼	0.4047(1)	0.0327(3)
O5	2.01		0.37631(3)	¼	0.4063(1)	0.0333(3)
O6	1.95		0.70958(3)	¼	0.4051(1)	0.0307(3)
O7	2.08		0.11918(3)	¼	0.2716(1)	0.0324(3)
O8	1.95		0.45245(3)	¼	0.2723(1)	0.0308(3)
O9	2.19		0.78577(3)	¼	0.2724(1)	0.0338(3)
O10	1.92		0.13000(4)	¾	0.4580(1)	0.0332(3)
O11	1.83		0.46455(4)	¾	0.4603(1)	0.0323(3)
O12	1.93		0.79798(4)	¾	0.4599(1)	0.0345(3)

Note: BV values calculated from the bond-valence curves of Brese and O'Keeffe (1991).

TABLE 3. Anisotropic-displacement parameters ($Å^2$) for the selected kudryavtsevaite crystal.

Atom	U_{11}	U_{22}	U_{33}	U_{13}
A1	0.0362(3)	0.0366(2)	0.0367(6)	−0.0004(3)
A2	0.0320(3)	0.0315(2)	0.0329(6)	0.0002(3)
A3	0.0358(3)	0.0358(2)	0.0366(6)	−0.0003(3)
M1	0.0293(2)	0.0302(1)	0.0316(4)	−0.0003(2)
M2	0.0265(1)	0.02675(6)	0.0275(2)	−0.0001(1)
M3	0.0297(1)	0.02992(7)	0.0307(3)	−0.0002(1)
M4	0.0265(1)	0.02667(6)	0.0277(3)	−0.0001(1)
M5	0.0285(1)	0.02822(7)	0.0294(3)	0.0001(1)
M6	0.0295(1)	0.02934(7)	0.0310(3)	−0.0001(1)
O1	0.0325(5)	0.0340(3)	0.0334(9)	0.0013(5)
O2	0.0338(5)	0.0327(3)	0.0349(8)	−0.0001(5)
O3	0.0350(5)	0.0343(3)	0.0365(9)	−0.0001(5)
O4	0.0313(4)	0.0320(3)	0.035(1)	0.0001(5)
O5	0.0320(4)	0.0326(3)	0.035(1)	0.0004(5)
O6	0.0301(4)	0.0292(3)	0.033(1)	0.0002(5)
O7	0.0313(4)	0.0311(3)	0.035(1)	0.0012(5)
O8	0.0303(4)	0.0299(3)	0.032(1)	0.0002(5)
O9	0.0329(4)	0.0331(3)	0.035(1)	0.0007(5)
O10	0.0334(5)	0.0325(3)	0.034(1)	−0.0002(5)
O11	0.0316(5)	0.0310(3)	0.034(1)	0.0007(5)
O12	0.0336(5)	0.0340(3)	0.036(1)	−0.0001(5)

TABLE 5. Selected interatomic distances (Å) for the selected kudryavtsevaite crystal.

A1–O5	2.242(1)	A2–O4	2.230(1)	A3–O6	2.321(1)
A1–O7 (×2)	2.450(1)	A2–O8 (×2)	2.480(1)	A3–O9 (×2)	2.403(1)
A1–O1	2.643(1)	A2–O2	2.641(1)	A3–O3	2.612(1)
A1–O6 (×2)	2.646(1)	A2–O4 (×2)	2.662(1)	A3–O5 (×2)	2.664(1)
Mean	2.513	Mean	2.526	Mean	2.511
M1–O8	1.928(1)	M2–O9	1.925(1)	M3–O7	1.926(1)
M1–O1 (×2)	1.9275(7)	M2–O2 (×2)	1.9447(8)	M3–O3 (×2)	1.9333(7)
M1–O11	1.988(1)	M2–O10	2.025(1)	M3–O12	1.997(1)
M1–O11 (×2)	2.0998(8)	M2–O12 (×2)	2.0915(8)	M3–O10 (×2)	2.1060(8)
Mean	1.995	Mean	2.004	Mean	2.000
M4–O1	1.997(1)	M5–O2	1.981(1)	M6–O3	1.983(1)
M4–O4 (×2)	1.9134(7)	M5–O5 (×2)	1.9221(7)	M6–O6 (×2)	1.9258(7)
M4–O10	2.010(1)	M5–O11	2.050(1)	M6–O12	2.052(1)
M4–O7 (×2)	2.0465(7)	M5–O8 (×2)	2.0457(7)	M6–O9 (×2)	2.0370(7)
Mean	1.988	Mean	1.994	Mean	1.993

To check the presence of H_2O/OH in kudryavtsevaite, a crystal was studied using a Renishaw RM2000 microRaman instrument, coupled with a diode laser source emitting at 785 nm. The laser beam was focused and Raman signal collected using a ×50 microscope objective attached to a Leica microscope DM LM. The beam power was 3.5 mW, the laser spot size was adjusted to 1.5 μm. Raman scattering was filtered by a double holographic Notch filter system and collected by an air-cooled CCD detector. The acquisition time was 100 s. No evidence of Raman peaks in the region $3300-3900$ cm^{-1} was detected (Fig. 2). Thus, according to the Raman results, the refined site scatterings and the bond valence sums (Table 2) as well as the charge-balance requirements, all the iron was considered as trivalent.
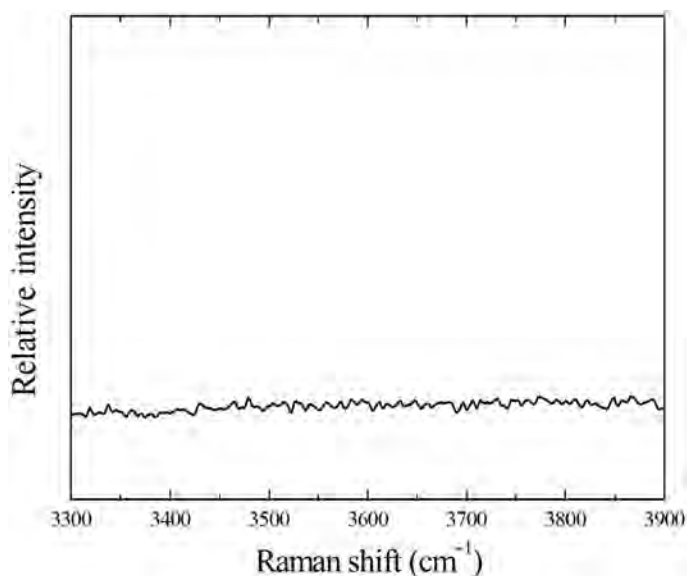

FIG. 2. Raman spectrum (unoriented crystal) of kudryavtsevaite in the $3300-3900$ cm^{-1} region.

TABLE 6. Experimental X-ray powder diffraction data (Å) for kudryavtsevaite.

I_{obs}	d_{obs}	d_{calc}	h	k	l
100	**7.17**	**7.1642**	**3**	**0**	**1**
5	6.93	6.9251	4	0	0
15	5.68	5.6781	0	0	2
70	**4.84**	**4.8368**	**3**	**0**	**2**
30	3.585	3.5821	6	0	2
10	3.504	3.5025	3	0	3
35	**2.973**	**2.9707**	**9**	**0**	**1**
50	**2.841**	**2.8391**	**0**	**0**	**4**
5	2.715	2.7137	3	0	4
50	**2.706**	**2.7059**	**9**	**0**	**2**
50	**2.541**	**2.5420**	**3**	**1**	**2**
70	**2.450**	**2.4494**	**6**	**1**	**1**
15	2.389	2.3881	9	0	3
45	**2.296**	**2.2945**	**6**	**1**	**2**
10	2.107	2.1067	9	1	1
15	2.090	2.0910	6	1	3
10	2.085	2.0868	9	0	4
10	2.037	2.0380	6	0	5
15	2.005	2.0057	9	1	2
10	1.881	1.8798	6	1	4
30	1.866	1.8655	9	1	3
30	1.828	1.8275	9	0	5
10	1.792	1.7911	12	0	4
5	1.750	1.7513	6	0	6
30	1.684	1.6836	6	1	5
10	1.645	1.6452	12	1	3
20	1.576	1.5755	3	1	6
10	1.555	1.5561	15	1	1
5	1.525	1.5250	18	0	1
10	1.515	1.5140	15	1	2
20	1.494	1.4940	0	2	0
5	1.464	1.4636	12	0	6
15	1.450	1.4509	15	1	3
10	1.433	1.4329	15	0	5
10	1.425	1.4257	0	1	7
5	1.409	1.4090	3	1	7
10	1.358	1.3583	18	1	1
5	1.322	1.3221	0	2	4
5	1.308	1.3079	9	2	2

Note: the strongest intensities are given in bold.

TABLE 7. Electron microprobe data (mean and ranges in wt.% of oxides) together with standard deviations (SD) and probe standards for kudryavtsevaite.

	Wt.%	Range	SD
Na_2O	16.46	16.32−16.61	0.15
CaO	1.01	0.85−1.23	0.03
MgO	5.31	4.98−5.65	0.05
Fe_2O_3	22.24	22.01−22.74	0.32
Cr_2O_3	1.05	0.80−1.23	0.06
Al_2O_3	0.03	0.00−0.06	0.02
TiO_2	53.81	52.79−54.11	0.50
Total	99.91	99.02−100.52	

sharing double chains and share a corner with another M. The A sites show a somewhat distorted octahedral coordination with distances in the range 2.230−2.664 Å. The $A3$ site shows the shortest mean bond distance (i.e. 2.511 Å), in agreement with a minor amount of Ca replacing Na. The octahedral sites are almost identical to one another, showing mean bond distances in the range 1.988−2.004 Å, which is not surprising, considering the similar ionic radii of the cations (i.e. Mg, Fe^{3+} and Ti) entering the M sites.

The kudryavtsevaite structure closely resembles that of synthetic $NaA^{3+}M^{4+}O_4$ compound (with $A = Fe^{3+}$ and Al and $M = Ti^{4+}$) described by Müller-Buschbaum and Frerichs (1993) [a = 9.230(2), b = 2.957(3), c = 11.318(2) Å, space group $Pnma$], which represents a calcium ferrite ($CaFe_2O_4$) derivative structure. The main difference is the tripling of the a axis in kudryavtsevaite due to ordering of the cations in the different octahedral sites. In this light, the kudryavtsevaite structure can be considered as a superstructure of the $NaA^{3+}M^{4+}O_4$ structure type.

Kudryavtsevaite and the associated freudenbergite seem to be products of the reaction of Mg-rich ilmenite with alkaline oxidized fluid or melt of metasomatic type.

Discussion

The structure of kudryavtsevaite (Fig. 3) consists of edge-sharing and corner-sharing octahedral chains (M atoms) running along the b axis, with the A atoms filling the tunnels formed by the chains. Six independent octahedral sites are present in the structure and all show a similar crystal-chemical environment: they form edge-
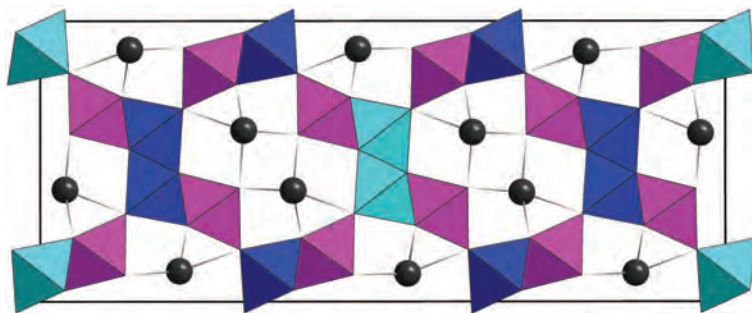
Acknowledgements

FIG. 3. The crystal structure of kudryavtsevaite viewed along [010]. The horizontal direction is the *a* axis. *A* sites are depicted as black spheres, *M* sites are shown as polyhedra. Light blue, dark blue and violet octahedra stand for *M*1 (Mg-dominant), *M*2-*M*3 (Fe^{3+}-dominant) and *M*4-*M*6 (Ti-dominant), respectively.

References

Albee, A.L. and Ray, L. (1970) Correction factors for electron probe analysis of silicate, oxides, carbonates, phosphates, and sulfates. *Analytical Chemistry*, **48**, 1408−1414.

Bence, A.E. and Albee, A.L. (1968) Empirical correction factors for the electron microanalysis of silicate and oxides. *Journal of Geology*, **76**, 382−403.

Brese, N.E. and O'Keeffe, M. (1991) Bond-valence parameters for solids. *Acta Crystallographica*, **B47**, 192−197.

Dawson, J.B. and Hawthorne, J.B. (1973) Magmatic sedimentation and carbonatitic differentiation in kimberlite sills at Benfontein, South Africa. *Journal of Geological Society of London*, **129**, 61−85.

Gernon, T.M., Fontana, G., Field, M., Sparks, R.S.J., Brown, R.J. and Mac Niocaill C. (2009) Pyroclastic flow deposits from a kimberlite eruption: The Orapa South Crater, Botswana. *Lithos*, **112**, 566−578.

Haggerty, S.E. (1983*a*) A freudenbergite-related mineral in granulites from Liberia. *Nueus Jahrbuch für Mineralogie Monatshefte*, **1983**, 375−384.

Haggerty, S.E. (1983*b*) The mineral chemistry of new titanates from the Jagersfontein kimberlite, South Africa: Implications for mantle metasomatism in the upper mantle. *Geochimica et Cosmochimica Acta*, **47**, 1833−1854.

Haggerty, S.E. and Gurney, J.J. (1984) Zircon-bearing nodules from the upper mantle. *EOS*, **65**, 301.

Ibers, J.A. and Hamilton, W.C. (editors) (1974) *International Tables for X-ray Crystallography*, vol. IV, 366 pp. Kynock, Dordrecht, The Netherlands.

Müller-Buschbaum, H. and Frerichs, D. (1993) Zur Existenz des $CaFe_2O_4$-Typs von Verbindungen der Zusammensetzung $Na\,A^{3+}M^{4+}O_4$. Röntgenstrukturanalysen von $NaFeTiO_4$ und $Na_{0,7}(Fe,Al)_{0,7}Ti_{1,3}O_4$. *Journal of Alloys and Compounds*, **199**, L5−L8.

Oxford Diffraction (2006) *CrysAlis* RED (Version 1.171.31.2) and ABSPACK in *CrysAlis* RED. Oxford Diffraction Ltd, Abingdon, Oxfordshire, England.

Patchen, A.D., Taylor, L.A. and Pokhilenko, N. (1997) Ferrous freudenbergite in ilmenite megacrysts: A unique paragenesis from the Dalnaya kimberlite, Yakutia. *American Mineralogist*, **82**, 991−1000.

Sheldrick, G.M. (2008) A short history of SHELX. *Acta Crystallographica*, **A64**, 112−122.