Article

Chromium Members of the Pumpellyite Group: Shuiskite-(Cr), Ca$_2$CrCr$_2$[Si$_4$O$_6$][Si$_2$O$_6$(OH)](OH)$_2$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 Ca$_2$CrCr$_2$[Si$_4$O$_6$][Si$_2$O$_6$(OH)](OH)$_2$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 clinochlore, and uvarovite. Shuiskite-(Cr) forms long prismatic to acicular crystals up to 0.1 × 0.5 × 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 (–), α = 1.757(5), β = 1.788(4), γ = 1.794(6), 2V (meas.) = 45(10)°, 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$_2$O$_3$ 5.41, Cr$_2$O$_3$ 28.50, TiO$_2$ 0.18, SiO$_2$ 33.86, H$_2$O 5.82, total 98.27. The empirical formula calculated based on the sum of eight metal cations and Si atoms per formula unit is Ca$_{2.02}$Mg$_{0.42}$Cr$_{3.19}$Al$_{0.56}$Ti$_{0.01}$Si$_{3.00}$O$_{10.52}$(OH)$_{3.43}$. The simplified formula is Ca$_2$(Cr,Mg)(Cr,Al)$_2$[Si$_4$O$_6$][Si$_2$O$_6$(OH)$_2$](OH)$_2$. Shuiskite-(Cr) is monoclinic, C2/m, a = 19.2436(6), b = 5.9999(2), c = 8.8316(3) Å, β = 97.833(3)°, V = 1010.17(6) Å$^3$, 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 [SiO$_4$] and [Si$_2$O$_6$(OH)] groups and Ca-centred polyhedra. The mineral species shuiskite, ideally Ca$_2$MgCr$_2$[Si$_4$O$_6$][Si$_2$O$_6$(OH)](OH)$_3$, was renamed to shuiskite-(Mg) by the decision of the IMA CNMNC. The shuiskite solid solution series with the general formula Ca$_2$XCr$_2$[Si$_4$O$_6$][Si$_2$O$_6$(OH)$_2$](OH)$_2$(OH)$_2$(OH), which includes shuiskite-(Mg) and shuiskite-(Cr) with X = 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 $\text{Cr}^{3+}$, while $Y = \text{Al}, \text{Mn}^{3+}, \text{Fe}^{3+}, \text{V}^{3+}$ and $\text{Cr}^{3+}$. 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: $^Y\text{Al}$—pumpellyite (the name first proposed by Palache and Vassar [2]), $^\text{YFe}^{3+}$—julgoldite [3], $^\text{YMn}^{3+}$—okhotskite [4], and $^\text{YV}^{3+}$—poppite [5]. Minerals with predominant $\text{Cr}^{3+}$ 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 $\text{Mg}$ 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 $\text{Cr}$ and low $\text{H}_2\text{O}$ content; however, the distribution of $\text{Cr}$ 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 $\text{Cr}$ is a dominant cation at both the $X$ and $Y$ sites, making it a new pumpellyite-group mineral shuiskite-(Cr), ideally $\text{Ca}_2\text{CrCr}_2[\text{SiO}_4][\text{Si}_2\text{O}_6(\text{OH})_2](\text{OH})_2\text{O}$, 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 $\text{Mg}$ prevailing at the $X$ site and, thus, the ideal formula $\text{Ca}_2\text{MgCr}_2[\text{SiO}_4][\text{Si}_2\text{O}_6(\text{OH})_2](\text{OH})_2\text{O}$, 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-(Mg) and shuiskite-(Cr) with $X = \text{Mg}$ and $\text{Cr}^{3+}$, 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 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 $0.1 \times 0.5 \times 7 \text{ mm}$, 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.

![Cruciform twins](image)

**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 clinochlore 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, CoKα 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 (MoKα radiation). The structure was solved by direct methods and refined on the basis of 2793 independent reflections with I > 2σ(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/cm$^3$.

Shuiskite-(Cr) is optically biaxial (–), $\alpha = 1.757(5)$, $\beta = 1.788(6)$, $\gamma = 1.794(6)$, $2V$ (meas.) = 45(10)$^\circ$, $2V$ (calc.) = 46$^\circ$ (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: $Z$’ $b$ 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$_{0.42}$Cr$_{3+}$1.99 Al$_{0.56}$Ti$_{0.01}$Si$_{3.00}$O$_{10.57}$OH), or, taking into account the crystal structure data (see below): Ca$_{2.02}$(Cr$_{0.56}$Mg$_{0.42}$)$_{2}$[Si$_{4}$O$_{12}$](Cr$_{3}$Al$_{0.56}$Ti$_{0.01}$)$_{2}$Si$_{3}$O$_{10}$H$_{3}$. The simplified formula is Ca$_{2}$[(Cr,Mg)$_{(Cr,Al)}$_{2}][SiO$_{4}$][Si$_{2}$O$_{6}$(OH,O)](OH,O)(OH)$_{2}$.

| 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  | Calculated from the stoichiometry. |
| Total       | 98.27|       |                   |

The ideal end-member formula is Ca$_{2}$Cr$_{2}$[Si$_{4}$O$_{12}$][Si$_{2}$O$_{6}$(OH)](OH)$_{2}$O, which requires CaO 20.49, Cr$_{2}$O$_{3}$ 41.64, SiO$_{2}$ 32.93, H$_{2}$O 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 H$_{2}$O molecules (in the range 1550–1750 cm$^{-1}$) and CO$_{3}^{2–}$ anions (1350–1550 cm$^{-1}$) are absent in the IR spectra of shuiskite-(Cr) and shuiskite-(Mg).
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 $X$Cr···O(9)–Si(3) or $X$Cr···O(2)–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 $V = 1010.87(2)$ Å$^3$.

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

| $I_{\text{meas}}$ | $d_{\text{meas}}$ | $I_{\text{calc}}^{1}$ | $d_{\text{calc}}^{2}$ | $hkl$ |
|-----------------|-----------------|-----------------|-----------------|------|
| 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              | 4.739           | 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.

| hkl   | $d_{calc}^1$ | $d_{calc}^2$ | $hkt$ |
|-------|--------------|--------------|-------|
| 75 3  | 3.785        | 202          |       |
| 3 14  | 3.546        | 11–2         |       |
| 14 1  | 3.467        | 40–2         |       |
| 4 18  | 3.409        | 112          |       |
| 13 1  | 3.245        | 31–2         |       |
| 4 18  | 3.140        | 51–1         |       |
| 18 12 | 3.024        | 402          |       |
| 12 100| 3.000        | 020          |       |
| 100 12| 2.916, 2.914, 2.902 | 003, 511, 20–3 |       |
| 14 2| 2.864, 2.862 | 601, 220     |       |
| 12 8| 2.838        | 021          |       |
| 52 2| 2.756, 2.753, 2.747 | 60–2, 22–1, 51–2 |       |
| 10 31| 2.688        | 221          |       |
| 31 10| 2.643        | 11–3         |       |
| 48 12| 2.539        | 420          |       |
| 39 2| 2.487, 2.474, 2.468 | 42–1, 022, 71–1 |       |
| 8 1| 2.441        | 22–2         |       |
| 8 10| 2.383, 2.383 | 80–1, 800    |       |
| 31 6| 2.351        | 222          |       |
| 12 7| 2.326        | 313          |       |
| 3 6| 2.296        | 51–3         |       |
| 12 3| 2.269        | 42–2         |       |
| 27 8| 2.224        | 80–2         |       |
| 8 14| 2.198        | 20–4         |       |
| 12 14| 2.187, 2.181 | 004, 620     |       |
| 4 2| 2.165        | 62–1         |       |
| 23 12| 2.130        | 422          |       |
| 12 2| 2.099        | 40–4         |       |
| 8 2| 2.072, 2.072, 2.071 | 11–4, 621, 204 |       |
| 2 1| 2.047        | 513          |       |
| 4 4| 2.033, 2.029 | 31–4, 62–2   |       |
| 4 4| 2.017        | 71–3         |       |
| 8| 1.9336, 1.9286 | 131, 60–4    |       |
| 14 20| 1.8859, 1.883 | 314, 622     |       |
| 20 4| 1.8607        | 82–1, 820    |       |
| 4| 1.8496        | 423          |       |
| 2 3| 1.8309        | 62–3         |       |
| 3| 1.7674        | 024          |       |
| 5| 1.7538        | 71–4         |       |
| 19| 1.7194        | 42–4, 514    |       |
| 2 6| 1.6996        | 604          |       |
| 8| 1.6793, 1.6765 | 31–5, 111–1  |       |
| 10| 1.6542        | 13–3         |       |
| 9| 1.6097        | 1020, 73–1, 424 |       |
| 35| 1.5897        | 1200         |       |
| 16| 1.5697        | 102–2        |       |
| 16| 1.551         | 1021         |       |
| 16| 1.5208        | 22–5         |       |
| 10| 1.5120        | 804          |       |
| 42| 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).

| Crystal system, space group, Z | Monoclinic, C2/m, 4 |
|-------------------------------|---------------------|
| a (Å)                        | 19.2436(6)          |
| b (Å)                        | 5.9999(2)           |
| c (Å)                        | 8.8316(3)           |
| β (°)                        | 97.833(3)           |
| V (Å³)                       | 1010.17(6)          |
| Diffractometer               | Xcalibur S CCD      |
| θ range (°)                  | 2.94 – 34.79        |
| Crystal size (mm³)           | 0.049 × 0.053 × 0.377 |
| Absorption coefficient µ (mm⁻¹) | 3.618          |
| F₀₀₀                         | 1028                |
| h, k, l range                | −30 ≤ h ≤ 29, −9 ≤ k ≤ 9, −13 ≤ l ≤ 14 |
| Reflections collected        | 3579                |
| Unique reflections | 2793                |
| Number of refined parameters | 127                 |
| Weighting scheme             | 1/σ²(Fo2) + 0.0434P² + 5.7592, P = (Fo² + 2Fc²)/3 |
| R₁                           | 0.0469              |
| wR₂(all)                     | 0.1088              |
| GoF                          | 1.076               |
| Δρ(max)/Δρ(min) (e/Å³)       | 1.342/−1.706        |

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

| Site    | x     | y     | z     | Ueq  | s.o.f. |
|---------|-------|-------|-------|------|--------|
| Ca(1)   | 0.339454(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) | 1      |
| Y       | 0.49532(3)  | 0.24730(9) | 0.25394(6) | 0.00457(16) | 1      |
| 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) | 0.0049(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)    | 0.45771(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)    | 0.17886(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)   | 0.31327(17) | 0     | 0.0865(4) | 0.0123(6) | 1      |
| O(11)   | 0.18416(16) | 0     | 0.4971(3) | 0.0077(5) | 1      |

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

| Cat(1)     | O(11)   | 2.324(3) X | O(11)   | 1.961(2) Si(1) | O(11)   | 1.598(2) X |
|------------|---------|------------|---------|----------------|---------|------------|
| O(3)       | 2.353(2) | 2          | O(11)   | 1.961(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>   | 2.062          |         |            |
| Y          | 2.402   |            |         |                |         |            |
|          |         | Y          | O(7)    | 1.941(2)       | O(2)    | 1.640(2) × 2 |
| Cat(2)     | O(11)   | 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)       | 2.462(2) | 2          | O(3)    | 1.963(2)       |         |            |
| O(9)       | 2.512(3) |            | O(6)    | 1.979(2)       | Si(3)   | 1.621(2) × 2 |
| O(6)       | 2.082(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)   |
|            |         |            |         |                |         | 1.640      |
Shuiskite-(Cr), ideally Ca₂Cr₂Cr₂[SiO₄][Si₂O₆(OH)](OH)₂O, is structurally similar to the other pumpellyite-group minerals. Its crystal structure is based on a pair of chains of edge-sharing Cr-bearing pumpellyite-group minerals [7,15–17].

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 means that disilicate groups [Si₂O₆(OH,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 indicate that these sites are occupied by hydroxyl groups, while the O(10) and O(11) sites have mixed O(10) and O(11) sites have mixed OH occupancies (1.27 and 1.24 vu, respectively) (Table 6). The mixed occupancy at the O(10) site means that disilicate groups [Si₂O₆(OH,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 O²⁻ anions. Both BVS and IR data indicate the absence of H₂O⁰ 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 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 [Si₂O₆(OH,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 O²⁻ anions. Both BVS and IR data indicate the absence of H₂O⁰ 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) Ca₂(Cr_{0.52}Mg_{0.48})(Cr_{1.40}Al_{0.60})[SiO₄][Si₂O₆(OH)](OH)₂⁴O_{0.52} is in a good agreement with the empirical formula Ca₂.02(Cr_{0.56}Mg_{0.42})Σ_{2.98}(Cr_{1.43}Al_{0.56}Ti_{0.01})Σ_{2.00}Si_{3.00}O_{10.57}(OH)_{3.43}.

### Table 6. Bond valence calculations ¹ for shuiskite-(Cr).

|      | Ca(1) | Ca(2) | X     | Y     | Si(1) | Si(2) | Si(3) | Σ     |
|------|-------|-------|-------|-------|-------|-------|-------|-------|
| O(1) | 0.36  | × 21  | 0.51  | 1.07  | × 21  | 1.94  |       |
| O(2) | 0.24  | × 21  | 0.25  | 1.07  | × 21  | 1.80  |       |
| O(3) | 0.30  | × 21  | 0.49  | 0.96  | × 21  | 1.80  |       |
| O(4) | 0.26  |       | 0.40  | 0.91  |       | 1.97  |       |
| O(5) | 0.51  | × 21  | 0.91  |       |       | 1.02  |       |
| O(6) | 0.08  |       | 0.47  | 0.93  |       | 1.95  |       |
| O(7) | 0.52  | × 21  | 0.93  |       |       | 1.04  |       |
| O(8) | 0.20  |       |       | 0.89  |       | 1.98  |       |
| O(9) | 0.19  | × 21  |       | 0.89  |       | 1.80  |       |
| O(10)| 0.26  |       |       | 1.01  |       | 1.27  |       |
| O(11)| 0.32  | × 21  |       | 1.01  |       | 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].

![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 occupations are labelled. The unit cell is outlined.](image-url)
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 $^7$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$_2$O$_3$), 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$_2$O$_3$), 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), $\text{Ca}_2\text{MgCr}_2\text{[SiO}_4\text{][Si}_2\text{O}_6\text{(OH,O)}\text{](OH)}_2\text{(OH,O)}$ [7]. As the present study shows, when the Cr content increases further (up to 28.5 wt.% Cr$_2$O$_3$), Cr becomes the predominant cation at both X and Y sites, forming shuiskite-(Cr), a mineral with the simplified formula $\text{Ca}_2\text{CrCr}_2\text{[SiO}_4\text{][Si}_2\text{O}_6\text{(OH,O)}\text{](OH)}_2\text{(OH,O)}$ 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.

| 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     | $C2/m$         | $C2/m$         |
| $a$, Å          | 19.2436(6)     | 19.2156(7)     |
| $b$, Å          | 5.9999(2)      | 5.9779(2)      |
| $c$, Å          | 8.8316(3)      | 8.8268(3)      |
| $\beta$, °      | 97.833(3)      | 97.785(3)      |
| $V$, Å$^3$      | 1010.17(6)     | 1004.59(6)     |
| $Z$             | 4              | 4              |
| $D$, g/cm$^3$   | 3.432 (calc)   | 3.24 (meas)    |
|                 | 3.238 (calc)   |                |
| Strongest reflections of the powder |                     |
| X-ray diffraction pattern: |                     |
| $d$, Å (I)      | 2.755 (52)     | 2.22 (40)      |
|                 | 2.539 (48)     | 2.12 (40)      |
|                 | 2.470 (39)     | 1.593 (100)    |
|                 | 1.5013 (42)    | 1.487 (80)     |
| References      | This work [6,7]|                |

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

A pumpellyite-group mineral with a high content of Cr (up to 26.5 wt.% Cr$_2$O$_3$) 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](http://www.mdpi.com/2075-163X/10/5/390/s1), CIF file: shuiskite-(Cr).cif.
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