

Article

Chromium Members of the Pumpellyite Group: Shuiskite-(Cr), $\text{Ca}_2\text{CrCr}_2[\text{SiO}_4][\text{Si}_2\text{O}_6(\text{OH})](\text{OH})_2\text{O}$, a New Mineral, and Shuiskite-(Mg), a New Species Name for Shuiskite

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Abstract: A new pumpellyite-group mineral shuiskite-(Cr), ideally $\text{Ca}_2\text{CrCr}_2[\text{SiO}_4][\text{Si}_2\text{O}_6(\text{OH})](\text{OH})_2\text{O}$, was found at the Rudnaya mine, Glavnoe Saranovskoe deposit, Middle Urals, Russia. It occurs on the walls of 0.5 to 1 cm thick fractures in chromitite, filled with calcite, Cr-bearing clinocllore, and uvarovite. Shuiskite-(Cr) forms long prismatic to acicular crystals up to $0.1 \times 0.5 \times 7$ mm elongated along [010] and slightly flattened on [100]. The crystals are commonly combined into radial, sheaf-like aggregates. Most observed crystals are simple twins with a (001) composition plane. Shuiskite-(Cr) is greenish-black under daylight or purplish-black under incandescent light. It is optically biaxial (-), $\alpha = 1.757(5)$, $\beta = 1.788(6)$, $\gamma = 1.794(6)$, $2V$ (meas.) = $45(10)^\circ$, $2V$ (calc.) = 46° (589 nm). The D_{calc} is 3.432 g/cm^3 . The IR spectrum is reported. The chemical composition (wt.%) is CaO 21.33, MgO 3.17, Al_2O_3 5.41, Cr_2O_3 28.50, TiO_2 0.18, SiO_2 33.86, H_2O 5.82, total 98.27. The empirical formula calculated based on the sum of eight metal cations and Si atoms per formula unit is $\text{Ca}_{2.02}\text{Mg}_{0.42}\text{Cr}^{3+}_{1.99}\text{Al}_{0.56}\text{Ti}_{0.01}\text{Si}_{3.00}\text{O}_{10.57}(\text{OH})_{3.43}$. The simplified formula is $\text{Ca}_2(\text{Cr,Mg})(\text{Cr,Al})_2[\text{SiO}_4][\text{Si}_2\text{O}_6(\text{OH,O})](\text{OH,O})(\text{OH})_2$. Shuiskite-(Cr) is monoclinic, $C2/m$, $a = 19.2436(6)$, $b = 5.9999(2)$, $c = 8.8316(3)$ Å, $\beta = 97.833(3)^\circ$, $V = 1010.17(6)$ Å³, and $Z = 4$. The crystal structure, solved from single-crystal X-ray diffraction data ($R = 0.0469$), is based on a pair of chains of edge-sharing Cr-centred octahedra running along the b axis, linked together via the $[\text{SiO}_4]$ and $[\text{Si}_2\text{O}_6(\text{OH})]$ groups and Ca-centred polyhedra. The mineral species shuiskite, ideally $\text{Ca}_2\text{MgCr}_2[\text{SiO}_4][\text{Si}_2\text{O}_6(\text{OH})](\text{OH})_3$, was renamed to shuiskite-(Mg) by the decision of the IMA CNMNC. The shuiskite solid solution series with the general formula $\text{Ca}_2\text{XCr}_2[\text{SiO}_4][\text{Si}_2\text{O}_6(\text{OH,O})](\text{OH})_2(\text{OH,O})$, which includes shuiskite-(Mg) and shuiskite-(Cr) with $X = \text{Mg}$ and Cr^{3+} , respectively, appeared in the pumpellyite group.

Keywords: shuiskite-(Cr); shuiskite-(Mg); shuiskite series; new mineral; pumpellyite group; crystal structure; Saranovskoe chromite deposit; Urals; Russia

1. Introduction

The pumpellyite-group members are low-grade metamorphic and hydrothermal minerals with the general formula $\text{Ca}_2\text{XY}_2\text{Si}_3\text{O}_{14-n}(\text{OH})_n$, where $X = \text{Mg}, \text{Al}, \text{Mn}^{2+}, \text{Mn}^{3+}, \text{Fe}^{2+}, \text{Fe}^{3+}, \text{V}^{3+}$ and Cr^{3+} , while $Y = \text{Al}, \text{Mn}^{3+}, \text{Fe}^{3+}, \text{V}^{3+}$ and Cr^{3+} . In accordance with the IMA-accepted nomenclature [1], pumpellyite-group members are named based on the combination of the predominant cations at the Y (root name) and X (suffix-modifier) sites. Minerals with different cations predominant at the Y site have the different root names: ^YAl —pumpellyite (the name first proposed by Palache and Vassar [2]), $^Y\text{Fe}^{3+}$ —julgoldite [3], $^Y\text{Mn}^{3+}$ —okhotskite [4], and $^Y\text{V}^{3+}$ —poppiite [5]. Minerals with predominant Cr^{3+} at the Y site have the root name (series name) shuiskite [6]. To date, the shuiskite series existed only formally and included one mineral species, shuiskite, with Mg as a dominant cation at the X site [6,7]; therefore, a suffix-modifier has not been used.

In 1985, a paper came out describing a variety of shuiskite with a high Cr and low H_2O content; however, the distribution of Cr between the X and Y sites was not determined [8]. One of the authors of the present study (O.I.) was the senior author of the cited work and was able to find that specimen. We studied it in detail and showed that Cr is a dominant cation at both the X and Y sites, making it a new pumpellyite-group mineral shuiskite-(Cr), ideally $\text{Ca}_2\text{CrCr}_2[\text{SiO}_4][\text{Si}_2\text{O}_6(\text{OH})](\text{OH})_2\text{O}$, as described in this paper. We proposed to name this new mineral species shuiskite-(Cr), and rename shuiskite to shuiskite-(Mg) as a mineral species with Mg prevailing at the X site and, thus, the ideal formula $\text{Ca}_2\text{MgCr}_2[\text{SiO}_4][\text{Si}_2\text{O}_6(\text{OH})](\text{OH})_3$, in accordance with the IMA-accepted nomenclature [1].

Both the new mineral shuiskite-(Cr), its name, and the new name for shuiskite were approved by the IMA Commission on New Minerals, Nomenclature and Classification (IMA2019-117). Therefore, the name shuiskite was transferred from a species name to a root name, and the shuiskite series with the general formula $\text{Ca}_2\text{XCr}_2[\text{SiO}_4][\text{Si}_2\text{O}_6(\text{OH},\text{O})](\text{OH})_2(\text{OH},\text{O})$, that includes shuiskite-(Mg) and shuiskite-(Cr) with $X = \text{Mg}$ and Cr^{3+} , respectively, appeared in the pumpellyite group.

The holotype specimen of shuiskite-(Cr) was deposited in the collection of the Fersman Mineralogical Museum of the Russian Academy of Sciences, Moscow, Russia with the registration number 5481/1. A part of the holotype was deposited in the collection of the Canadian Museum of Nature, Ottawa, Canada with the catalogue number CMNMC 87302.

2. Materials and Methods

2.1. Occurrence and General Appearance

The specimen that became a holotype of shuiskite-(Cr) was found in 1979 by V.A. Kuznetsov, a local geologist, at the Rudnaya underground chromite mine (level 280 m), located in the town of Sarany, Perm Krai, Middle Urals, Russia. This mine operates at the Glavnoe (Main) Saranovskoe deposit belonging to the Saranovskaya group of chromite deposits [8]. The Glavnoe Saranovskoe chromite deposit is also known as Saranovskoe (the Saranovskii mine, or, colloquially, Sarany, or Sarani), and should not be confused with the Biserskoe (the Yuzhno-Saranovskoe, or Southern Saranovskoe) deposit, where shuiskite-(Mg) was first found [6]. Both Biserskoe and Glavnoe Saranovskoe deposits belong to the Saranovskaya group of chromite deposits; Biserskoe is located 4 km south of Glavnoe Saranovskoe [9].

Shuiskite-(Cr) forms long prismatic to acicular crystals up to $0.1 \times 0.5 \times 7$ mm, elongated along [010] and usually slightly flattened on [100] (Figure 1a,b). The major crystal forms are pinacoids {100}, {001}, {102}, and $\{-102\}$. The crystals are commonly combined into radial, sheaf-like aggregates.

Most observed crystals are simple twins with a (001) composition plane (Figure 1b), identical to the “cruciform twins” described by Coombs [10] for pumpellyite.

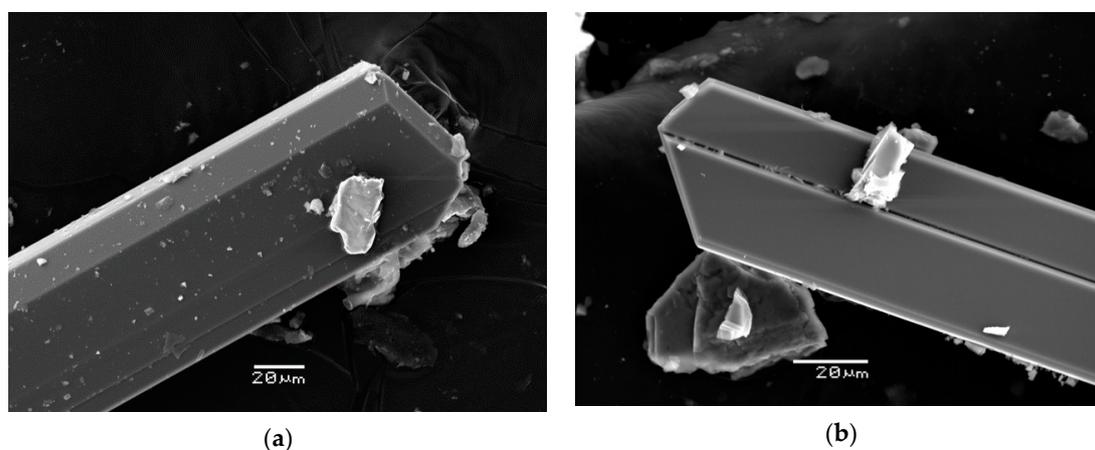


Figure 1. Crystal of shuiskite-(Cr) (a) and a twin with a (001) composition plane (b). SEM (SE) images.

Shuiskite-(Cr) occurs together with pink Cr-bearing clinocllore and bright green uvarovite on the walls of 0.5 to 1 cm thick fractures in chromitite, filled with colourless calcite.

2.2. Analytical Methods

Chemical data for shuiskite-(Cr) were obtained using a Tescan VEGA-II XMU scanning electron microscope equipped with an EDS INCA Energy 450 and a WDS INCA-Wave 700 (Institute of Experimental Mineralogy, Chernogolovka, Russia) with an acceleration voltage of 20 kV, a beam current of 10 nA, and a beam diameter of 5 μm. The following standards were used: wollastonite (Ca), Mg (MgO), Al (Al₂O₃), Cr (Cr), Ti (Ti), Si (SiO₂). H₂O content was not determined directly because of the paucity of the available material. CO₂ content was not measured because bands that could be assigned to C–O vibrations are absent in the infrared (IR) spectrum of shuiskite-(Cr).

IR absorption spectra of shuiskite-(Cr) and shuiskite-(Mg) were obtained from powdered samples mixed with dried KBr, pelletized, and analysed using an ALPHA FTIR spectrometer (Bruker Optics) at a resolution of 4 cm^{−1}. Sixteen scans were collected. The IR spectrum of an analogous pellet of pure KBr was used as a reference.

Powder X-ray diffraction data were collected with a Rigaku R-AXIS Rapid II single-crystal diffractometer (St. Petersburg State University, St. Petersburg, Russia) equipped with a cylindrical image plate detector using Debye–Scherrer geometry ($d = 127.4$ mm, CoK α radiation). The data were integrated using the software package Osc2Tab [11].

Single-crystal X-ray studies were carried out using an Oxford Xcalibur S diffractometer (Moscow State University, Moscow, Russia) equipped with a CCD detector (MoK α radiation). The structure was solved by direct methods and refined on the basis of 2793 independent reflections with $I > 2\sigma(I)$ to $R1 = 0.0469$ using the SHELXL-2018/3 program package [12]. The structure was refined using the dataset containing the specific twin information, i.e., the overlapping as well as the non-overlapping reflections (so-called HKLF 5 format), as a two-component twin with a domain ratio of 87:13.

3. Results

3.1. Physical Properties and Optical Data

Shuiskite-(Cr) is transparent in thin crystals and translucent in thicker ones. It changes colour depending on the light source like alexandrite, the chromian variety of chrysoberyl, and some other Cr-bearing minerals: in aggregates, shuiskite-(Cr) is greenish-black under daylight or purplish-black under incandescent light; in separate crystals, it is green to light-green and purple or greyish-purple,

respectively. The streak is grey-green. The lustre is vitreous. The mineral is non-fluorescent under ultraviolet rays. The Mohs hardness is 6. Cleavage is {001} distinct. The fracture is uneven. The density, calculated using the empirical formula and unit-cell volume refined from the single-crystal XRD data, is 3.432 g/cm³.

Shuiskite-(Cr) is optically biaxial (−), $\alpha = 1.757(5)$, $\beta = 1.788(6)$, $\gamma = 1.794(6)$, $2V$ (meas.) = 45(10)°, $2V$ (calc.) = 46° (589 nm). It shows strong crossed dispersion. For thicker prismatic crystals, pleochroism is strong and the absorption scheme is as follows: X (greyish) < Y (light greyish-green) < Z (brown). For thinner crystals, pleochroism is weaker: X (light greyish to nearly colourless) < Y (light greyish) < Z (light greyish-brown). Optical orientation is as follows: $Z \wedge b$ is $\approx 12^\circ$.

3.2. Chemical Data

Chemical data for shuiskite-(Cr) are given in Table 1. The empirical formula, calculated on the basis of the sum of eight metal cations and Si atoms per formula unit (*pfu*) and (O+OH) = 14 *pfu* (the O/OH ratio is calculated by charge balance), is Ca_{2.02}Mg_{0.42}Cr³⁺_{1.99}Al_{0.56}Ti_{0.01}Si_{3.00}O_{10.57}(OH)_{3.43} or, taking into account the crystal structure data (see below): Ca_{2.02}(Cr_{0.56}Mg_{0.42}) Σ _{0.98}(Cr_{1.43}Al_{0.56}Ti_{0.01}) Σ _{2.00}Si_{3.00}O_{10.57}(OH)_{3.43}. The simplified formula is Ca₂(Cr,Mg)(Cr,Al)₂[SiO₄][Si₂O₆(OH,O)](OH,O)(OH)₂.

Table 1. Chemical data (in wt %, average of 5 analyses) for shuiskite-(Cr).

Constituent	Mean	Range	Standard Deviation
CaO	21.33	20.98–21.62	0.26
MgO	3.17	2.32–3.78	0.54
Al ₂ O ₃	5.41	4.78–5.93	0.46
Cr ₂ O ₃	28.50	27.61–29.89	0.99
TiO ₂	0.18	0.00–0.68	0.29
SiO ₂	33.86	33.44–34.24	0.33
H ₂ O	5.82 ¹		
Total	98.27		

¹ Calculated from the stoichiometry.

The ideal end-member formula is Ca₂CrCr₂[SiO₄][Si₂O₆(OH)](OH)₂O, which requires CaO 20.49, Cr₂O₃ 41.64, SiO₂ 32.93, H₂O 4.94, total 100 wt.%.

Shuiskite-(Cr) does not react with a diluted aqueous HCl solution at room temperature.

3.3. Infrared Spectroscopy

The IR spectra of shuiskite-(Cr) and shuiskite-(Mg) are similar (Figure 2); both show rather strong IR bands of O–H-stretching (in the range from 2900 to 3520 cm^{−1}), Si–O-stretching (900–1040 cm^{−1}), as well as O–Si–O bending (560–640 cm^{−1}) vibrations. The bands in the ranges 520–526 and 360–490 cm^{−1} correspond to Al–O-stretching vibrations and to mixed modes involving Si–O–Si bending and (Cr,Mg)–O stretching vibrations, respectively. The band assignment was made in accordance with Chukanov and Chervonnyi [13].

The bands at 827–836 cm^{−1}, and possibly the weak band at 681 cm^{−1}, may be tentatively assigned to M···O–H modes (where M is a metal cation at the X or Y site), but these bands may also correspond to mixed vibrations involving M···O–H angles and silicate groups. The weak bands in the ranges 1110–1160 and 1930–1950 cm^{−1} correspond to overtones or combination modes. The wavenumbers of the weak bands at 2207 and 2180 cm^{−1} are too high for a first overtone or a combination mode. The presence of these bands in the IR spectra can be explained by the presence of silanol groups Si–OH, confirming structural data that show a significant protonation of O (10).

Characteristic bands of H–O–H bending vibrations of H₂O molecules (in the range 1550–1750 cm^{−1}) and CO₃^{2−} anions (1350–1550 cm^{−1}) are absent in the IR spectra of shuiskite-(Cr) and shuiskite-(Mg).

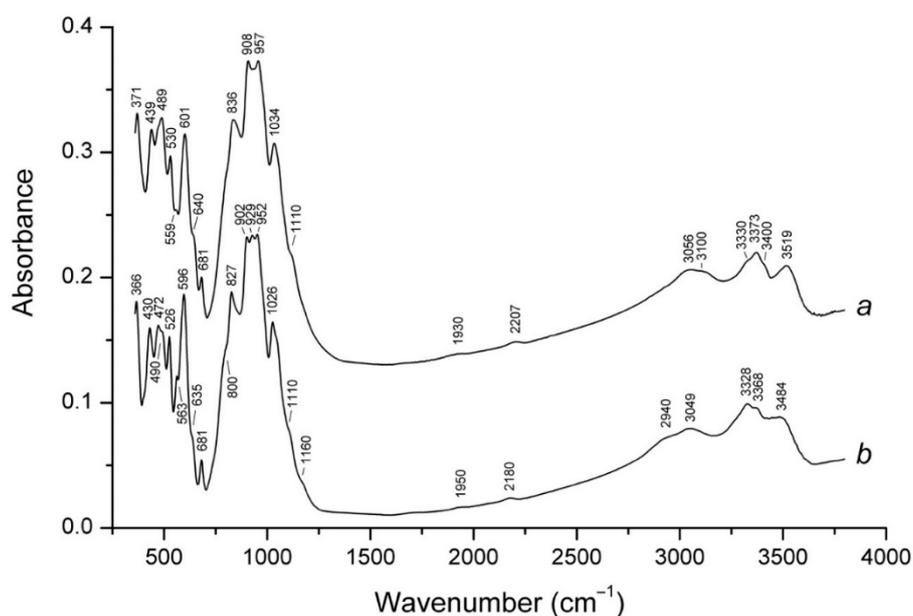


Figure 2. Powder infrared absorption spectra of (a) shuiskite-(Mg) from the Biserskoe chromite deposit, Middle Urals, Russia and (b) shuiskite-(Cr).

The main differences between the IR spectra of shuiskite-(Cr) and shuiskite-(Mg) are as follows:

1. The bands in the range of O–H-stretching vibrations (in the range from 2900 to 3520 cm^{-1}) in the IR spectrum of shuiskite-(Cr) are shifted towards lower frequencies as compared to shuiskite-(Mg), which corresponds to stronger hydrogen bonds formed by the OH groups in the former mineral;
2. The strong absorption maximum at 929 cm^{-1} observed in the IR spectrum of shuiskite-(Cr) is absent in the spectrum of shuiskite-(Mg). Consequently, this band can be hypothetically assigned to Si–O-stretching vibrations of $^X\text{Cr}\cdots\text{O}(9)\text{--Si}(3)$ or $^X\text{Cr}\cdots\text{O}(2)\text{--Si}(2)$;
3. The low-frequency shifts in the bands of shuiskite-(Cr) relative to those of shuiskite-(Mg) in the range 360–490 cm^{-1} (mixed modes involving (Cr,Mg)–O stretching vibrations) are due to the fact that Cr^{3+} cation is heavier than Mg^{2+} .

3.4. Powder X-Ray Diffraction Data

The indexed powder X-ray diffraction data are given in Table 2. Parameters of the monoclinic unit cell refined from the powder data are as follows: $a = 19.2399(2)$, $b = 6.0006(1)$, $c = 8.8393(1)$ Å, $\beta = 97.880(1)^\circ$, and $V = 1010.87(2)$ Å³.

Table 2. Powder X-ray diffraction data (d in Å) for shuiskite-(Cr). The strongest reflections are given in bold.

I_{meas}	d_{meas}	I_{calc}^1	d_{calc}^2	hkl
16	9.53	18	9.53	200
8	8.74	7	8.75	001
4	6.93	4	6.93	20–1
7	6.05	9	6.05	201
9	4.883	9	4.882	11–1
34	4.759	39	4.766	400
36	4.707	45	4.702	111
6	4.442	7	4.448	40–1
18	4.375	23	4.375	002
5	4.059	6	4.059	31–1
3	3.960	4	3.965	401

Table 2. Cont.

I_{meas}	d_{meas}	I_{calc}^1	d_{calc}^2	hkl
75	3.783	69	3.785	202
3	3.545	2	3.546	11–2
14	3.468	16	3.467	40–2
4	3.409	4	3.409	112
1	3.239	1	3.245	31–2
4	3.138	4	3.140	51–1
18	3.023	18	3.024	402
12	3.000	10	3.000	020
100	2.913	18, 100, 19	2.916, 2.914, 2.902	003, 511, 20–3
14	2.861	2, 18	2.864, 2.862	601, 220
12	2.839	15	2.838	021
52	2.755	61, 8, 5	2.756, 2.753, 2.747	60–2, 22–1, 51–2
10	2.688	10	2.688	221
31	2.643	41	2.643	11–3
48	2.539	70	2.539	420
39	2.470	6, 21, 30	2.487, 2.474, 2.468	42–1, 022, 71–1
8	2.442	13	2.441	22–2
4	2.384	4, 2	2.383, 2.383	80–1, 800
31	2.352	41	2.351	222
12	2.327	15	2.326	313
6	2.298	8	2.296	51–3
3	2.270	2	2.269	42–2
27	2.225	31	2.224	80–2
8	2.198	6	2.198	20–4
14	2.186	10, 8	2.187, 2.181	004, 620
4	2.164	4	2.165	62–1
23	2.13	31	2.130	422
12	2.099	13	2.099	40–4
8	2.073	4, 3, 2	2.072, 2.072, 2.071	11–4, 621, 204
2	2.049	2	2.047	513
4	2.030	1, 3	2.033, 2.029	31–4, 62–2
4	2.019	5	2.017	71–3
8	1.9309	4, 8	1.9336, 1.9286	131, 60–4
14	1.8842	5, 14	1.8859, 1.883	314, 622
20	1.8667	4, 25	1.866, 1.8659	82–1, 820
4	1.8499	4	1.8496	423
2	1.8320	3	1.8309	62–3
3	1.7693	3	1.7674	024
5	1.7528	6	1.7518	71–4
19	1.7194	16, 6	1.7200, 1.7194	42–4, 514
6	1.6990	6	1.6969	604
10	1.6783	4, 8	1.6793, 1.6765	31–5, 111–1
9	1.6551	13	1.6542	13–3
35	1.6017	5, 3, 56	1.6090, 1.6086, 1.6007	1020, 73–1, 424
16	1.5897	19	1.5887	1200
20	1.5705	27	1.5697	102–2
5	1.5524	5	1.551	1021
3	1.5232	3	1.5208	22–5
10	1.5124	11	1.5120	804
42	1.5013	29, 38	1.5009, 1.5000	82–4, 040

¹ For the calculated pattern, only reflections with intensities ≥ 1 are given; ² For the unit-cell parameters calculated from single-crystal data.

3.5. Single-Crystal X-Ray Diffraction Data and Description of The Crystal Structure

The single-crystal X-ray diffraction data were indexed in the $C2/m$ space group with the following unit-cell parameters: $a = 19.2436(6)$, $b = 5.9999(2)$, $c = 8.8316(3)$ Å, $\beta = 97.833(3)^\circ$, and $V = 1010.17(6)$ Å³. The details on the data collection and structure refinement are given in Table 3. The Coordinates and equivalent displacement parameters of the atoms are given in Table 4, selected interatomic distances in Table 5, and bond valence calculations in Table 6. The crystallographic information file (CIF) for shuiskite-(Cr) is available as Supplementary Material (see below).

Table 3. Crystal data, data collection information and structure refinement details for shuiskite-(Cr).

Formula Derived from the Structure Refinement	$\text{Ca}_2(\text{Cr}_{0.52}\text{Mg}_{0.48})(\text{Cr}_{1.40}\text{Al}_{0.60})[\text{SiO}_4][\text{Si}_2\text{O}_6(\text{OH})](\text{OH})_{2.48}\text{O}_{0.52}$
Crystal system, space group, Z	Monoclinic, C2/m, 4
<i>a</i> (Å)	19.2436(6)
<i>b</i> (Å)	5.9999(2)
<i>c</i> (Å)	8.8316(3)
β (°)	97.833(3)
<i>V</i> (Å ³)	1010.17(6)
λ (MoK α) (Å), <i>T</i> (K)	0.71073, 293
Diffractometer	Xcalibur S CCD
θ range (°)	2.94–34.79
Crystal size (mm ³)	0.049 × 0.053 × 0.377
Absorption coefficient μ (mm ⁻¹)	3.618
F_{000}	1028
<i>h, k, l</i> range	$-30 \leq h \leq 29, -9 \leq k \leq 9, -13 \leq l \leq 14$
Reflections collected	3579
Unique reflections [$I > 2\sigma(I)$]	2793
Number of refined parameters	127
Weighting scheme	$1/[\sigma^2(F_o^2) + (0.0434P)^2 + 5.7592], P = [(F_o)^2 + 2(F_c)^2]/3$
R1	0.0469
wR2 _{all} (F ²)	0.1088
GoF	1.076
$\Delta\rho_{\text{max}}/\Delta\rho_{\text{min}}$ (e/Å ³)	1.342/−1.706

Table 4. Coordinates and equivalent displacement parameters (U_{eq} , in Å²) of atoms and site occupancy factors (s.o.f.) for shuiskite-(Cr).

Site	<i>x</i>	<i>y</i>	<i>z</i>	U_{eq}	s.o.f.
Ca(1)	0.33945(4)	1/2	0.25177(10)	0.00834(17)	1
Ca(2)	0.15486(5)	1/2	0.18808(11)	0.01106(18)	1
X	1/4	1/4	1/2	0.0054(3)	Cr _{0.516(8)} Mg _{0.484(9)}
Y	0.49532(3)	0.24730(9)	0.25394(6)	0.00457(16)	Cr _{0.700(7)} Al _{0.300(8)}
Si(1)	0.09159(6)	0	0.05128(13)	0.0050(2)	1
Si(2)	0.24812(6)	0	0.16523(13)	0.0060(2)	1
Si(3)	0.40195(6)	0	0.46535(13)	0.0048(2)	1
O(1)	0.07386(11)	0.2230(4)	0.1373(2)	0.0083(4)	1
O(2)	0.24643(11)	0.2293(4)	0.2657(2)	0.0080(4)	1
O(3)	0.41468(11)	0.2209(4)	0.3671(3)	0.0081(4)	1
O(4)	0.44434(16)	1/2	0.1303(3)	0.0064(5)	1
O(5) = OH	0.45671(16)	0	0.1265(4)	0.0086(5)	1
O(6)	0.04507(16)	1/2	0.3709(3)	0.0074(5)	1
O(7) = OH	0.03450(18)	0	0.3737(4)	0.0105(6)	1
O(8)	0.17686(15)	0	0.0349(4)	0.0083(5)	1
O(9)	0.17653(16)	1/2	0.4751(4)	0.0090(5)	1
O(10) = OH,O	0.31327(17)	0	0.0665(4)	0.0123(6)	1
O(11) = OH,O	0.18416(16)	0	0.4971(3)	0.0077(5)	1

Table 5. Selected interatomic distances (Å) in the structure of shuiskite-(Cr).

Ca(1)	O(11)	2.324(3)	X	O(11)	1.961(2)	Si(1)	O(1)	1.598(2) × 2
	O(3)	2.353(2) × 2		O(11)	1.9613(19)		O(4)	1.657(3)
	O(4)	2.412(3)		O(9)	2.052(2) × 2		O(8)	1.667(3)
	O(2)	2.433(2) × 2		O(2)	2.065(2) × 2	<Si(1)-O>		1.630
	O(8)	2.508(3)	<X-O>		2.026			
<Ca(1)-O>		2.402				Si(2)	O(10)	1.622(3)
			Y	O(7)	1.941(2)		O(2)	1.640(2) × 2
Ca(2)	O(1)	2.281(2) × 2		O(5)	1.947(2)		O(8)	1.666(3)
	O(10)	2.410(3)		O(1)	1.950(2)	<Si(2)-O>		1.642
	O(2)	2.426(2) × 2		O(3)	1.963(2)			
	O(9)	2.512(3)		O(6)	1.979(2)	Si(3)	O(3)	1.621(2) × 2
	O(6)	2.828(3)		O(4)	2.040(2)		O(6)	1.652(3)
<Ca(2)-O>		2.452	<Y-O>		1.970		O(9)	1.666(3)
						<Si(3)-O>		1.640

Table 6. Bond valence calculations¹ for shuiskite-(Cr).

	Ca(1)	Ca(2)	X	Y	Si(1)	Si(2)	Si(3)	Σ
O(1)		$0.36 \times 2\downarrow$		0.51	$1.07 \times 2\downarrow$			1.94
O(2)	$0.24 \times 2\downarrow$	$0.25 \times 2\downarrow$	$0.35 \times 2\downarrow$			$0.96 \times 2\downarrow$		1.80
O(3)	$0.30 \times 2\downarrow$						$1.01 \times 2\downarrow$	1.80
O(4)	0.26			$0.40 \times 2\rightarrow$	0.91			1.97
O(5)				$0.51 \times 2\rightarrow$				1.02
O(6)		0.08		$0.47 \times 2\rightarrow$			0.93	1.95
O(7)				$0.52 \times 2\rightarrow$				1.04
O(8)	0.20				0.89	0.89		1.98
O(9)		0.19	$0.36 \times 2\downarrow \times 2\rightarrow$				0.89	1.80
O(10)		0.26				1.01		1.27
O(11)	0.32		$0.46 \times 2\downarrow \times 2\rightarrow$					1.24
Σ	1.86	1.75	2.34	2.90	3.94	3.82	3.84	

¹ Bond-valence parameters were taken from [14].

Shuiskite-(Cr), ideally $\text{Ca}_2\text{CrCr}_2[\text{SiO}_4][\text{Si}_2\text{O}_6(\text{OH})](\text{OH})_2\text{O}$, is structurally similar to the other pumpellyite-group minerals. Its crystal structure is based on a pair of chains of edge-sharing X- and Y-centred octahedra running along the *b* axis. The octahedra are linked together via orthosilicate groups $[\text{SiO}_4]$, disilicate groups $[\text{Si}_2\text{O}_6(\text{OH})]$, and Ca-centred polyhedra (Figure 3). The X site is occupied by $0.52\text{Cr} + 0.48\text{Mg}$, with the average $\langle\text{X-O}\rangle$ distance of 2.026 Å, while the Y site is occupied by $0.70\text{Cr} + 0.30\text{Al}$, with the average $\langle\text{Y-O}\rangle$ distance of 1.970 Å.

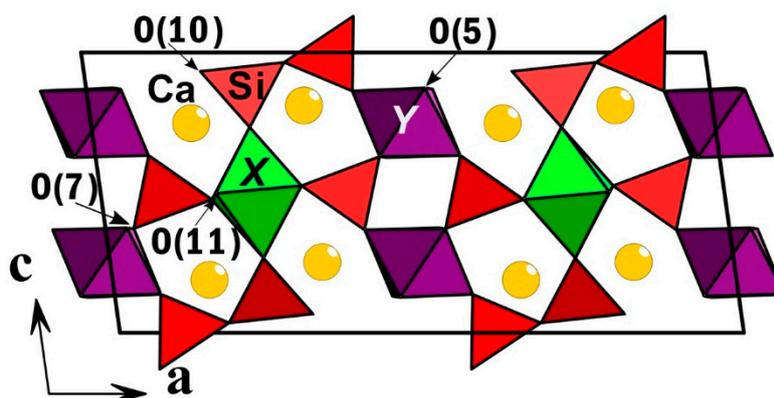


Figure 3. General view of the crystal structure of shuiskite-(Cr). Anion sites with full [O(5) and O(7)] or partial [O(10) and O(11)] OH occupancies are labelled. The unit cell is outlined.

The bond-valence sums (BVS) at the O(5) (1.02 valence units (*vu*)) and O(7) (1.04 *vu*) sites indicate that these sites are occupied by hydroxyl groups, while the O(10) and O(11) sites have mixed O/OH occupancies (1.27 and 1.24 *vu*, respectively) (Table 6). The mixed occupancy at the O(10) site means that disilicate groups $[\text{Si}_2\text{O}_6(\text{OH},\text{O})]$ are present. Weak bands at 2207 and 2180 cm^{-1} in the IR spectra of shuiskite-(Cr) confirm the presence of silanol groups Si–OH (Figure 2b). The remaining ten oxygen sites are occupied by O^{2-} anions. Both BVS and IR data indicate the absence of H_2O^0 in shuiskite-(Cr). The distribution of OH groups in shuiskite-(Cr) is similar to that found in other Cr-bearing pumpellyite-group minerals [7,15–17].

The obtained structural formula of shuiskite-(Cr) $\text{Ca}_2(\text{Cr}_{0.52}\text{Mg}_{0.48})(\text{Cr}_{1.40}\text{Al}_{0.60})[\text{SiO}_4][\text{Si}_2\text{O}_6(\text{OH})](\text{OH})_{2.48}\text{O}_{0.52}$ is in a good agreement with the empirical formula $\text{Ca}_{2.02}(\text{Cr}_{0.56}\text{Mg}_{0.42})\Sigma_{0.98}(\text{Cr}_{1.43}\text{Al}_{0.56}\text{Ti}_{0.01})\Sigma_{2.00}\text{Si}_{3.00}\text{O}_{10.57}(\text{OH})_{3.43}$.

4. Discussion

Our data show that Cr^{3+} can be the predominant cation at both the Y and X sites in pumpellyite-group minerals, resulting in the formation of the second $^{\text{Y}}\text{Cr}$ -dominant member of the pumpellyite group—shuiskite-(Cr).

All the works on Cr-enriched pumpellyite-group minerals show that Cr is distributed between both the X and Y sites; however, the distribution is uneven. At a relatively low Cr content (up to 16–17 wt.% Cr_2O_3), Cr prefers the X site rather than the Y site resulting in the formation of a Cr-rich variety of pumpellyite-(Mg), $\text{Ca}_2(\text{Mg,Cr})(\text{Al,Cr})_2[\text{SiO}_4][\text{Si}_2\text{O}_6(\text{OH,O})](\text{OH})_2(\text{OH,O})$, studied on samples from the Glavnoe Saranovskoe deposit [7,15–17]. With the increase in the total Cr content (22–23 wt.% Cr_2O_3), the affinity of the X site for Cr decreases. Cr becomes the predominant cation at the Y site, while the X site remains Mg-dominant, resulting in the formation of shuiskite-(Mg), $\text{Ca}_2(\text{Mg,Cr})(\text{Cr,Al})_2[\text{SiO}_4][\text{Si}_2\text{O}_6(\text{OH,O})](\text{OH})_2(\text{OH,O})$ [7]. As the present study shows, when the Cr content increases further (up to 28.5 wt.% Cr_2O_3), Cr becomes the predominant cation at the both X and Y sites, forming shuiskite-(Cr), a mineral with the simplified formula $\text{Ca}_2(\text{Cr,Mg})(\text{Cr,Al})_2[\text{SiO}_4][\text{Si}_2\text{O}_6(\text{OH,O})](\text{OH})_2(\text{OH,O})$ and the ideal formula $\text{Ca}_2\text{CrCr}_2[\text{SiO}_4][\text{Si}_2\text{O}_6(\text{OH})](\text{OH})_2\text{O}$. For comparison of shuiskite-(Mg) and shuiskite-(Cr), see Table 7. As proposed by Yoshiasa and Matsumoto [18], the substitution of Mg for Cr^{3+} at the X site in pumpellyite-group minerals follows the mechanism $\text{Mg}^{2+} + \text{OH}^- \rightarrow \text{Cr}^{3+} + \text{O}^{2-}$ with corresponding anion substitutions at the O(11) site.

Table 7. Comparative data for shuiskite-(Cr) and shuiskite-(Mg).

Mineral	Shuiskite-(Cr)	Shuiskite-(Mg)
Formula	$\text{Ca}_2\text{CrCr}_2[\text{SiO}_4][\text{Si}_2\text{O}_6(\text{OH})](\text{OH})_2\text{O}$	$\text{Ca}_2\text{MgCr}_2[\text{SiO}_4][\text{Si}_2\text{O}_6(\text{OH})](\text{OH})_3$
Crystal system	Monoclinic	Monoclinic
Space group	$C2/m$	$C2/m$
<i>a</i> , Å	19.2436(6)	19.2156(7)
<i>b</i> , Å	5.9999(2)	5.9779(2)
<i>c</i> , Å	8.8316(3)	8.8268(3)
β , °	97.833(3)	97.785(3)
<i>V</i> , Å ³	1010.17(6)	1004.59(6)
<i>Z</i>	4	4
<i>D</i> , g/cm ³	3.432 (calc)	3.24 (meas) 3.238 (calc)
Strongest reflections of the powder X-ray diffraction pattern: <i>d</i> , Å (<i>l</i>)	4.707 (36)	2.90 (90)
	3.783 (75)	2.73 (70)
	2.913 (100)	2.64 (50)
	2.755 (52)	2.46 (50)
	2.539 (48)	2.22 (40)
	2.470 (39)	2.12 (40)
	1.5013 (42)	1.593 (100) 1.487 (80)
References	This work	[6,7]

A pumpellyite-group mineral with a high content of Cr (up to 26.5 wt.% Cr_2O_3) and an Mg content as low as 3.0 wt.% MgO was reported by Mevel and Kienast [19] from the Roche Noire massif, Auvergne-Rhône-Alpes, France. This could be the second occurrence of shuiskite-(Cr); however, a structural study is needed to determine the distribution of Cr between the X and Y sites and identify the mineral species.

Shuiskite-(Cr) is one of only twenty known minerals with both Cr and Si as the dominant constituents [20].

Supplementary Materials: The following are available online at <http://www.mdpi.com/2075-163X/10/5/390/s1>, CIF file: shuiskite-(Cr).cif.

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