

# Chukhrovite-(Ca), $\text{Ca}_{4.5}\text{Al}_2(\text{SO}_4)\text{F}_{13}\cdot 12\text{H}_2\text{O}$ , a new mineral species from the Val Cavallizza Pb–Zn–(Ag) mine, Cuasso al Monte, Varese province, Italy

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**Abstract:** Chukhrovite-(Ca),  $\text{Ca}_{4.5}\text{Al}_2(\text{SO}_4)\text{F}_{13}\cdot 12\text{H}_2\text{O}$ , is the Ca-dominant species of the chukhrovite mineral group. It occurs at the Val Cavallizza Pb–Zn–Ag mine, Cuasso al Monte, Varese province, Italy. Chukhrovite-(Ca) is found as low temperature hydrothermal crystallizations covering the surfaces of brittle fractures crosscutting a marcasite and REE-bearing fluorite vein. Associated minerals include marcasite, gypsum, and hydrated Fe oxides. This new calcium aluminofluoride forms sharp octahedra up to 150  $\mu\text{m}$  in diameter. Crystals are translucent to transparent, colourless to white, with a white streak and a vitreous lustre. Chukhrovite-(Ca) is isotropic with  $n = 1.432(1)$ , and is non-fluorescent either under short-wave (254 nm) or long-wave (366 nm) ultraviolet light. The mineral is brittle with a Mohs hardness of 3.5(5), and without a distinct cleavage or fracture. Its density, calculated from the single-crystal unit-cell parameters and assuming 12  $\text{H}_2\text{O}$  molecules per formula unit, is 2.23  $\text{g}/\text{cm}^3$ . The empirical formula, based on 3 (Al + S) atoms per formula unit and calculated from an average of five selected point analyses, is:  $(\text{Ca}_{4.33}\text{Na}_{0.11}\text{Fe}_{0.03})_{\Sigma 4.47}\text{Al}_{2.10}(\text{S}_{0.90}\text{O}_{3.72})\text{F}_{13.10}\cdot 5.98\text{H}_2\text{O}$ , with the water content calculated by difference to 100 %. Chukhrovite-(Ca) is cubic with space group  $Fd\bar{3}$ ; its single-crystal unit-cell parameters are  $a = 16.749(1)$  Å and  $V = 4698.6(1)$  Å<sup>3</sup>, for  $Z = 8$ . The eight strongest lines in the X-ray powder diffraction pattern are [ $d$  in Å ( $hkl$ ): 9.665 (100) 111, 5.921 (31) 022, 5.053 (16) 113, 4.190 (10) 004, 3.226 (15) 333 and 115, 2.556 (10) 533, 2.182 (12) 355 and 137, 1.915 (17) 626]. The mineral, which has been approved by the CNMNC under number IMA 2010-081, is named chukhrovite-(Ca), since it corresponds to the Ca-rich equivalent of chukhrovite-(REE) (REE = Ce, Nd, Y), in which REE are replaced by Ca.

**Key-words:** chukhrovite-(Ca), new mineral species, calcium aluminofluoride, chukhrovite group, Val Cavallizza mine, Cuasso al Monte, central Southern Alps, Italy.

## 1. Introduction

The chukhrovite group includes four extremely rare Ca- and REE-bearing aluminofluoride mineral species. Chukhrovite-(Y),  $\text{Ca}_3(\text{Y,Ce})\text{Al}_2(\text{SO}_4)\text{F}_{13}\cdot 12\text{H}_2\text{O}$ , was discovered in 1950 in the oxidized zone of the Kara-Oba tungsten deposit (Kazakhstan), and described as colourless to white cubo-octahedral crystals up to 1 cm diameter, associated with halloysite, gearsutite, fluorite, creedite, anglesite, and “limonite” (Ermilova *et al.*, 1960; Pekov, 1998). Chukhrovite-(Ce),  $\text{Ca}_3(\text{Ce,Y})\text{Al}_2(\text{SO}_4)\text{F}_{13}\cdot 12\text{H}_2\text{O}$ , was found for the first time at the Yaroslavskoye tin deposit (Primorsk Territory, Russia), where it forms milky-white cubo-octahedral crystals up to 1.5 mm in diameter, associated with fluorite, tourmaline, ralstonite,

yaroslavite, muscovite, and jarosite (Novikova, 1973; Pekov, 1998). Its occurrence was also notified in Grube Clara (Germany) by Walenta (1978), and, more recently, at Gamskalgraben (Austria) by Niedermayr *et al.* (2008).

The REE-free mineral species meniaylovite,  $\text{Ca}_4\text{AlSi}(\text{SO}_4)\text{F}_{13}\cdot 12\text{H}_2\text{O}$ , was described as white to yellowish crystals produced by volcanic exhalations of the Tolbachik volcano (Kamchatka territory, Russia) and of the Eldfell volcano (Heimaey island, Iceland) (Vergasova *et al.*, 2004; Mitolo *et al.*, 2008). The last identified mineral species belonging to the chukhrovite group is chukhrovite-(Nd),  $\text{Ca}_3(\text{Nd,Y})\text{Al}_2(\text{SO}_4)\text{F}_{13}\cdot 12\text{H}_2\text{O}$ , which forms colourless to white crystals from 0.05 up to 0.4 mm diameter, associated with chukhrovite-(Y) in the Kara-Oba deposit (Pautov *et al.*, 2005). These four mineral species are cubic with space

group  $Fd\bar{3}$ ; their unit-cell parameters are 16.800(5), 16.800(5), 16.722(2), and 16.759(3) Å, respectively.

In 1993, during a field campaign in the Val Cavallizza mine, Cuasso al Monte, Varese province, north Italy, we found octahedral colourless crystals covering the surfaces of brittle fractures crosscutting a marcasite and REE-bearing fluorite vein. Mineralogical analyses of these crystals showed that they correspond to a REE-free calcium aluminofluoride belonging to the chukhrovite group. The mineral was consequently named chukhrovite-(Ca), since it corresponds to the Ca-rich equivalent of chukhrovite-(REE) (REE = Ce, Nd, Y), in which REE are replaced by Ca. Both the mineral and the name were approved by the IMA Commission on New Minerals, Nomenclature and Classification (IMA # 2010-081, Vignola *et al.*, 2011).

This paper presents the mineralogical description of new species chukhrovite-(Ca). The electron-microprobe, structural, optical, and spectroscopic analyses were performed on two co-type specimens extracted from the same hand sample collected in 1993. These two co-types are stored in the mineralogical collection of the Museum of Natural History of Milano (Italy), catalogue number M37901, and in the mineralogical collection of the Laboratory of Mineralogy of the University of Liège (Belgium), catalogue number 20383.

## 2. Occurrence, general appearance, and physical properties

Chukhrovite-(Ca) was found in 1993 by two of the authors (P.V. and P.G.) in the Val Cavallizza mine, Cuasso al Monte, Varese province, north Italy (45°54'01" N; 8°51'41" E). The Val Cavallizza Pb–Zn–(Ag) mineralization, discovered in 1869, was mined from 1901 to 1903 for Pb and Ag (Bozzoli, 1905). The last survey workings, operated by the RiMin society, date back to the 1951–1953 period; then the mine was completely abandoned. Chukhrovite-(Ca) occurs as low temperature hydrothermal crystallizations covering the surfaces of brittle fractures, crosscutting a marcasite and REE-bearing fluorite vein hosted by the late Hercynian NYF-miarolitic pink porphyritic granite of Cuasso al Monte (Pezzotta *et al.*, 2005). The mineral is associated with marcasite, REE-bearing fluorite, gypsum, hydrated Fe oxides, as well as minor galena and sphalerite.

Chukhrovite-(Ca) forms colourless to whitish, transparent to translucent, sharp octahedral crystals up to 100–150 µm diameter (Fig. 1). Twinning along the [001] axis, with a rotation of 90° (iron cross law), is widespread, while spinel law twins are rare. Chukhrovite-(Ca) is isotropic with  $n = 1.432(1)$  (measured with a microrefractometer spindle-stage; Medenbach, 1985), shows a vitreous lustre, a white streak, and is non-fluorescent either under short-wave (254 nm) or long-wave (366 nm) ultraviolet light. The mineral is brittle with a Mohs hardness of 3.5(5), and without a distinct cleavage or fracture. Due to small grain size, the density was not directly measured; the density value calculated from the

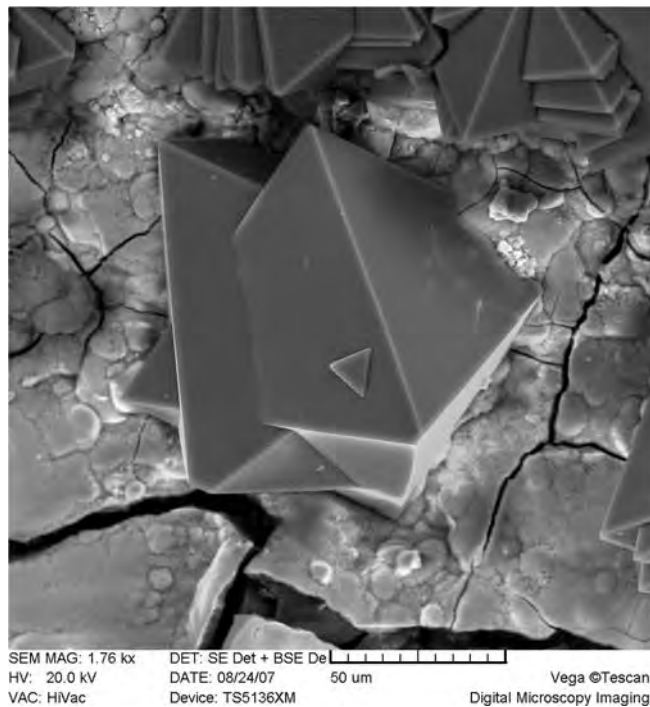


Fig. 1. Octahedral crystals of chukhrovite-(Ca).

empirical formula and single-crystal unit-cell parameters, assuming 12 H<sub>2</sub>O molecules per formula unit, is 2.23 g/cm<sup>3</sup>. The compatibility index,  $1 - (K_p/K_c) = 0.011$ , is superior. For the compatibility calculations, we used the  $K_i$  constants calculated for fluorides by Pauly (1982) (CaF<sub>2</sub>, AlF<sub>3</sub>, NaF), as well as the constants calculated for oxides by Mandarino (1981) (FeO, CaO, SO<sub>3</sub>, H<sub>2</sub>O).

## 3. Chemical composition

Quantitative chemical analyses were performed on polished thin sections of chukhrovite-(Ca), using a JEOL JXA-8200 electron microprobe working in wavelength-dispersion mode, at the laboratory of the Department of Earth Sciences, University of Milan. The system was operated using an accelerating voltage of 10 kV, a beam current of 5 nA, a spot size of 5 µm, and a counting time of 30 s on the peaks and 10 s on the background. Natural minerals (grossular for Si, Ca and Al, galena for S, omphacite for Na, and fayalite for Fe), as well as synthetic REE(PO<sub>4</sub>) (for REE) and RbMnF<sub>3</sub> (for F), served as standards. The raw data were corrected for matrix effects using the  $\Phi\rho Z$  method from the JEOL series of programs.

The mean analytical results are reported in Table 1. H<sub>2</sub>O was not determined directly due to the small amount of material, and the water content was calculated by difference to 100 wt%. This content significantly differs from that calculated from the structural data (see below), which corresponds to 31.80 wt% H<sub>2</sub>O; this difference is due to water loss under the electron beam, during the electron-microprobe measurement. CO<sub>2</sub> is absent from the mineral,

Table 1. Electron-microprobe analysis of chukhrovite-(Ca).

Constituent	Wt%	Range	Stand. dev.	Cation numbers	
SiO <sub>2</sub>	0.03	(0.00–0.07)	0.02	Si <sub>apfu</sub>	0.003
SO <sub>3</sub>	10.64	(9.44–11.82)	0.52	S	0.904
Al <sub>2</sub> O <sub>3</sub>	15.72	(13.13–17.07)	0.85	Al	2.096
REE <sub>2</sub> O <sub>3</sub>	<i>b.d.l.</i>	–	–	REE	–
FeO	0.34	(0.01–0.98)	0.26	Fe	0.032
CaO	35.74	(34.11–37.05)	0.78	Ca	4.332
Na <sub>2</sub> O	0.49	(0.16–0.77)	0.18	Na	0.107
F	36.61	(34.17–39.50)	1.35	F	13.100
H <sub>2</sub> O <sup>a</sup>	15.85			H <sub>2</sub> O	5.979
O = F	–15.42				
Total	100.00				

Note: Average of 5 point analyses. Cation numbers were calculated on the basis of 3 (Al + S) per formula unit.

<sup>a</sup>The water content was calculated by difference to 100 %.

as shown by the infrared and Raman spectra, as well as by the structural data (see below). The empirical formula, calculated on the basis of 3 (Al + S) atoms per formula unit, is: (Ca<sub>4.33</sub>Na<sub>0.11</sub>Fe<sub>0.03</sub>)<sub>Σ4.47</sub>Al<sub>2.10</sub>(S<sub>0.90</sub>O<sub>3.72</sub>)F<sub>13.10</sub>·5.98H<sub>2</sub>O. The simplified formula, in which the ideal water content obtained from the structural data is used, corresponds to Ca<sub>4.5</sub>Al<sub>2</sub>(SO<sub>4</sub>)F<sub>13</sub>·12H<sub>2</sub>O, which requires: CaO 28.18, Al<sub>2</sub>O<sub>3</sub> 22.77, SO<sub>3</sub> 8.94, F 27.58, H<sub>2</sub>O 24.15, O ≡ F –11.61, total 100.00 wt%.

#### 4. X-ray diffraction data and crystal structure determination

The X-ray powder diffraction (XRPD) pattern of chukhrovite-(Ca) has been obtained using a high-resolution Panalytical X'pert Pro X-ray powder diffractometer equipped with an X'Celerator-type detector at the Department of Geological Sciences and Geotechnologies of the University of Milan-Bicocca. Operating conditions were: Ni-filtered CuK $\alpha$  radiation, 40 kV, 40 mA, 2 $\theta$ -range from 5° to 105°, step size 0.017° 2 $\theta$ , counting time 300 s per step. Silicon NIST 640c was used as internal standard, and the refinement of unit-cell parameters, as well as indexing of reflections, were performed using the least-squares indexing program CELREF 3, beta version (LMGP Suite of Programs for the interpretation of X-ray Experiments, by Jean Laugier and Bernard Bochu, ENSP/Laboratoire des Matériaux et du Génie Physique. <http://www.inpg.fr/LMGP>). The refined unit-cell parameter for space group *Fd* $\bar{3}$  is  $a = 16.736(7)$  Å, and  $V = 4687.6(3)$  Å<sup>3</sup>, for  $Z = 8$ . The complete list of indexed reflections is reported in Table 2. The eight strongest measured lines are [ $d$  in Å ( $hkl$ ): 9.665 (100) 111, 5.921 (31) 022, 5.053 (16) 113, 4.190 (10) 004, 3.226 (15) 333 and 115, 2.556 (10) 533, 2.182 (12) 355 and 137, 1.915 (17) 626.

The X-ray structural study was carried out on an Oxford Diffraction Gemini PX Ultra 4-circle diffractometer equipped with a Ruby CCD-area detector, on a chukhrovite-(Ca) crystal measuring 120  $\mu$ m in length. Forty frames with a spatial resolution of 1° were collected by the  $\phi/\omega$

Table 2. X-ray powder diffraction data for chukhrovite-(Ca).

$hkl$	$d_{meas}$	$d_{calc}^a$	$hkl$
<b>100</b>	9.665	9.663	1 1 1
<b>31</b>	5.921	5.917	0 2 2
<b>16</b>	5.053	5.046	1 1 3
7	4.841	4.831	2 2 2
<b>10</b>	4.190	4.184	0 0 4
3	3.842	3.840	3 1 3
6	3.418	3.416	2 2 4
<b>15</b>	3.226	3.221	3 3 3, 1 1 5
2	2.963	2.959	0 4 4
4	2.831	2.829	3 1 5
4	2.794	2.789	2 4 4
7	2.650	2.646	2 0 6
<b>10</b>	2.556	2.552	5 3 3
<1	2.530	2.523	2 2 6
6	2.413	2.416	4 4 4
2	2.346	2.344	1 5 5, 1 1 7
7	2.240	2.237	2 4 6
<b>12</b>	2.182	2.179	3 5 5, 1 3 7
1	2.031	2.030	4 4 6
1	1.974	1.972	2 2 8, 6 0 6
2	1.927	1.933	5 1 7, 5 5 5
<b>17</b>	1.915	1.920	6 2 6
<1	1.874	1.871	0 4 8
1	1.840	1.837	5 3 7, 1 1 9
6	1.829	1.826	4 2 8
1	1.787	1.784	4 6 6
7	1.754	1.755	9 1 3
5	1.640	1.641	10 0 2, 2 6 8
1	1.613	1.611	6 6 6, 2 2 10
<1	1.562	1.561	5 3 9
1	1.511	1.509	7 5 7, 1 1 1
2	1.416	1.415	6 2 10
1	1.358	1.358	2 2 12, 10 4 6
1	1.281	1.280	5 5 11, 3 9 9, 11 1 7, 1 1 13
1	1.254	1.251	7 7 9, 11 3 7
1	1.250	1.251	3 1 13
<1	1.224	1.224	9 5 9, 3 3 13
<1	1.207	1.208	8 8 8
<1	1.182	1.183	14 0 2, 6 8 10, 10 0 10
<1	1.129	1.131	1 7 13, 11 7 7, 13 5 5
2	1.092	1.092	15 1 3

Note: <sup>a</sup>Unit-cell parameter refined from the X-ray powder data:  $a = 16.736(7)$  Å. The bold characters indicate the 8 most intense peaks.

scan technique, with a counting time of 1.5 s per frame, in the range  $6.88^\circ < 2\theta < 52.60^\circ$ . A total of 1064 reflections were extracted from these frames, corresponding to 365 unique reflections. The unit-cell parameter refined from these reflections is  $a = 16.749(1) \text{ \AA}$  ( $V = 4698.6(1) \text{ \AA}^3$ ), and is in good agreement with that refined from the X-ray powder data. Data were corrected for Lorentz, polarisation and absorption effects, the latter with an empirical method using the SCALE3 ABSPACK scaling algorithm included in the CrysAlisRED package (Oxford Diffraction, 2007).

The crystal structure of chukhrovite-(Ca) (Fig. 2) was refined in space group  $Fd\bar{3}$ . The starting atomic coordinates were those of synthetic Ca-rich chukhrovite (Mathew *et al.*, 1981), and scattering curves for neutral atoms, together with anomalous dispersion corrections, were taken from the International Tables for X-ray Crystallography, Vol. C (Wilson, 1992). In the final refinement cycle, all atoms were refined anisotropically, except the hydrogen atoms which were refined isotropically. The final  $R_1$  value is 0.0466. Further details concerning the intensity data collection and refinement are listed in Table 3; atomic coordinates, site occupancy factors, and anisotropic displacement parameters are reported in Table 4; bond distances are presented in Table 5.

The structure can be described as a compact assembly of  $\text{AlF}_6$  octahedra,  $\text{SO}_4$  tetrahedra, and large Ca sites (Fig. 2). The Ca sites are surrounded by F atoms and water molecules, forming distorted octahedra [Ca(2), bond distances 2.190–2.629 Å] or distorted pentagonal bipyramids [Ca(1), bond distances 2.317–2.455 Å] (Table 5). These Ca sites are connected together by corner- or edge-sharing, and are connected to the  $\text{AlF}_6$  regular octahedra (Al–F = 1.803 Å) by corner-sharing. The  $\text{SO}_4$  tetrahedra (S–O = 1.481 Å) occur within cavities in the structure, and are linked *via* hydrogen bonds to the water molecules (Fig. 3). Both

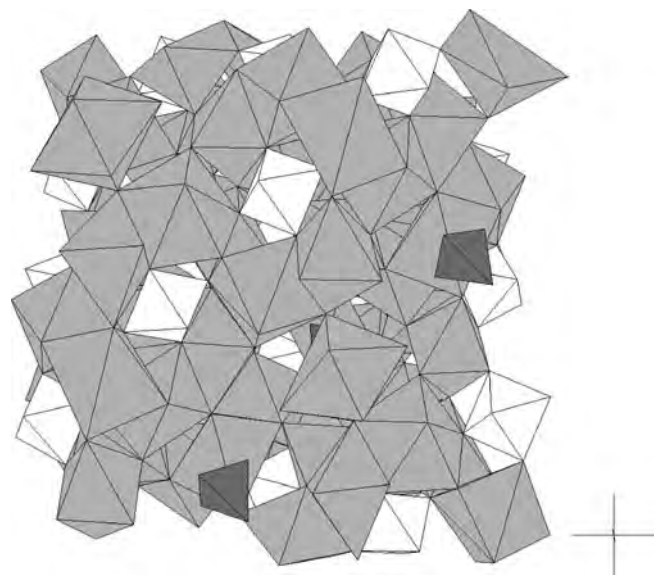


Fig. 2. The crystal structure of chukhrovite-(Ca), projected along the  $a$  axis. The  $\text{AlF}_6$  octahedra are white, the Ca polyhedra are light grey, and the  $\text{SO}_4$  tetrahedra are dark grey.

Table 3. Experimental details for the single-crystal X-ray diffraction study of chukhrovite-(Ca).

Crystal shape	Octahedron
Crystal size (mm)	0.120
Crystal colour	Colourless
$a$ (Å)	16.749(1)
$Vol.$ (Å <sup>3</sup> )	4698.6(1)
Space group	$Fd\bar{3}$
$Z$	8
Diffractometer	Oxford Diffraction Gemini PX Ultra with Ruby CCD-area detector
Operating conditions	50 kV, 40 mA
Radiation (Å)	MoK $\alpha$ ( $\lambda = 0.7107 \text{ \AA}$ )
Scan mode	$\phi/\omega$ scan
$2\theta_{\text{min.}}$ , $2\theta_{\text{max.}}$	$6.88^\circ$ , $52.60^\circ$
Range of indices	$-11 \leq h \leq 17$ , $-19 \leq k \leq 14$ , $-16 \leq l \leq 6$
Measured intensities	1064
Unique reflections	365
Observed [ $I > 2\sigma(I)$ reflections]	332
Absorption corrections	Empirical (SCALE3 ABSPACK scaling algorithm)
$\mu$ (mm <sup>-1</sup> )	1.362
<i>l.s.</i> refinement program	SHELX-97 (Sheldrick, 2008)
Refined parameters	43
$R_1$ ( $F_o > 2\sigma(F_o)$ )	0.0399
$R_1$ (all)	0.0466
$wR_2$ (all)	0.1239
$S$ (goodness of fit)	1.014
Max $\Delta/\sigma$ in the last <i>l.s.</i> cycle	0.000
Max peak and hole in the final $\Delta F$ map ( $e/\text{\AA}^3$ )	+ 0.529 and -1.014

hydrogen atoms of the asymmetric unit are involved in hydrogen bonds: each water molecule is consequently hydrogen bonded to an oxygen atom of the  $\text{SO}_4$  ion, and to a fluorine atom of the  $\text{AlF}_6$  octahedron (Fig. 3).

Refinement of the site occupancy factor for the Ca(2) site indicates that this site is only partially occupied by Ca, thus explaining the relatively high displacement parameters observed (Table 4). This low site population of ca. 9 % corresponds to 0.55 atoms per formula unit (*a.p.f.u.*), and is in good agreement with the chemical composition of the mineral. Indeed, the structural data indicate the presence of 4 Ca *a.p.f.u.* on the Ca(1) site, and of 0.55 Ca *a.p.f.u.* on the Ca(2) site, thus totalizing an amount of 4.55 Ca atoms, very close to the 4.47 (Ca + Na + Fe) *a.p.f.u.* measured with the electron microprobe. Bond-valence sums, calculated from the values of Brown & Altermatt (1985), are 2.99 (Al), 5.89 (S), 1.86 (Ca(1)), and 1.88 (Ca(2)); their good fit with the ideal values confirm the reliability of the assigned site populations.

## 5. Spectroscopic properties

The infrared spectrum of chukhrovite-(Ca) (Fig. 4) was collected with a Nicolet NEXUS spectrometer, in the

Table 4. Final fractional atom coordinates, anisotropic displacement parameters ( $\text{\AA}^2$ ), and site occupancy factors (S.O.F.) for chukhrovite-(Ca).

Atom	Wyckoff	x	y	z	S.O.F.	$U_{eq}$	$U_{11}$	$U_{22}$	$U_{33}$	$U_{23}$	$U_{13}$	$U_{12}$
Ca(1)	32 e	0.29285 (4)	0.29285 (4)	0.29285 (4)	1/3	0.0205 (5)	0.0205 (5)	0.0205 (5)	0.0205 (5)	-0.0019 (2)	-0.0019 (2)	-0.0019 (2)
Ca(2)	48 f	-0.125	0.375	0.6030 (9)	0.046(3)	0.052 (6)	0.06 (1)	0.041 (9)	0.06 (1)	0	0	-0.004 (6)
Al	16 d	0.5	0.5	0.5	1/6	0.0174 (6)	0.0174 (6)	0.0174 (6)	0.0174 (6)	-0.0031 (5)	-0.0031 (5)	-0.0031 (5)
S	8 a	0.125	0.125	0.125	1/12	0.0269 (8)	0.0269 (8)	0.0269 (8)	0.0269 (8)	0	0	0
F(1)	8 b	0.375	0.375	0.375	1/12	0.017 (1)	0.017 (1)	0.017 (1)	0.017 (1)	0	0	0
F(2)	96 g	0.2197 (1)	0.3400 (1)	0.4494 (1)	1	0.0290 (7)	0.030 (1)	0.024 (1)	0.033 (1)	0.0104 (8)	-0.0021 (8)	-0.0031 (8)
O	32 e	0.0740 (1)	0.0740 (1)	0.0740 (1)	1/3	0.031 (1)	0.031 (1)	0.031 (1)	0.031 (1)	-0.002 (1)	-0.002 (1)	-0.002 (1)
O(W)	96 g	0.1556 (2)	0.2436 (2)	0.3071 (2)	1	0.0401 (8)	0.034 (2)	0.055 (2)	0.031 (2)	0.002 (2)	-0.002 (2)	-0.018 (1)
H(1)	96 g	0.132 (4)	0.213 (3)	0.276 (4)	1	0.08 (2)						
H(2)	96 g	0.151 (4)	0.213 (4)	0.350 (4)	1	0.09 (2)						

Table 5. Interatomic distances ( $\text{\AA}$ ) for chukhrovite-(Ca).

Al-F(2) ( $\times 6$ )	1.803 (2)	S-O ( $\times 4$ )	1.481 (4)
Ca(1)-F(2) ( $\times 3$ )	2.317 (2)	Ca(2)-OW ( $\times 2$ )	2.190 (6)
Ca(1)-F(1)	2.383 (1)	Ca(2)-F(2) ( $\times 2$ )	2.39 (1)
Ca(1)-OW ( $\times 3$ )	2.455 (3)	Ca(2)-OW' ( $\times 2$ )	2.629 (6)
H(1)-OW	0.84 (1)	H(2)-OW	0.88 (1)
OW-O	2.819 (3)	OW-F(2)	2.819 (4)

400–4000  $\text{cm}^{-1}$  region. Absorption bands corresponding to vibrations of the  $\text{SO}_4$  group are located at 864 ( $\nu_1 \text{SO}_4$ ), 1077, and 1165  $\text{cm}^{-1}$  ( $\nu_3 \text{SO}_4$ ), whereas  $\text{H}_2\text{O}$  bending vibrations occur at 1618  $\text{cm}^{-1}$ , and  $\text{H}_2\text{O}$  stretching modes at 3233, 3349, 3504, and 3631  $\text{cm}^{-1}$ . Starting from these  $\text{H}_2\text{O}$  stretching wavenumbers, the correlation established by Libowitsky (1999) served to estimate the OW...O distances between oxygen atoms involved in hydrogen bonds. These distances are in the range 2.72–2.90  $\text{\AA}$ , in very good agreement with the OW...O distance of 2.819(3)  $\text{\AA}$  observed by single-crystal X-ray diffraction (Table 5).

The Raman spectrum (Fig. 5) was collected in the 100–3600  $\text{cm}^{-1}$  region using a Jobin-Yvon Horiba Labram spectrometer (linearly-polarized He-Ne laser,  $\lambda = 632.8 \text{ nm}$ ), equipped with an Olympus microscope. The spectrum is characterized by absorption bands related to the vibration of the sulphate group, at 449 ( $\nu_2 \text{SO}_4$ ), 553 ( $\nu_4 \text{SO}_4$ ), 977 ( $\nu_1 \text{SO}_4$ ), and 1112  $\text{cm}^{-1}$  ( $\nu_3 \text{SO}_4$ ). Vibrations of the water molecules occur at 1632 ( $\text{H}_2\text{O}$  bending), 3270, 3440, 3470, and 3560  $\text{cm}^{-1}$  ( $\text{H}_2\text{O}$  stretching). Low frequency bands, between 181 and 430  $\text{cm}^{-1}$ , are attributed to cations and lattice modes.

## 6. Discussion

Chukhrovite-(Ca) belongs to the chukhrovite group (Dana classification 12.01.05, Halides – Compound halides with miscellaneous anions – Chukhrovite group. Strunz classification 03.CG.10, Halides – Complex halides – Aluminiumfluorides with  $\text{CO}_3$ ,  $\text{SO}_4$ ,  $\text{PO}_4$ ), and corresponds to the Ca-rich equivalent of chukhrovite-(REE) (REE = Ce, Nd, Y)  $[\text{Ca}_3(\text{REE})\text{Al}_2(\text{SO}_4)\text{F}_{13}\cdot 12\text{H}_2\text{O}]$  in which REE are replaced by Ca, according to the substitution mechanism  $0.5 \square + 1 \text{REE}^{3+} = 0.5 \text{Ca}^{2+} + 1 \text{Ca}^{2+}$ . Chukhrovite-(Ca) also corresponds to the Al-rich equivalent of meniyailovite  $[\text{Ca}_4\text{AlSi}(\text{SO}_4)\text{F}_{13}\cdot 12\text{H}_2\text{O}]$ , in which calcium is inserted according to the substitution mechanism  $0.5 \square + \text{Si}^{4+} = 0.5 \text{Ca}^{2+} + \text{Al}^{3+}$ .

All members of the chukhrovite mineral group crystallize in space group  $Fd\bar{3}$ , with unit-cell parameters decreasing from the REE-bearing members to chukhrovite-(Ca). The shortest unit-cell parameter belongs to menyailovite (Table 6). X-ray powder diffraction patterns of chukhrovite-group minerals are similar, with the most intense peak located around  $d = 9.70 \text{ \AA}$ , except for chukhrovite-(Y) for which the most intense peak is located at  $d = 2.193 \text{ \AA}$ . Interestingly, only chukhrovite-(Ca) shows two fairly intense peaks at  $d = 5.053$  and  $1.915 \text{ \AA}$  (Table 6).

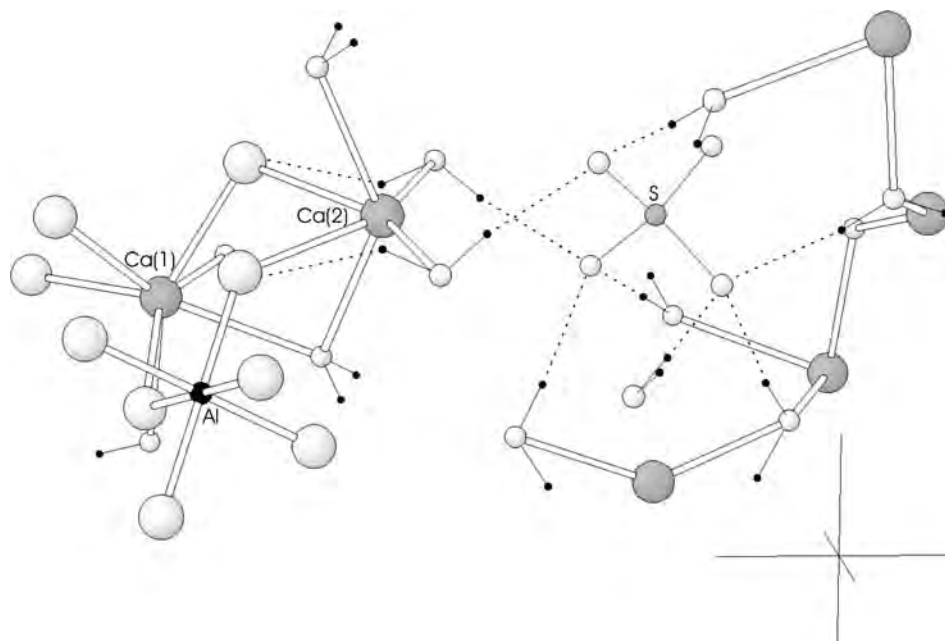


Fig. 3. The hydrogen bonding scheme in the crystal structure of chukhrovite-(Ca). Large black atoms = Al, small black atoms = H, large grey atoms = Ca, small grey atoms = S, large white atoms = F, and small white atoms = O and OW. The hydrogen bonds are dotted.

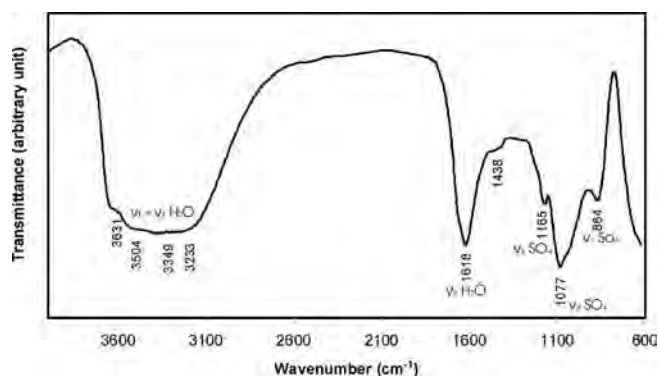


Fig. 4. Infrared spectrum of chukhrovite-(Ca).

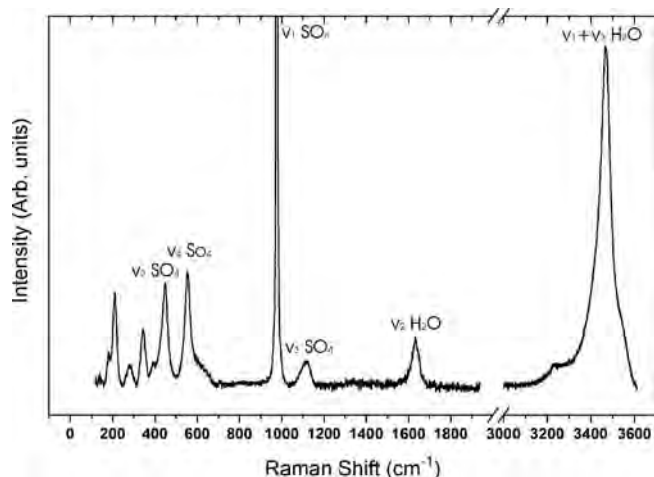


Fig. 5. Raman spectrum of chukhrovite-(Ca).

Compared to the structural data published for the synthetic  $\text{Ca}_4\text{AlSi}(\text{SO}_4)\text{F}_{13}\cdot 12\text{H}_2\text{O}$  compound (Mathew et al., 1981), the sample of chukhrovite-(Ca) investigated herein shows a supplementary Ca(2) position, located at  $-0.125\ 0.375\ 0.6030(9)$  (Table 1). This supplementary Ca position can be explained by the large Ca-content of the natural sample, which reaches 4.43 Ca *a.p.f.u.* (see above). The topology of this site (Fig. 2 and 3) corresponds to a distorted octahedron, in which Ca is coordinated by 4 water molecules and two F(2) atoms (Table 5). This coordination polyhedron is significantly different from that observed around the 7-coordinated Ca(1) atom, which rather corresponds to a distorted pentagonal bipyramid (Fig. 2 and 3).

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Table 6. Comparison of the physical properties for minerals of the chukhrovite group.

Mineral Reference	Chukhrovite-(Ca) This work	Chukhrovite-(Y) [1, 2]	Chukhrovite-(Ce) [3, 4]	Chukhrovite-(Nd) [5]	Menyailovite [6]
Ideal formula	$\text{Ca}_{4.5}\text{Al}_2(\text{SO}_4)\text{F}_{13} \cdot 12\text{H}_2\text{O}$	$\text{Ca}_3\text{YAl}_2(\text{SO}_4)\text{F}_{13} \cdot 12\text{H}_2\text{O}$	$\text{Ca}_3\text{CeAl}_2(\text{SO}_4)\text{F}_{13} \cdot 12\text{H}_2\text{O}$	$\text{Ca}_3\text{NdAl}_2(\text{SO}_4)\text{F}_{13} \cdot 12\text{H}_2\text{O}$	$\text{Ca}_4\text{AlSi}(\text{SO}_4)\text{F}_{13} \cdot 12\text{H}_2\text{O}$
Space group	$Fd\bar{3}$	$Fd\bar{3}$	$Fd\bar{3}$	$Fd\bar{3}$	$Fd\bar{3}$
<i>a</i> (Å)	16.749(1)	16.800(5)	16.800 (5)	16.759(3)	16.722(2)
Z	8	8	8	8	8
Strong X-ray lines	9.665 (100) 5.921 (31) 5.053 (16) 4.190 (10) 3.226 (15) 2.831 (4) 2.650 (7) 2.556 (10) 2.240 (7) 2.182 (12) 1.915 (17) 1.829 (6)	4.256 (70) 3.261 (90) 2.843 (80) 2.664 (70) 2.572 (90)	4.20 (50) 3.22 (70)	9.7 (100) 5.92 (70)	4.173 (40) 3.219 (70)
Density	2.25 (calc.)	1.834 (100) 1.684 (80)	1.824 (50)	1.827 (50)	1.824 (50)
<i>n</i>	1.432(1)	2.34(7) 1.43(1)	1.443(2)	2.42(3) 1.443(2)	2.25 1.430
Hardness	3.5(5)	3	White	3.5–4	–
Colour	Colourless	Colourless, white, lilac	White	Colourless, white	–
Morphology	{111}	{100}{111}	–	{100}{111}	–

Note: [1] Ermilova *et al.* (1960), [2] Fleischer (1960), [3] Walenta (1978), [4] Fleischer *et al.* (1980), [5] Pautov *et al.* (2005), [6] Vergasova *et al.* (2004).

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