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TANIAJACOITE AND STRONTIORUIZITE, TWO NEW MINERALS ISOSTRUCTURAL WITH RUIZITE FROM THE N'CHWANING III MINE, KALAHARI MANGANESE FIELD, SOUTH AFRICA

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ABSTRACT

Two new mineral species, taniajacoite and strontioruizite, ideally $SrCaMn^{3+}{}_2Si_4O_{11}(OH)_4{\cdot}2H_2O$ and $Sr_2Mn^{3+}{}_2Si_4O_{11}(OH)_4{\cdot}2H_2O$, respectively, have been identified from the N'Chwaning III mine, Kalahari manganese field, South Africa. Both minerals occur as brown radiating groups or aggregates of acicular or prismatic crystals, with individual crystals up to $0.15 \times 0.04 \times 0.02$ mm for taniajacoite and $1.3 \times 0.2 \times 0.2$ mm for strontioruizite. Minerals associated with taniajacoite include sugilite, aegirine, pectolite, richterite, potassic-ferri-leakeite, and lipuite, whereas those associated with strontioruizite include sugilite, potassic-magnesio-arfvedsonite, and lipuite. Both taniajacoite and strontioruizite are brown in transmitted light, transparent with very light brown streak and vitreous luster. They are brittle and have a Mohs hardness of 5–5.5; cleavage is good on {010} and no parting or twinning is observed macroscopically. The measured and calculated densities are 3.05(2) and 3.09 g/cm^3, respectively, for taniajacoite and 3.20(2) and 3.16 g/cm^3 for strontioruizite. Optically, both taniajacoite and strontioruizite are biaxial (–), with $\alpha = 1.686(2)$, $\beta = 1.729(2)$, $\gamma = 1.746(2)$ (white light), $2V$ (meas.) = 63.7(5)°, $2V$ (calc.) = 62.5° for the former and $\alpha = 1.692(2)$, $\beta = 1.734(2)$, $\gamma = 1.747(2)$ (white light), $2V$ (meas.) = 59.1(5)°, $2V$ (calc.) = 56.6° for the latter. The calculated compatibility index based on the empirical formula is 0.008 for taniajacoite and 0.015 for strontioruizite. An electron microprobe analysis yielded an empirical formula (based on 17 O *apfu*) of $Sr(Ca_{0.81}Sr_{0.19})_{\Sigma 1.00}(Mn^{3+}{}_{1.90}Fe^{3+}{}_{0.15}Al_{0.01})_{\Sigma 2.06}Si_{3.96}O_{11}(OH)_4{\cdot}2H_2O$ for taniajacoite and $(Sr_{1.61}Ca_{0.42})_{\Sigma 2.03}(Mn^{3+}{}_{1.95}Fe^{3+}{}_{0.05})_{\Sigma 2.00}Si_{3.98}O_{11}(OH)_4{\cdot}2H_2O$ for strontioruizite.

Taniajacoite and strontioruizite are isostructural with ruizite. Strontioruizite, like ruizite, is monoclinic with space group $C2$ and unit-cell parameters $a = 9.1575(4)$, $b = 6.2857(4)$, $c = 12.0431(6)$ Å, $\beta = 91.744(4)°$, and $V = 692.90(6)$ Å^3, whereas taniajacoite is triclinic, with space group $C1$ and $a = 9.1386(5)$, $b = 6.2566(3)$, $c = 12.0043(6)$ Å, $\alpha = 90.019(4)$, $\beta = 91.643(4)$, $\gamma = 89.900(4)°$, and $V = 686.08(6)$ Å^3. Their structures are characterized by chains of edge-sharing MnO_6 octahedra extended along [010], which are linked together by corner-shared SiO_4 tetrahedra in four-membered $[Si_4O_{11}(OH)_2]$ linear clusters, giving rise to a so-called "hetero-polyhedral framework". The large cations Sr^{2+} and Ca^{2+} occupy the seven-coordinated interstices. Unlike monoclinic ruizite and strontioruizite, taniajacoite with Sr:Ca ≈ 1:1 is triclinic, owing to the ordering of Sr^{2+} and Ca^{2+} into two crystallographically distinct sites, indicating an incomplete solid solution between Ca and Sr endmembers. The unit-cell volumes for ruizite, taniajacoite, and strontioruizite appear to vary linearly with the Sr/(Ca + Sr) ratio.

Keywords: taniajacoite, strontioruizite, crystal structure, X-ray diffraction, Raman spectra.

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Introduction

Two new mineral species, taniajacoite and strontioruizite, ideally $SrCaMn^{3+}{}_2Si_4O_{11}(OH)_4{\cdot}2H_2O$ and $Sr_2Mn^{3+}{}_2Si_4O_{11}(OH)_4{\cdot}2H_2O$, respectively, have been found at the N'Chwaning III mine, Kalahari manganese field, Northern Cape province, South Africa. Taniajacoite is named in honor of its finders, Mrs. Tania and Mr. Jaco van Nieuwenhuizen, who are mineral collectors and the owners of "*Crystal Spring Minerals CC*" in South Africa (Cairncross 2020). Strontioruizite is named for the dominant presence of Sr over Ca in ruizite, $Ca_2Mn^{3+}{}_2Si_4O_{11}(OH)_4{\cdot}2H_2O$. The two new minerals and their names have been approved by the Commission on New Minerals, Nomenclature and Classification (CNMNC) of the International Mineralogical Association (IMA 2014-107 for taniajacoite and IMA 2017-045 for strontioruizite). The cotype samples of the two new minerals have been deposited at the University of Arizona Mineral Museum (Catalogue # 20009 and #21486) and the RRUFF Project (deposition # R140945 and R160085).

Both taniajacoite and strontioruizite are isostructural with ruizite, a sorosilicate mineral that was originally reported from the Christmas mine, Gila County, Arizona, USA by Williams & Duggan (1977) as monoclinic in space group $P2_1/c$, with unit cell parameters $a = 11.95$, $b = 6.17$, $c = 9.03$ Å, $\beta = 91.38°$. The ideal chemistry was proposed as $CaMn(SiO_3)_2(OH){\cdot}2H_2O$. The structure of ruizite was first determined by Hawthorne (1984) based on space group $A2$, in the same setting as that reported by Williams & Duggan (1977), using a crystal from the Wessels mine, Kalahari manganese field, Northern Cape province, South Africa. The structure refinement yielded $R = 5.6\%$ for an isotropic displacement model in which positions of three of the four hydrogen atoms were located. Refinement of anisotropic displacement parameters for non-H atoms was not successful. The ideal chemical formula was revised to $Ca_2Mn^{3+}{}_2[Si_4O_{11}(OH)_2](OH)_2(H_2O)_2$. Moore *et al.* (1985) re-examined the ruizite structure using a sample from the N'Chwaning mine, Kalahari manganese field, Northern Cape province, South Africa, and reported space group $C2/m$, with a different setting: $a = 9.064$, $b = 6.171$, $c = 11.976$ Å, $\beta = 91.38°$. Although they refined the structure with anisotropic displacement parameters for non-H atoms ($R = 8.4\%$), most of the resulting displacement ellipsoids were unreasonable or non-positive definite and no H atoms were located. Recently, Fendrich *et al.* (2016) conducted a redetermination of the ruizite structure using a crystal from the Wessels mine. With all non-H atoms refined anisotropically and all H atoms located, their data ($R_1 = 3.0\%$) confirmed that the space group of ruizite is $C2$, rather than $C2/m$.

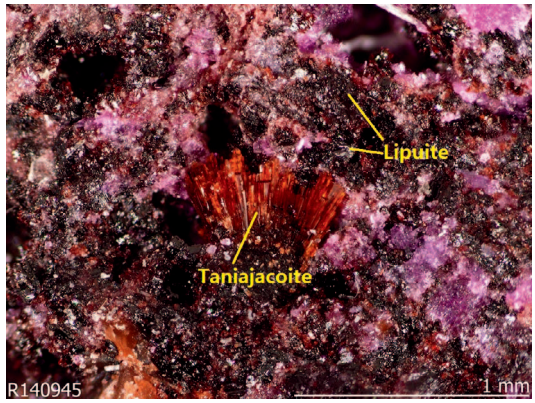

FIG. 1. A microscopic view of acicular brown taniajacoite crystals, associated with purple sugilite and dark-red brown lipuite.

This paper describes the physical and chemical properties of taniajacoite and strontioruizite and their crystal structures determined from single-crystal X-ray diffraction data, as well as their structural variations with chemical composition in the $Ca_2Mn^{3+}{}_2Si_4O_{11}(OH)_4{\cdot}2H_2O$–$Sr_2Mn^{3+}{}_2Si_4O_{11}(OH)_4{\cdot}2H_2O$ system.

Sample Description and Experimental Methods

Occurrence, physical and chemical properties, and Raman spectra

Both taniajacoite and strontioruizite were found on specimens collected from the N'Chwaning III mine, Kalahari manganese field, Northern Cape province, Republic of South Africa (27°7′50.81"S

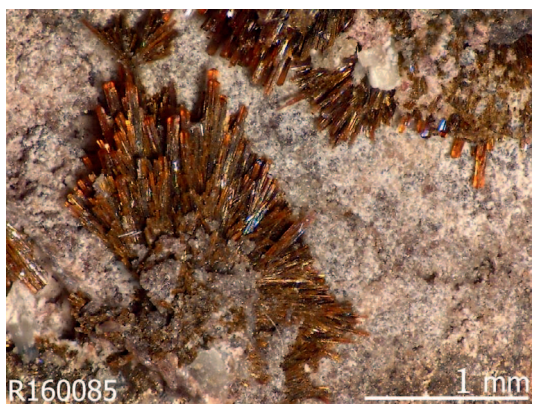

FIG. 2. A microscopic view of acicular brown strontioruizite crystals.

TABLE 1. COMPARISON OF MINERALOGICAL DATA FOR RUIZITE, TANIAJACOITE, AND STRONTIORUIZITE

	Ruizite	Taniajacoite	Strontioruizite
Ideal chemical formula	$Ca_2Mn^{3+}{}_2Si_4O_{11}(OH)_4 \cdot 2H_2O$	$SrCaMn^{3+}{}_2Si_4O_{11}(OH)_4 \cdot 2H_2O$	$Sr_2Mn^{3+}{}_2Si_4O_{11}(OH)_4 \cdot 2H_2O$
Crystal symmetry	Monoclinic	Triclinic	Monoclinic
Space group	*C*2	*C*1	*C*2
a (Å)	9.0360 (3)	9.1386(5)	9.1575(4)
b (Å)	6.1683 (2)	6.2566(3)	6.2857(4)
c (Å)	11.9601 (4)	12.0043(6)	12.0431(6)
α (°)	90	90.019(4)	90
β (°)	91.433 (2)	91.643(4)	91.744(4)
γ (°)	90	89.900(4)	90
V (Å^3)	666.41 (4)	686.08(6)	692.90(6)
Z	2	2	2
ρ_{meas}, ρ_{cal}(g/cm^3)	2.9(1), 3.00	3.05(2), 3.09	3.20(2), 3.16
Optical data			
Biaxial	(–)	(–)	(–)
α	1.663	1.686(2)	1.692(2)
β	1.715	1.729(2)	1.734(2)
γ	1.734	1.746(2)	1.747(2)
$2V_{meas}$, $2V_{calc}$ (°)	60.2, 60.7	63.7(5), 62.5	59.1(5), 56.6
Dispersion	$r > \nu$, strong	$r > \nu$, strong	$r > \nu$, strong
Crystal size (mm)	0.06 × 0.04 × 0.04	0.06 × 0.03 × 0.02	0.07 × 0.07 × 0.06
2θ range for data collection	≤65.12	≤60.00	≤65.04
No. of reflections collected	4997	6547	9249
No. of independent reflections	2038	3099	2178
No. of reflections with $I > 2\sigma(I)$	1732	2176	2009
No. of parameters refined	127	147	128
R(int)	0.029	0.051	0.024
Final R_1, wR_2 factors [$I > 2\sigma(I)$]	0.030, 0.065	0.054, 0.108	0.020, 0.048
Goodness-of-fit	1.06	1.013	1.071
Crystal locality	Wessels Mine	N'Chwaning III Mine	N'Chwaning III Mine
Reference	Fendrich *et al.* (2016)	This study	This study

TABLE 2. DETERMINED CHEMICAL COMPOSITIONS FOR TANIAJACOITE AND STRONTIORUIZITE

Constituent	Taniajacoite (average of 14 analyses)	Strontioruizite (average of 15 analyses)	Standard
SiO_2	36.85(33)	36.06	Forsterite $Mg_2(SiO_4)$
Al_2O_3	0.06(3)	n.d.	Anorthite $Ca(Al_2Si_2O_8)$
Mn_2O_3	23.29(56)	23.15(5)	Rhodonite $CaMn^{2+}{}_3Mn^{2+}(Si_5O_{15})$
Fe_2O_3	1.84(63)	0.65(3)	Fayalite $Fe^{2+}{}_2(SiO_4)$
SrO	19.15(83)	25.17(6)	Synthetic $SrTiO_3$
CaO	7.03(53)	3.54(4)	Diopside $CaMgSi_2O_6$
H_2O^+	11.17	10.85(4)	Added*
Total	99.39(68)	99.42(31)	

Note: * The H_2O content was added based on ($4OH + 2H_2O$) determined from the structure refinements.

22°50′28.83"E). Taniajacoite occurs as brown radiating groups or aggregates of acicular or prismatic crystals (Fig. 1), with individual crystals up to 0.15 × 0.04 × 0.02 mm. Associated minerals include sugilite, aegirine, pectolite, richterite, potassic-ferri-leakeite, and lipuite. Strontioruizite occurs as brown, elongate crystals clustered together, some with divergent habits (Fig. 2). The crystals are oriented approxi-

TABLE 3A. POWDER X-RAY DIFFRACTION DATA FOR TANIAJACOITE

I%	d_{meas}	d_{calc}	h	k	l
100.0	12.142	11.999	0	0	1
19.9	5.164	5.166	1	1	0
10.3	5.119	5.158	1	$\bar{1}$	0
13.8	4.752	4.766	$\bar{1}$	1	1
14.4	4.575	4.567	2	0	0
25.4	4.239	4.229	2	0	1
7.8	3.998	4.000	0	0	3
2.6	3.891	3.883	1	1	2
5.5	3.696	3.685	2	0	$\bar{2}$
38.0	3.134	3.138	1	1	3
8.4	3.029	3.027	0	2	$\bar{1}$
8.1	2.980	3.000	0	0	4
7.5	2.925	2.967	2	0	3
30.8	2.771	2.774	0	2	$\bar{2}$
4.9	2.690	2.686	3	1	$\bar{1}$
11.2	2.605	2.613	1	1	$\bar{4}$
11.3	2.600	2.611	$\bar{1}$	1	4
14.1	2.538	2.541	2	0	$\bar{4}$
17.6	2.363	2.358	2	2	2
2.3	2.217	2.232	4	0	1
13.0	2.151	2.152	2	$\bar{2}$	3
3.2	2.070	2.048	$\bar{3}$	1	4
15.0	2.002	2.008	4	0	$\bar{3}$
6.3	1.902	1.904	0	2	5
2.0	1.874	1.875	1	1	$\bar{6}$
2.6	1.843	1.843	4	0	$\bar{4}$
2.6	1.805	1.808	1	3	3
6.3	1.787	1.792	4	0	4
4.3	1.735	1.753	4	2	2
5.5	1.683	1.685	0	2	$\bar{6}$
6.6	1.670	1.661	4	2	3
3.8	1.647	1.631	4	0	5
4.0	1.594	1.594	2	2	$\bar{6}$
16.1	1.562	1.564	0	4	0
3.5	1.504	1.500	0	0	8
5.8	1.484	1.480	4	2	$\bar{5}$
4.9	1.467	1.478	$\bar{4}$	2	5
3.2	1.434	1.437	6	0	$\bar{3}$
2.6	1.413	1.413	2	0	8
2.9	1.385	1.390	4	0	$\bar{7}$
2.0	1.374	1.365	6	2	$\bar{1}$
1.4	1.350	1.343	6	2	$\bar{2}$
3.5	1.330	1.333	2	4	$\bar{4}$
2.9	1.243	1.243	7	1	2
2.9	1.226	1.227	0	2	$\bar{9}$

TABLE 3B. POWDER X-RAY DIFFRACTION DATA FOR STRONTIORUIZITE

I%	$d_{meas.}$	$d_{calc.}$	h	k	l
35	5.135	5.182	1	1	0
42	4.762	4.789	$\bar{1}$	1	1
41	4.549	4.577	2	0	0
46	4.219	4.235	2	0	1
23	4.019	4.013	0	0	3
8	3.896	3.894	1	1	2
14	3.691	3.698	$\bar{2}$	0	2
15	3.199	3.199	$\bar{1}$	1	3
100	3.143	3.146	1	1	3
21	3.046	3.064	$\bar{2}$	0	3
39	2.972	2.973	2	0	3
61	2.785	2.786	0	2	2
33	2.751	2.745	3	1	0
37	2.693	2.692	$\bar{3}$	1	1
28	2.661	2.66	3	1	1
41	2.62	2.622	$\bar{1}$	1	4
28	2.59	2.591	2	2	0
35	2.549	2.55	$\bar{2}$	0	4
22	2.52	2.524	2	2	1
			$\bar{3}$	1	2
6	2.469	2.472	3	1	2
8	2.397	2.395	$\bar{2}$	2	2
35	2.366	2.365	2	2	2
17	2.232	2.236	4	0	1
18	2.197	2.198	$\bar{1}$	1	5
33	2.162	2.16	2	2	3
13	2.056	2.056	$\bar{3}$	1	4
30	2.012	2.014	$\bar{4}$	0	3
11	1.909	1.911	0	2	5
5	1.88	1.882	$\bar{1}$	1	6
4	1.848	1.849	$\bar{4}$	0	4
6	1.835	1.835	$\bar{4}$	2	1
11	1.793	1.795	4	0	4
18	1.779	1.781	$\bar{4}$	2	2
12	1.755	1.756	4	2	2
18	1.72	1.72	0	0	7
13	1.692	1.691	0	2	6
21	1.665	1.665	4	2	3
11	1.627	1.626	$\bar{2}$	0	7
7	1.6	1.6	$\bar{2}$	2	6
13	1.569	1.571	0	4	0
12	1.506	1.505	0	0	8
16	1.485	1.485	$\bar{4}$	2	5
14	1.475	1.473	2	4	1
9	1.44	1.44	3	1	7
7	1.416	1.417	2	0	8
8	1.394	1.395	$\bar{4}$	0	7
12	1.367	1.368	$\bar{6}$	2	1
9	1.345	1.346	$\bar{6}$	2	2
14	1.338	1.338	$\bar{2}$	4	4

mately parallel to the matrix surface, suggesting that they crystallized in a narrow fracture/joint in the host matrix. Associated minerals include sugilite, potassic-magnesio-arfvedsonite, and lipuite. The largest strontioruizite crystal on the sample is $1.3 \times 0.2 \times 0.2$ mm. Taniajacoite and strontioruizite are found on

TABLE 4A. ATOMIC COORDINATES AND DISPLACEMENT PARAMETERS FOR STRONTIORUIZITE

Atom	*x*	*y*	*z*	U_{iso}	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
M	0.70695(2)	0.01489(7)	0.26375(2)	0.01236(6)	0.0161(1)	0.0128(1)	0.0083(2)	–0.0011(2)	0.0027(1)	–0.0046(2)
Mn	0.25005(7)	0.26637(12)	0.00001(6)	0.00709(6)	0.0079(1)	0.0069(1)	0.0066(1)	0.0005(1)	0.0015(1)	0.0003(1)
Si1	0.03705(5)	0.01596(24)	0.14977(4)	0.00670(9)	0.0068(2)	0.0078(2)	0.0056(2)	–0.0014(5)	0.0003(2)	0.0008(5)
Si2	0.10478(6)	0.00539(24)	0.39818(5)	0.0103(1)	0.0132(2)	0.0125(4)	0.0052(2)	0.0000(4)	–0.0003(2)	–0.0018(5)
O1	0.8749(1)	0.0163(5)	0.0925(1)	0.0097(3)	0.0080(6)	0.0111(7)	0.0097(6)	0.0011(14)	–0.0018(4)	–0.0021(13)
O2	0.0003(2)	0.0194(6)	0.2848(1)	0.0118(3)	0.0108(6)	0.0173(8)	0.0074(6)	0.0008(14)	–0.0002(5)	–0.0002(13)
O3	0.1325(3)	0.2294(4)	0.1265(2)	0.0099(5)	0.0102(11)	0.0089(14)	0.0106(12)	–0.0012(10)	0.0031(10)	–0.0009(10)
O4	0.8684(3)	0.8039(4)	0.8746(2)	0.0091(5)	0.0103(11)	0.0107(14)	0.0065(11)	–0.0006(10)	0.0008(10)	–0.0023(10)
O5	0	–0.0468(5)	0.5	0.0236(7)	0.0338(16)	0.0268(19)	0.0109(12)	0	0.0099(11)	0
O6	0.2253(2)	–0.1751(4)	0.3884(2)	0.0152(4)	0.0170(9)	0.0165(11)	0.0120(9)	0.0006(8)	–0.0026(7)	0.0042(8)
O7	0.1732(3)	0.2423(4)	0.4143(2)	0.0231(5)	0.0371(14)	0.0170(12)	0.0145(11)	–0.0006(9)	–0.0108(9)	–0.0074(10)
O8	0.3653(2)	0.0160(6)	0.0454(1)	0.0091(3)	0.0077(6)	0.0092(7)	0.0103(6)	0.0010(14)	0.0004(5)	0.0032(14)
O9	0.4328(3)	0.0404(6)	0.2775(2)	0.0278(6)	0.0215(9)	0.0362(18)	0.0259(10)	–0.0009(14)	0.0061(8)	–0.0088(13)
H1	0.202(5)	0.253(8)	0.463(4)	0.04						
H2	0.413(4)	–0.017(10)	0.045(3)	0.04						
H3	0.384(4)	–0.053(7)	0.319(3)	0.04						
H4	0.408(5)	0.068(8)	0.232(3)	0.04						

Note: The site occupancies for the M site are (0.795Sr + 0.205Ca).

TABLE 4B. ATOMIC COORDINATES AND DISPLACEMENT PARAMETERS FOR TANIAJACOITE

Atom	*x*	*y*	*z*	U_{iso}	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
MA	0.2959(1)	0.0143(6)	0.7333(1)	0.019(1)	0.017(1)	0.031(1)	0.010(1)	0.000(2)	0.003(1)	0.001(2)
MB	0.7094(2)	0.0181(16)	0.2602(2)	0.012(1)	0.014(2)	0.015(2)	0.008(1)	–0.001(3)	0.003(1)	–0.003(4)
MnA	0.2510(7)	0.2685(10)	0.0031(5)	0.012(1)	0.014(3)	0.015(4)	0.007(3)	0.002(2)	–0.001(2)	0.000(3)
MnB	0.7489(6)	0.2674(11)	0.0017(5)	0.013(1)	0.008(2)	0.024(4)	0.006(3)	0.002(2)	0.003(2)	0.000(3)
Si1A	0.0386(7)	0.0146(25)	0.1543(4)	0.012(1)	0.010(3)	0.018(4)	0.008(2)	0.001(6)	–0.000(2)	0.001(6)
Si1B	0.9645(6)	0.0173(27)	0.8532(4)	0.013(2)	0.009(3)	0.027(5)	0.004(2)	0.004(6)	0.001(2)	0.009(6)
Si2A	0.1211(7)	0.0099(27)	0.3962(4)	0.018(2)	0.014(3)	0.033(5)	0.007(2)	–0.010(6)	0.001(2)	–0.005(7)
Si2B	–0.0886(7)	0.0116(26)	–0.4000(5)	0.014(2)	0.014(3)	0.024(4)	0.004(2)	0.005(6)	0.001(2)	–0.004(6)
O1A	0.8756(14)	0.0036(46)	0.0992(10)	0.012(3)						
O1B	–0.8749(14)	0.0115(54)	–0.0870(9)	0.013(3)						
O2A	0.0020(14)	0.0058(46)	0.2889(10)	0.014(3)						
O2B	0.0026(15)	0.0368(37)	–0.2834(10)	0.010(3)						
O3A	0.1340(29)	0.2299(42)	0.1319(22)	0.016(7)						
O3B	–0.1277(25)	0.2296(42)	–0.1209(19)	0.012(6)						
O4A	0.8663(27)	0.7952(45)	0.8745(20)	0.015(6)						
O4B	–0.8677(27)	0.8044(44)	–0.8714(20)	0.010(6)						
O5	0.0326(13)	–0.0439(21)	–0.4928(11)	0.020(4)						
O6A	0.2327(17)	–0.1810(28)	0.3811(12)	0.008(3)						
O6B	–0.2164(21)	–0.1641(34)	–0.4003(14)	0.022(4)						
O7A	0.1980(20)	0.2482(33)	0.4027(15)	0.021(4)						
O7B	–0.1559(17)	0.2420(27)	–0.4215(12)	0.016(4)						
O8A	0.3651(16)	0.0047(49)	0.0472(12)	0.017(3)						
O8B	–0.3678(14)	0.0126(51)	–0.0443(10)	0.009(3)						
O9A	0.4455(18)	0.0178(62)	0.2810(12)	0.028(4)						
O9B	–0.4227(19)	0.0554(32)	–0.2772(12)	0.023(4)						

Note: (1) The site occupancies for the MA and MB sites are Sr and (0.81Ca + 0.19Sr), respectively. (2) The A and B sets of atoms are related by a two-fold rotation in ruizite (Hawthorne 1984, Fendrich *et al.* 2016) and strontioruizite (this study).

TABLE 5. COMPARISON OF SELECTED BOND DISTANCES IN STRONTIORUIZITE, RUIZITE, AND TANIAJACOITE

Strontioruizite (this study)		Ruizite (Fendrich *et al.* 2016)		Taniajacoite (this study)			
	Distance (Å)		Distance (Å)		Distance (Å)		Distance (Å)
M–O6	2.462(2)	Ca–O6	2.348(4)	MA–O4A	2.51(3)	MB–O6A	2.383(18)
–O9	2.526(2)	–O9	2.386(4)	–O6B	2.57(2)	–O4B	2.48(3)
–O3	2.520(3)	–O3	2.422(5)	–O7B	2.567(16)	–O1A	2.493(12)
–O4	2.546(3)	–O4	2.433(4)	–O9B	2.592(18)	–O7A	2.41(2)
–O7	2.520(3)	–O7	2.449(4)	–O3B	2.58(2)	–O9A	2.432(16)
–O1	2.610(1)	–O1	2.557(2)	–O2B	2.686(14)	–O3A	2.46(2)
–O2	2.691(1)	–O2	2.606(3)	–O1B	2.699(12)	–O2A	2.687(14)
<M–O>	2.554	<Ca–O>	2.457	<MA–O>	2.601	<MB–O>	2.478
Mn–O3	1.906(3)	Mn–O3	1.906(4)	MnA–O4A	1.90(2)	MnB–O3B	1.89(2)
–O4	1.900(2)	–O4	1.909(4)	–O3A	1.92(3)	–O4B	1.90(3)
–O8	1.960(3)	–O8	1.949(5)	–O8B	1.95(3)	–O8A	1.90(3)
–O8′	1.963(3)	–O8′	1.951(5)	–O8A	2.01(3)	–O8B	1.978(22)
–O1	2.222(3)	–O1	2.184(4)	–O1A	2.17(2)	–O1B	2.17(3)
–O1′	2.223(3)	–O1	2.187(4)	–O1B	2.23(3)	–O1A	2.32(2)
<M–O>	2.029	<Mn–O>	2.014	<MnA–O>	2.030	<MnB–O>	2.028
Si1–O1	1.618(1)	Si1–O1	1.608(3)	Si1A–O4B	1.60(3)	Si1B–O3B	1.62(3)
–O4	1.621(3)	–O4	1.611(4)	–O1A	1.615(14)	–O1B	1.615(14)
–O3	1.630(3)	–O3	1.635(5)	–O3A	1.63(3)	–O2B	1.691(13)
–O2	1.671(1)	–O2	1.664(2)	–O2A	1.660(13)	–O4A	1.68(3)
<Si1–O>	1.635	<Si1–O>	1.629	<Si1A–O>	1.628	<Si1B–O>	1.648
Si2–O6	1.590(2)	Si2–O6	1.593(4)	Si2A–O6A	1.58(2)	Si2B–O7B	1.59(2)
–O5	1.614(1)	–O5	1.603(1)	–O5	1.614(15)	–O6B	1.61(2)
–O2	1.625(3)	–O2	1.640(3)	–O7A	1.65(2)	–O2B	1.615(13)
–O7	1.645(1)	–O7	1.642(4)	–O2A	1.663(13)	–O5	1.630(15)
<Si2–O>	1.618	<Si2–O>	1.620	<Si2A–O>	1.628	<Si2B–O>	1.609

chemically weathered manganese matrix. The observed mineral assemblages for the two new minerals probably resulted from hydrothermal activity. Conditions during metamorphism were in the range 270–420 °C at 0.2–1.0 kbar (Kleyenstuber 1984, Gutzmer & Beukes 1996). Details of the geology and mineralogy of the Kalahari manganese field have been reported by Kleyenstuber (1984), Von Bezing *et al*. (1991), and Gutzmer & Beukes (1996).

Both taniajacoite and strontioruizite are brown in transmitted light, transparent with very light brown streak and vitreous luster. They are brittle and have a Mohs hardness of 5–5.5; cleavage is good on {010} and no parting or twinning is observed macroscopically. Their optical data are given in Table 1, along with those for ruizite (Williams & Duggan 1977) for comparison. The calculated compatibility index based on the empirical formula is 0.008 (superior) for taniajacoite and 0.015 (superior) for strontioruizite (Mandarino 1981). The two new minerals are insoluble in water or hydrochloric acid.

The chemical compositions of strontioruizite and taniajacoite were determined using a CAMECA SX-100 electron microprobe (WDS mode, 15 kV, 10 nA, and a beam diameter of 1 μm). The standards used are listed in Table 2, along with the determined compositions. The resultant chemical formulae, calculated on the basis of 17 O atoms *pfu* (from the structure determination), is $Sr(Ca_{0.81}Sr_{0.19})_{\Sigma 1.00}(Mn^{3+}_{1.90}Fe^{3+}_{0.15}Al_{0.01})_{\Sigma 2.06}Si_{3.96}O_{11}(OH)_4{\cdot}2H_2O$ for taniajacoite and $(Sr_{1.61}Ca_{0.42})_{\Sigma 2.03}(Mn^{3+}_{1.95}Fe^{3+}_{0.05})_{\Sigma 2.00}Si_{3.98}O_{11}(OH)_4{\cdot}2H_2O$ for strontioruizite, which can be simplified as $SrCaMn^{3+}{}_2Si_4O_{11}(OH)_4{\cdot}2H_2O$ and $Sr_2Mn^{3+}{}_2Si_4O_{11}(OH)_4{\cdot}2H_2O$, respectively.

The Raman spectra of taniajacoite and strontioruizite were collected from randomly oriented crystals with a Thermo Almega microRaman system, using a solid-state laser with a frequency of 532 nm at the full power of 150 mW and a thermoelectric-cooled CCD

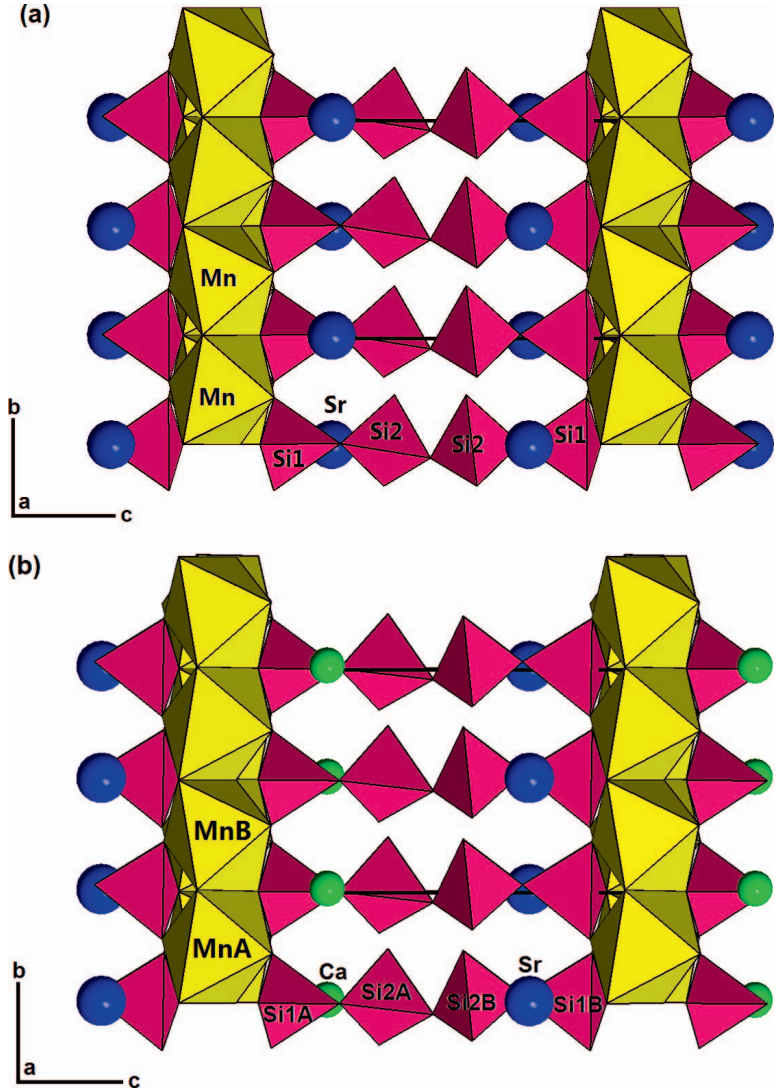

FIG. 3. Crystal structures of (a) strontioruizite and (b) taniajacoite, showing the four-membered corner-sharing SiO_4 tetrahedral clusters and the edge-sharing MnO_6 octahedral chains running parallel to [010].

detector. The laser is partially polarized with 4 cm^{-1} resolution and a spot size of 1 μm.

X-ray crystallography

The powder X-ray diffraction data for strontioruizite and taniajacoite (Table 3) were collected using a Rigaku D/Max Rapid IIR diffractometer employing Cu$K\alpha$ radiation at 45kV and 250 mA. The unit-cell parameters obtained from the powder X-ray diffraction data using the program of Downs *et al*. (1993) are: a = 9.1276 (8) Å, b = 6.2502 (4) Å, c = 11.9485 (11) Å, α = 89.853 (9)°, β = 91.807 (6)°, γ = 89.176 (10)°, V = 681.25 (7) $Å^3$ for triclinic taniajacoite and a = 9.149(3), b = 6.287(2), c = 12.044(2) Å, β = 91.73(3) °, V = 692.4(3) $Å^3$ for monoclinic strontioruizite.

Single-crystal X-ray diffraction data for taniajacoite and strontioruizite were collected with a Bruker X8 APEX2 CCD X-ray diffractometer equipped with graphite-monochromatized Mo$K\alpha$ radiation (50kV and 30 mA) with frame widths of 0.5° in ω and 30 s counting time per frame. All reflections were indexed on the basis of a triclinic unit cell for taniajacoite and a

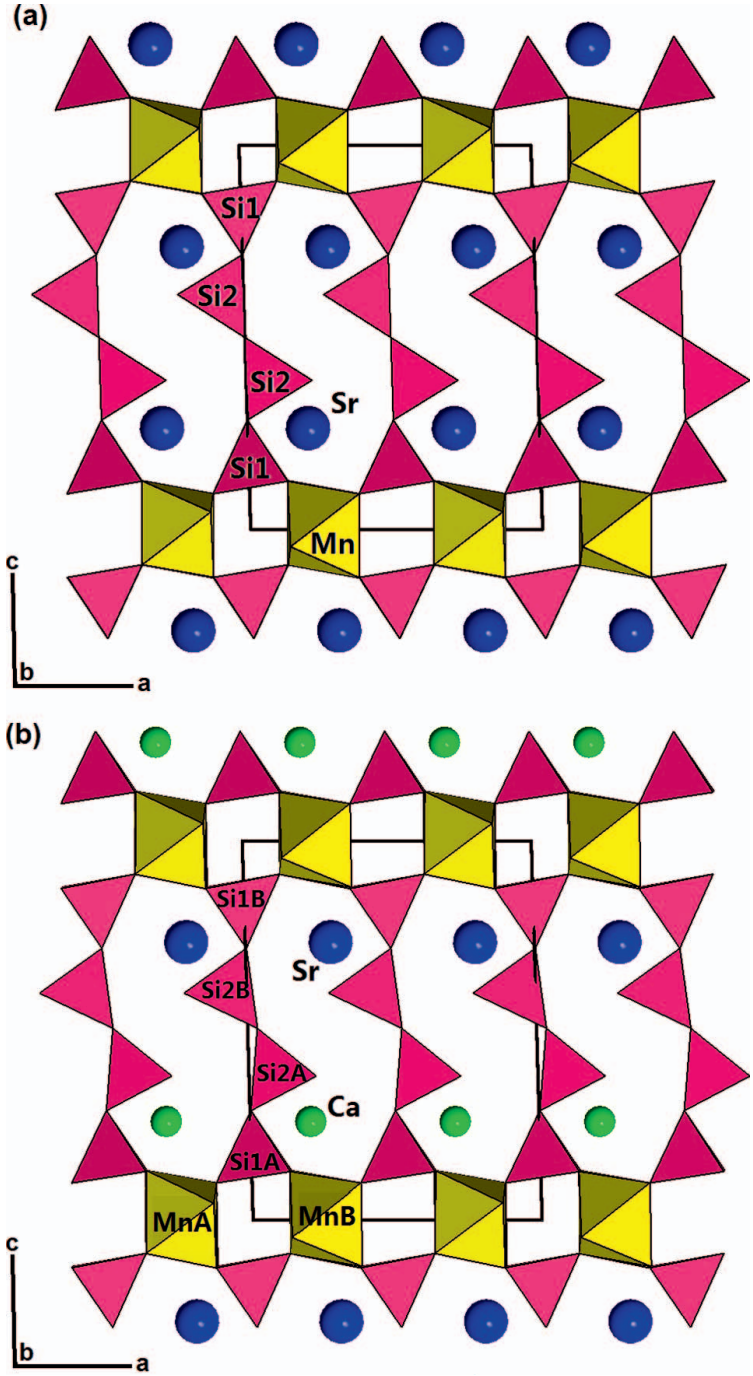

FIG. 4. Crystal structures of (a) strontioruizite and (b) taniajacoite, showing the linkage between the edge-sharing MnO_6 octahedral chains and four-membered corner-sharing SiO_4 tetrahedral clusters, with Sr/Ca atoms occupying the interstices.

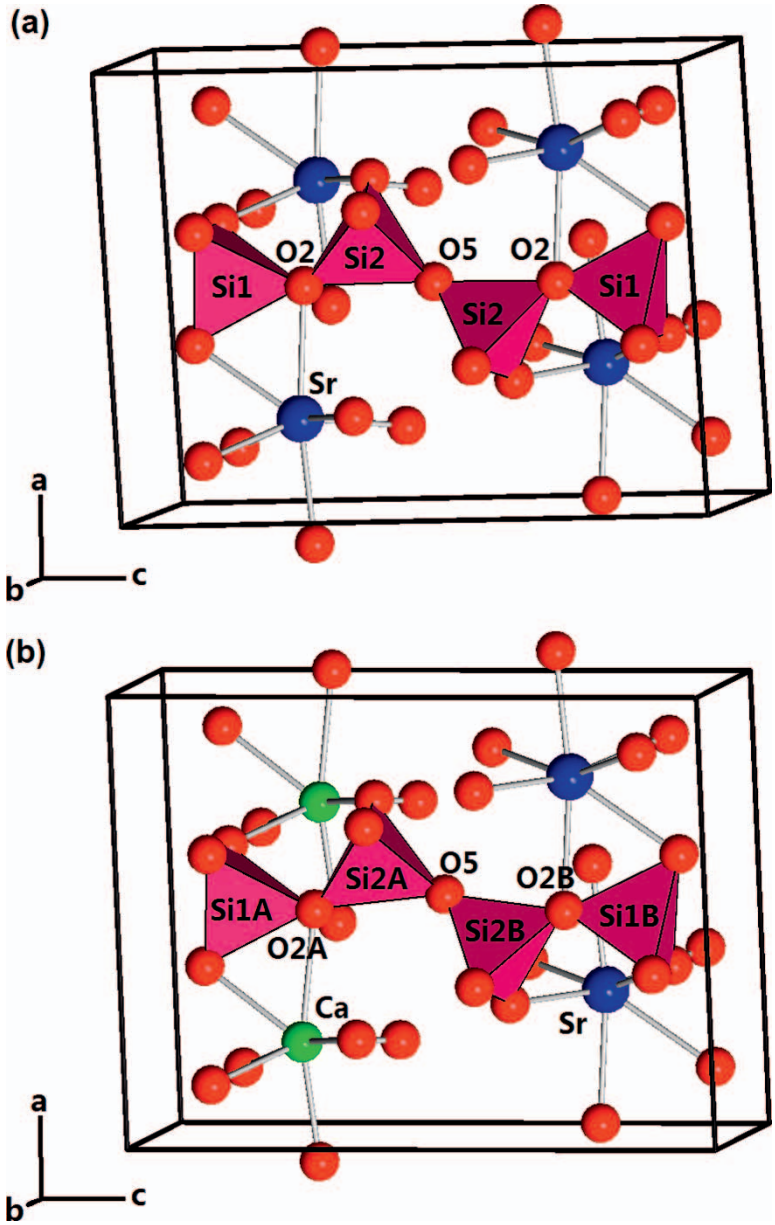

FIG. 5. Illustrations of coordinations for large cations Sr^{2+}/Ca^{2+} and linkage for the four-membered SiO_4 tetrahedral clusters in (a) strontioruizite and (b) taniajacoite.

monoclinic one for strontioruizite (Table 1). The intensity data were corrected for X-ray absorption using the Bruker program SADABS. The systematic absences of reflections suggested possible space group *C*1 or *C*$\bar{1}$ for taniajacoite and *C*2, *Cm*, or *C*2/*m* for strontioruizite. The choice of the non-standard *C*-lattice setting for triclinic taniajacoite is to facilitate direct structural comparisons with ruizite and strontioruizite (Table 1).

The crystal structures of taniajacoite and strontioruizite were solved and refined using SHELX2018 (Sheldrick 2015a, 2015b) based on space groups *C*1 and *C*2, respectively, because they produced the better refinement statistics in terms of bond lengths and

TABLE 6A. BOND-VALENCE SUMS FOR STRONTIORUIZITE

Atom	M	Mn	Si1	Si2A	Sum
O1	0.246	0.287	1.017		1.836
		0.286			
O2	0.197		0.880	0.945	2.022
O3	0.315	0.674	0.984		1.973
O4	0.292	0.685	1.008		1.985
O5				1.029 × 2 →	2.058
O6	0.367			1.097	1.464
O7	0.314			0.997	1.311
O8		0.583			1.16
		0.577			
O9	0.309				0.309
Sum	2.04	3.091	3.889	4.068	

Note: The bond valence sum for M was calculated based on (0.795 Sr + 0.205 Ca).

angles, atomic displacement parameters, and *R* factors for the respective structures. For simplicity, the chemical formulae $Sr(Ca_{0.81}Sr_{0.19})_{\Sigma 1.00}Mn_2Si_4O_{11}(OH)_4{\cdot}2H_2O$ for taniajacoite and $(Sr_{1.59}Ca_{0.41})_{\Sigma 2.00}Mn_2Si_4O_{11}(OH)_4{\cdot}2H_2O$ for strontioruizite were adopted during the refinements. In other words, the small amounts of Fe in both samples were treated as Mn in the refinements and all atomic sites were assumed to be fully occupied. Due to the pervasive twinning and the small crystal size (0.06 × 0.03 × 0.02 mm) for taniajacoite, the displacement ellipsoids of some oxygen atoms became non-positive-definite with the anisotropic refinement. Therefore, only cations were refined with anisotropic displacement parameters and all O atoms were refined isotropically. The H atoms were not located from the difference-Fourier maps. An attempt to refine the structure of taniajacoite in space group *C*2, as for ruizite and strontioruizite, not only resulted in a significant increase in the R_1 factor from 5.38% to 7.68%, but also unreasonably large displacement ellipsoids for the Si atoms and two O atoms, as well as non-positive definite ellipsoids for four (O2, O3, O4, and O7) out of nine symmetrically independent O atoms. Thus, the model with the *C*2 symmetry for taniajacoite was rejected. For strontioruizite, the

TABLE 6B. BOND-VALENCE SUMS FOR TANIAJACOITE

Atom	MA	MB	MnA	MnB	Si1A	Si1B	Si2A	Si2B	Sum
O1A		0.262	0.315	0.233	1.038				1.848
O1B	0.207		0.257	0.364		1.009			1.837
O2A		0.157			0.895		0.906		1.957
O2B	0.214					0.846		1.015	2.074
O3A		0.284	0.668		0.968				1.920
O3B	0.287			0.700		1.065			2.051
O4A	0.349		0.687			0.828			1.864
O4B		0.277		0.665	1.099				2.041
O5							1.013	1.004	2.017
O6A		0.358					1.121		1.479
O6B	0.289							1.053	1.342
O7A		0.337					0.923		1.260
O7B	0.292							1.125	1.417
O8A			0.509	0.671					1.180
O8B			0.596	0.556					1.151
O9A		0.309							0.309
O9B	0.283								0.283
Sum	1.920	1.984	3.031	3.188	4.000	3.748	3.963	4.197	

Note: The bond valence sum for Ca was calculated based on (0.81Ca + 0.19Sr).

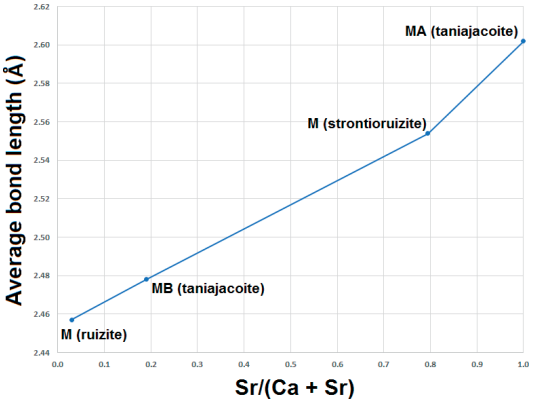

FIG. 6. Variations of the average bond distances (Å) for the seven-coordinated cations with Ca/Sr contents in ruizite, taniajacoite, and strontioruizite.

positions of all atoms were refined with anisotropic displacement parameters.

Because both strontioruizite and taniajacoite are non-centrosymmetric with β angles close to 90°, we also tested their structure refinements with pseudo-merohedral twin and inversion twin models. The results indicate that strontioruizite exhibits slight inversion twinning, with a twin ratio of 0.92 *versus* 0.08. However, taniajacoite shows both pseudo-merohedral and inversion twins. Its structure was, therefore, refined with four twin domains. The resultant twin ratios are 0.30 : 0.42 : 0.13 : 0.15, with the first two values for two domains due to pseudo-merohedral twinning and the last two due to inversion twinning of the first two domains. Final atom coordinates and displacement parameters for strontioruizite and taniajacoite are listed in Table 4 and selected bond-distances are given in Table 5.

CRYSTAL STRUCTURE DESCRIPTION AND DISCUSSION

Both taniajacoite and strontioruizite are isotypic with ruizite, which exhibits many structural similarities to the lawsonite group of minerals (Hawthorne 1984, Moore *et al.* 1985). Their structures are characterized by chains of edge-sharing MnO_6 octahedra parallel to [010], which are linked together by corner-sharing with SiO_4 tetrahedra in the four-membered $[Si_4O_{11}(OH)_2]$ linear clusters (Figs. 3 and 4), giving rise to a so-called "hetero-polyhedral framework" (Hawthorne 1984). The $[Si_4O_{11}(OH)_2]$ cluster in ruizite-type minerals is the only reported silicate cluster of this kind. The large cations Sr^{2+} and Ca^{2+} occupy the seven-coordinated interstices (Fig. 5). However, unlike the two endmembers ruizite and strontioruizite, which are monoclinic and have only one symmetrically independent site (the M site) for the large cations (Ca/Sr) (Hawthorne 1984, Fendrich *et al.* 2016), taniajacoite with Sr:Ca ≈ 1:1 is triclinic, owing to the ordering of the large Sr^{2+} (r = 1.21 Å) and relatively small Ca^{2+} (r = 1.06 Å) cations (Shannon 1976) into two crystallographically distinct sites (the MA and MB sites). These two sites are symmetrically equivalent by a two-fold rotation in ruizite and strontioruizite (Hawthorne 1984, Fendrich *et al.* 2016). In other words, there is no complete solid solution between ruizite and strontioruizite. The calculated bond-valence sums using the parameters from Brese & O'Keeffe (1991) (Table 6) indicate that the molecule at O9 is H_2O, whereas at O7 and O8 it is OH. Discounting hydrogen bonds, the O6 atoms are significantly under-bonded, which is clearly compensated for by the strong hydrogen bonds from O7 and O9 (Hawthorne 1984). The detailed hydrogen bonding scheme in strontioruizite resembles that in ruizite (Fendrich *et al.* 2016).

The major structural features of ruizite, taniajacoite, and strontioruizite, such as bond lengths and angles for the SiO_4 tetrahedra and MnO_6 octahedra, are very similar. The noticeable structural difference among them lies in the seven-coordinated large cation sites. In taniajacoite, the two distinct interstice sites, MA and MB, are occupied by Sr and (0.81Ca + 0.19Sr), respectively. The average bond distance for the MA site is 2.601 Å, longer than that (2.554 Å) for the M site in strontioruizite, which contains a little more Ca (0.795Sr + 0.205Ca). Similarly, the average bond distance (2.478 Å) for the MB site with 19% Sr in taniajacoite is longer than that (2.457 Å) for the M site in ruizite, which contains only 3% Sr. Figure 6 illustrates the variation of the average bond distance for the M site with the Sr content in ruizite, taniajacoite, and strontioruizite.

In the ruizite-type structure, the SiO_4 tetrahedra in the four-membered linear clusters are linked together by sharing one O5 and two O2 atoms, as illustrated in Figure 5. The Si2–$O5_{br}$–Si2 and Si1–$O2_{br}$–Si2 angles are 162.89° and 128.27°, respectively, for ruizite (Fendrich *et al.* 2016), and 156.56 and 132.68° for strontioruizite. The smaller Si1–$O2_{br}$–Si2 angle, as compared to the Si2–$O5_{br}$–Si2 angle, is attributed to the bonding of Ca with $O2_{br}$ from one side and with $O4_{nbr}$ (belonging to the $Si1O_4$ tetrahedron) and $O6_{nbr}$ (belonging to the $Si2O_4$ tetrahedron) from the other side (Fig. 5). Apparently, the substitution of large Sr^{2+} for small Ca^{2+} pushes Si1 and Si2 farther apart, and thus increases the Si1–$O2_{br}$–Si2 angle. Similar reasoning can be applied to taniajacoite, although the situation is a little more complicated, because of the ordering of Ca and Sr into two distinct sites (Fig. 5).

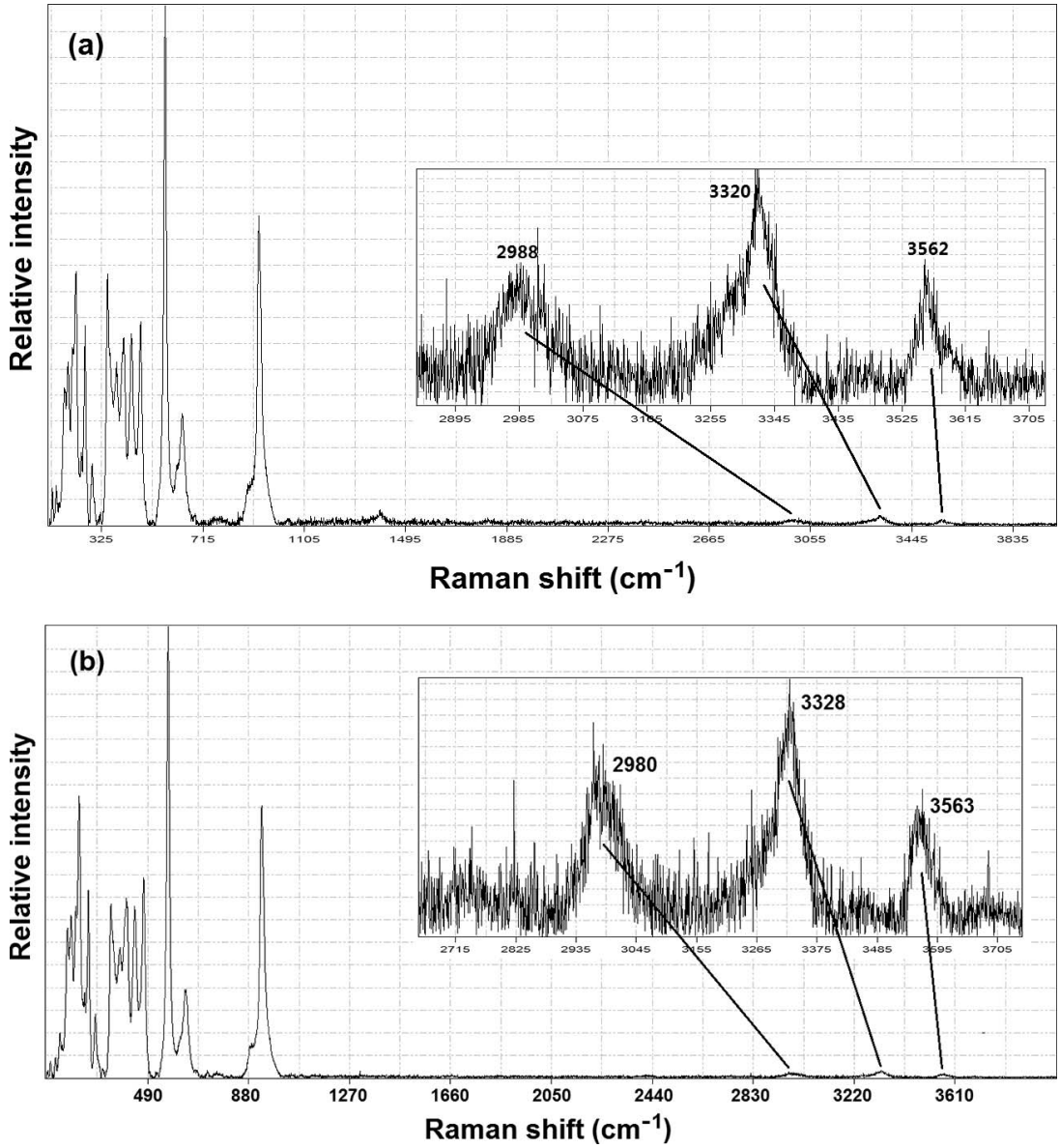

FIG. 7. Raman spectra of (a) strontioruizite and (b) taniajacoite.

Figure 7 is a plot of the Raman spectra for taniajacoite and strontioruizite, which show strong similarities to the Raman spectrum for ruizite (https://rruff.info/R130787) (Fendrich *et al*. 2016). A tentative assignment of the major Raman bands for taniajacoite and strontioruizite is made as follows based on the study of ruizite by Fendrich *et al*. (2016): Bands between 820 and 1060 cm^{-1} are attributable to the Si–O stretching vibrations within the SiO_4 groups and those from 530 to 760 cm^{-1} to the bending vibrations of O–Si–O within the SiO_4 groups and Si–O–Si between the SiO_4 tetrahedra. The bands below 500 cm^{-1} are mainly associated with the rotational and translational modes of SiO_4 tetrahedra, as well as the Mn–O and Ca/Sr–O interactions. The three weak broad bands between 2980 and 3563 cm^{-1} are due to the O–H stretching vibrations.

Although ruizite, taniajacoite, and strontioruizite exhibit similar colors and morphologies, making it difficult to distinguish them visually, their unit-cell

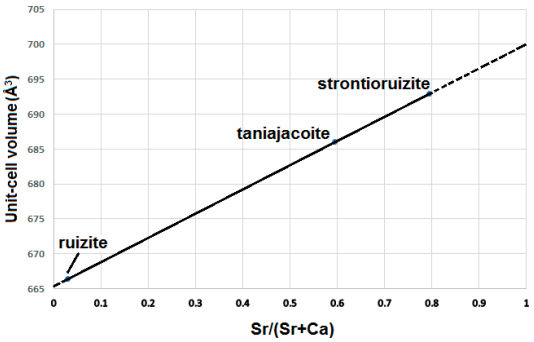

FIG. 8. The unit-cell volume (Å^3) as a function of the Sr/(Ca + Sr) ratio for the ruizite-strontioruizite system. The data for ruizite are from Fendrich *et al*. (2016).

volumes appear to vary linearly with the Sr/Ca ratio (Fig. 8), despite the limited data and a phase transformation between ruizite/strontioruizite and taniajacoite. A linear regression yielded an equation for the unit-cell volume (V) as a function of the Sr/(Ca + Sr) ratio (X): $V = 34.668X + 665.39$ (Å^3). Based on this equation, we can derive the unit-cell volumes of 665.4 and 700.1 (Å^3) for ideal ruizite and strontioruizite, respectively.

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