

# Kristjánite, $\text{KNa}_2\text{H}(\text{SO}_4)_2$ , a new fumarolic mineral from Iceland containing $[\text{SO}_4\text{-H-SO}_4]^{3-}$ anion in the crystal structure

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## Abstract

Kristjánite,  $\text{KNa}_2\text{H}(\text{SO}_4)_2$ , is a new mineral found in a high-temperature fumarole on Fimmvörðuháls, Iceland. It is monoclinic,  $P2_1/n$ ,  $a$ ,  $b$ ,  $c$  (Å) = 6.9625(1), 9.9953(1), 11.0928(2),  $\beta = 105.637(2)^\circ$ ,  $V = 743.40(2)$  Å<sup>3</sup>.

Kristjánite forms colourless transparent crystals up to about 100 μm in size in compact aggregates with metathénardite, belomarinaite, apthitalite, ivsite and an unknown mineral with tentative composition  $\text{K}_2\text{NaH}(\text{SO}_4)_2$ , or grows in white globules of smaller grains on their surface. The eight strongest maxima in a Powder X-Ray Diffraction diagram are



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[ $d(\text{\AA})_{\text{intensity}}$ ] 4.37<sub>6</sub>, 3.65<sub>3</sub>, 3.48<sub>8</sub>, 3.36<sub>10</sub>, 3.18<sub>8</sub>, 2.83<sub>4</sub>, 2.73<sub>4</sub> and 2.405<sub>2</sub>. The mineral represents a novel crystal structure type. In it, K is coordinated by eight O atoms, and two symmetrically independent Na atoms by seven O atoms. Two symmetrically independent S atoms are in tetrahedral coordination by O atoms. A close to linear, very short hydrogen bond (2.44 Å), connects the two to a SO<sub>4</sub>-H-SO<sub>4</sub> dimer. K and Na coordination polyhedra share vertices, edges and even faces forming with sulphate tetrahedra a tight structure with narrow [100] channels lined on two opposite sides by hydrogen bonds.

**Keywords:** kristjánite, new mineral, KNa<sub>2</sub>H(SO<sub>4</sub>)<sub>2</sub>, SO<sub>4</sub>-H-SO<sub>4</sub> dimer, Icelandic fumarole

## Introduction

An eruption on Fimmvörðuháls, the pass that lies between Mýrdalsjökul and Eyjafjallajökul glaciers in south Iceland, began in March 2010. In June, July and September of 2010, Dr. Kristján Jónasson from the Icelandic Institute of Natural History collected a number of fumarolic samples, which formed on the fresh lava at Fimmvörðuháls and sent some fragments to the X-ray Diffraction Laboratory of the Department of Geosciences and Natural Resource Management of the Copenhagen University for analyses. We recognized an unknown powder diffraction pattern in the sample collected on 28<sup>th</sup> June from a new crater called Magni. Dr. Kristján Jónasson measured the temperature at the collection spot to be 670° C.

The new mineral was found in the part of the sample consisting of a seemingly glassy, greenish mass of metathénardite mixed with the new mineral and small amounts of belomarinaite (KNaSO<sub>4</sub>), apthitalite [K<sub>3</sub>Na(SO<sub>4</sub>)<sub>2</sub>], ivsite [Na<sub>3</sub>H(SO<sub>4</sub>)<sub>2</sub>], thénardite and kröhnkite (the last two being most probably products of a transformation of metathénardite at low temperatures after collection), with several unattributed diffraction lines. Blades of

belomarinaite and white globules made of tiny crystals of the new mineral overgrow the 'glassy' mass (Fig. 1).

We named the new mineral after Kristján Jónasson. The type material is deposited in the mineral collection of the Icelandic Institute of Natural History, Urriðaholtstræti 6–8, 210 Garðabær, Iceland, catalogue number 24468. IMA Commission on New Minerals Nomenclature and Classification approved the mineral and its name as IMA No. 2022-131 (Balić-Žunić *et al.*, 2023).

### Experimental methods

Chemical analyses were performed using a Scanning Electron Microscope with Energy Dispersive Spectrometer (SEM-EDS) Quanta FEG 200 ESEM equipped with a detector from Oxford Instruments, SDD x-max 80 mm<sup>2</sup>, at the Nanocenter, Danish Technical University.

The instrument has a superb resolution and is good as possible to this type of sensitive material. Acceleration voltage = 15 kV; beam current = 0.5 nA; beam diameter = 1.5 μm.

Powder X-ray Diffraction (PXRD) measurements were carried out using a Bruker-AXS D8 Advance Powder Diffractometer, operating in the Bragg-Brentano reflection geometry. The instrument is equipped with a primary Ge111 monochromator producing a CuKα1 (1.54059 Å) radiation and a silicon-strip LynxEye detector. A small quantity of powdered material was spread on the zero-background quartz plate covered by a thin film of silica fat (to prevent the sample from gliding off the plate during measurement) embedded in a variable height sample holder. The mounted sample was gently pressed by a glass slide and adjusted on the linear focus of the instrument. The measurements were made on rotating sample in steps of 0.02° 2θ with measuring time of four seconds per step, over a 2θ range of 5 to 90°.

Among the grains found in debris fallen from the sample, one hemimorphic grain showed clear X-ray diffraction and gave unit cell parameters consistent with those of the new mineral

phase observed by PXRD. Single-crystal X-ray Diffraction (SXRD) was performed on Supernova diffractometer (Rigaku Oxford Diffraction) equipped with a micro (Mo) X-ray source (wavelength 0.71073 Å) and a Pilatus Dectris 200K area detector. Details of the crystal structure, measurement and refinement are in Table 1. CrysAlisPro 1.171.40.55a (Rigaku Oxford Diffraction, 2019) program was used for data collection, data reduction, unit cell refinement and absorption correction. Empirical absorption correction was performed using spherical harmonics, implemented in SCALE3 ABSPACK scaling algorithm. The program JANA (Petříček *et al.*, 2023), including Charge-flipping method SUPERFLIP program (Oszlányi and Sütő, 2004; Palatinus and Chapuis, 2007) was used for structure solution and refinement.

## Results

### *Chemical composition*

The chemical measurements were done on six spots on a polished, largely porous sample embedded in EPOXY containing kristjánite and a mineral with tentative composition  $\text{K}_2\text{NaH}(\text{SO}_4)_2$  (Fig. 2). The results of the chemical analysis on kristjánite are represented in Table 2. Besides the elements cited in the table, we also measured Mg, Al, Si, Ca, Ti, Fe and Cu. Their quantities were under the detection limits in kristjánite.

The empirical formula for kristjánite, calculated by the charge balance, is  $\text{K}_{0.88}\text{Na}_{1.65}\text{HS}_2\text{O}_{7.76}$  (according to structural analysis, the mineral contains 1 H per formula unit). The ideal formula is  $\text{KNa}_2\text{H}(\text{SO}_4)_2$ , which requires K 14.05 wt.%, Na 16.53 wt.%, H 0.36 wt.%, S 23.05 wt.% and O 46.01 wt.%.

### *Powder X-ray diffraction*

The best PXRD was obtained from the white globules from the surface of the sample. According to Rietveld quantitative calculation (program Topas V.6 from Bruker-AXS,

fundamental parameters used to define profile shapes) it contained 86 wt.% kristjánite with 7 wt.% kröhnkite, 4 wt.% thénardite and 3 wt.% apthitalite (Fig. 3). We suppose that kröhnkite and thénardite, which are low temperature phases, are products of the decomposition of metastable metathénardite after sample collection and preparation. The numerical PXRD data for kristjánite are in Table 3. The unit cell parameters obtained through PXRD analysis are:  $a = 6.9632(3) \text{ \AA}$ ,  $b = 9.9950(4) \text{ \AA}$ ,  $c = 11.0939(4) \text{ \AA}$ ,  $\beta = 105.638(2)^\circ$ .

#### *Single crystal X-ray diffraction*

The structure solution (program SUPERFLIP based on charge flipping method) revealed the positions of all non-hydrogen atoms. The position of hydrogen was obtained from difference Fourier map after one isotropic refinement of the model obtained by structure solution. The last refinement was made with anisotropic displacement parameters for all atomic sites except the H site that was kept isotropic. Table 4 gives the atomic sites' parameters, whereas the other details of structure refinement are in Table 1 and in the deposited cif file.

Sulfur atoms at the S1 and S2 sites are in tetrahedral coordination with 3 bond lengths of 1.46 Å and the fourth over 1.5 Å, which is the distance to the O atom (O5 in S1 or O6 in S2 coordination) involved in the hydrogen bond. H sits approximately on a straight line between them distances 1.08(3) Å to O6 and 1.37(3) Å to O5, bond angle 176(3)°. Its total valence is 1.103 (from bond valence sum). The SO<sub>4</sub>-H-SO<sub>4</sub> dimer is shown on Fig. 4.

The potassium atom at the K1 site is in a distorted bis-disphenoid [coordination number (CN) 8 with bonds between 2.8 and 3.1 Å].

The sodium atoms at the Na1 and Na2 sites are in a CN 7 coordination best described as a split octahedron (Na1-O bond distances 2.36 to 2.97 Å, Na2-O 2.37 to 2.99 Å).

Table 5 contains the parameters of the coordination polyhedra. In Table 6 are bond valence sums for oxygens and in Table 7 all bond lengths save those in hydrogen, described earlier.

The general appearance of the crystal structure is the following: Sulphate tetrahedra and alkali atoms are arranged in layers parallel (100). The layers are interconnected through K-O, Na-O and hydrogen bonds. Sulphate tetrahedra and alkali atoms also form two—sulphate—tetrahedra thick slabs parallel (001), interconnected by K-O and Na-O bonds (Fig. 5).

K1 and Na2 coordinations share two triangular faces and thus form relatively straight chains along [100]. Na2 coordinations additionally share a vertex with one of the neighboring chains and thus connect chains in (010) wrapped sheets. SO<sub>4</sub> tetrahedra interconnect the sheets. Na1 coordinations that, taken alone, form [010] zigzag chains by mutually sharing two of the vertices, additionally connect K-Na2 sheets and SO<sub>4</sub> groups through vertex, edge, and face sharing. The 3D arrangement of K, Na and S coordination polyhedra forms a tight structure that features narrow [100] channels around inversion centers at  $x,0,0$  and  $x,1/2,1/2$ , lined along the two narrow opposite sides by hydrogen bonds, and along the two longer by K and Na2 coordination polyhedra (Fig. 6).

## Discussion

Kristjánite belongs to the mineral crystal structure group 7AD: anhydrous sulphates with only large cations (Strunz and Nickel, 2001). It moreover contains SO<sub>4</sub>-H-SO<sub>4</sub> dimers where very short hydrogen bond (<2.5 Å) connects two SO<sub>4</sub> groups. In letovicite, (NH<sub>4</sub>)<sub>3</sub>H(SO<sub>4</sub>)<sub>2</sub> (Leclaire et al., 1985), Rb<sub>3</sub>H(SO<sub>4</sub>)<sub>2</sub> (Swain and Row, 2007) and K<sub>3</sub>H(SO<sub>4</sub>)<sub>2</sub> (Oh et al., 2019) the hydrogen is placed symmetrically, whereas in ivsite, Na<sub>3</sub>H(SO<sub>4</sub>)<sub>2</sub> (Joswig et al., 1982) and kristjánite it is asymmetrical but with a small difference between the donor and acceptor bonds (1.16, 1.28 Å in Na<sub>3</sub>H(SO<sub>4</sub>)<sub>2</sub> and 1.08, 1.37 Å in kristjánite). The differences in crystal structures between kristjánite and other structures with (SO<sub>4</sub>)-H-(SO<sub>4</sub>) dimers are profound and it thus represents a novel structure type.

## Conclusions

The new mineral, kristjánite, was found in association with metathénardite, belomarinaite, apthitalite and ivsite at a high-temperature fumarole ( $\geq 600^\circ\text{C}$ ) on Fimmvörðuháls, south Iceland. Its chemical formula is  $\text{KNa}_2\text{H}(\text{SO}_4)_2$ . It is most probably formed through a reaction between lava minerals (sanidine and augite) and  $\text{SO}_2$  and probably  $\text{H}_2\text{O}$  from volcanic gas. It has a unique crystal structure for which we could not find a closely related counterpart. It contains the  $\text{SO}_4\text{-H-SO}_4$  dimers featuring an almost straight linear and very short ( $< 2.5 \text{ \AA}$ ) hydrogen bond observed also in some other  $\text{A}_3\text{H}(\text{SO}_4)_2$  compounds (where A stands for large monovalent cations).

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Competing interests: The authors declare none.

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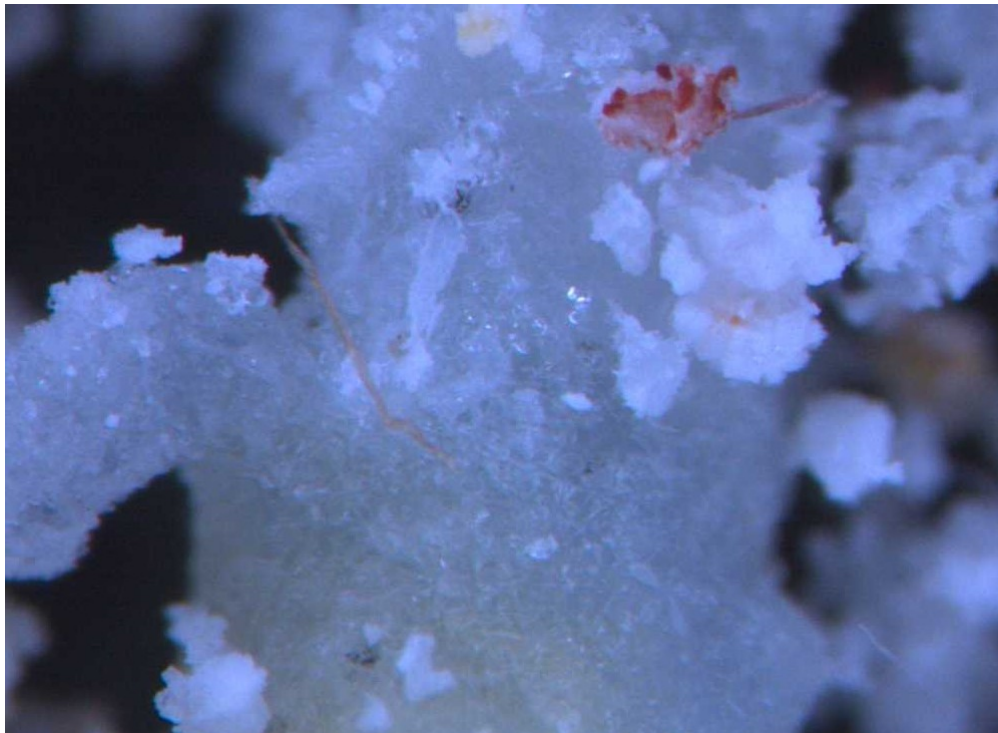
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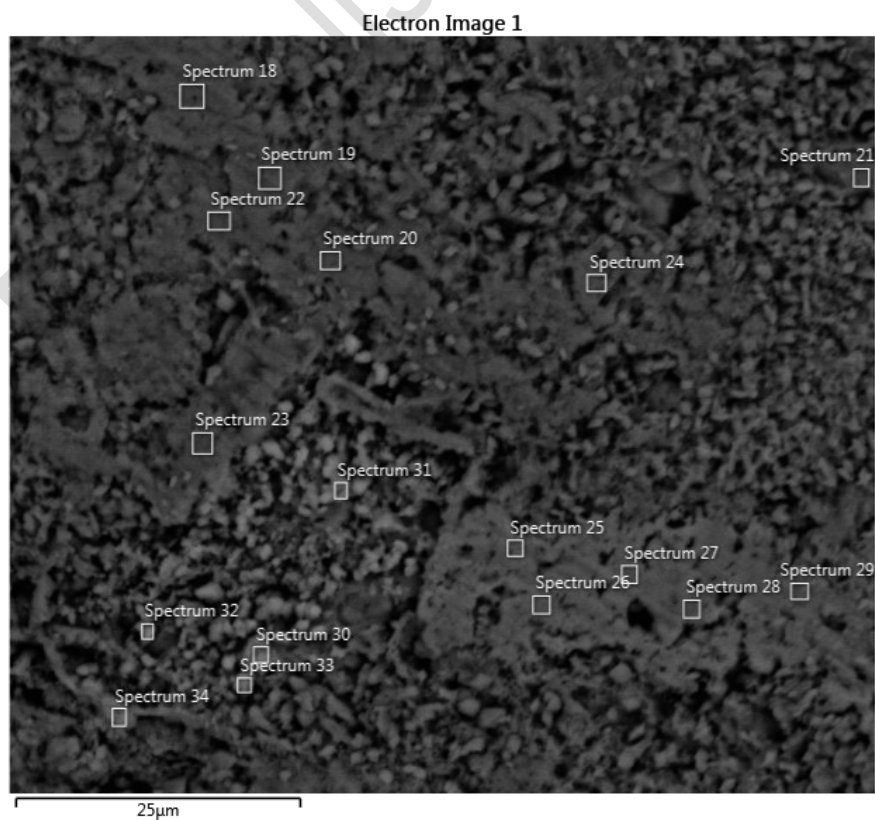


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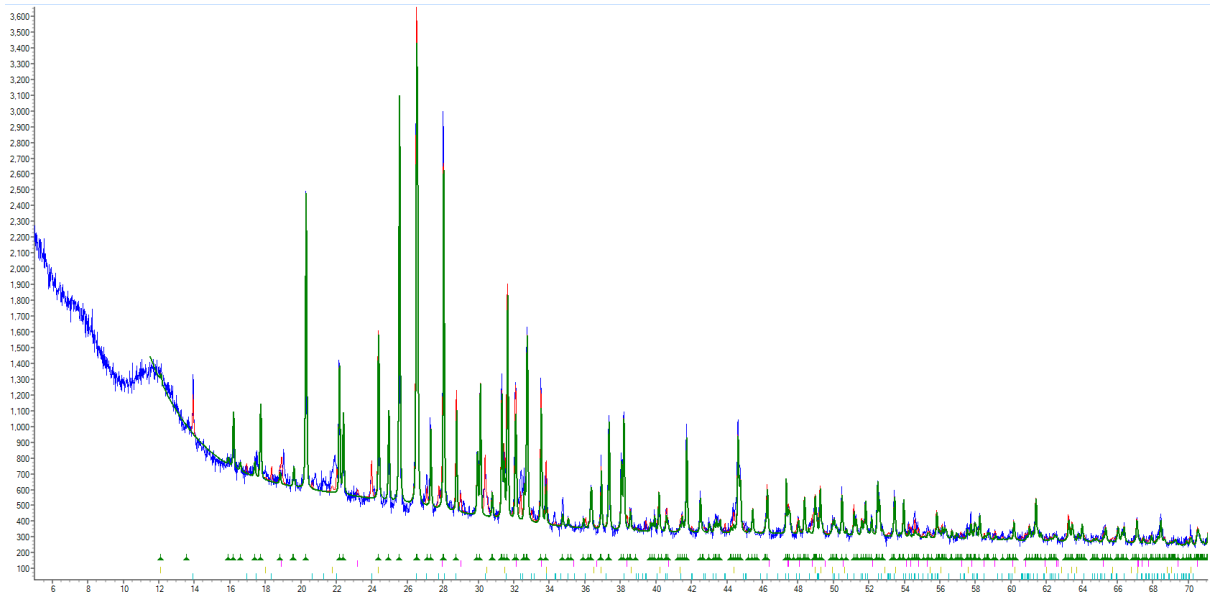
## Figure captions



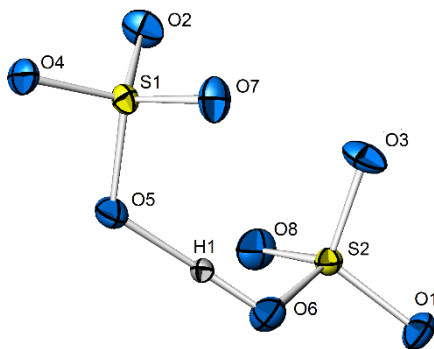
**Fig. 1.** White globules of kristjánite on the surface of a blade of belomarinaite. The actual width of photograph is 1 mm.



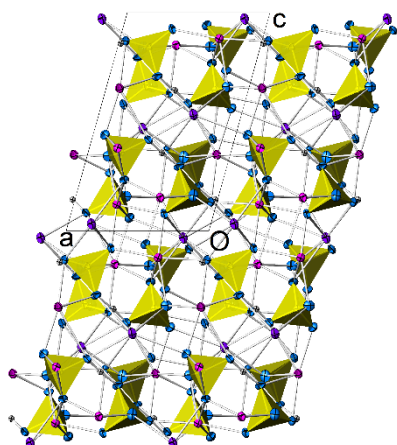
**Fig. 2.** Back-scattered electron image of the sample where chemical composition of kristjánite was determined. Spots 18-20 + 22-24: kristjánite. Spots 25-29: mineral with tentative composition  $K_2NaH(SO_4)_2$ .



**Fig. 3.** Powder X-ray diffraction diagram of a sample containing 86 wt% kristjánite with small amounts of kröhnkite and thénardite, probably formed from metathénardite on cooling and apthitalite (Rietveld analysis by program Topas V.6, Bruker-AXS). Green: calculated pattern of kristjánite, blue: experimental pattern, red: theoretical pattern.

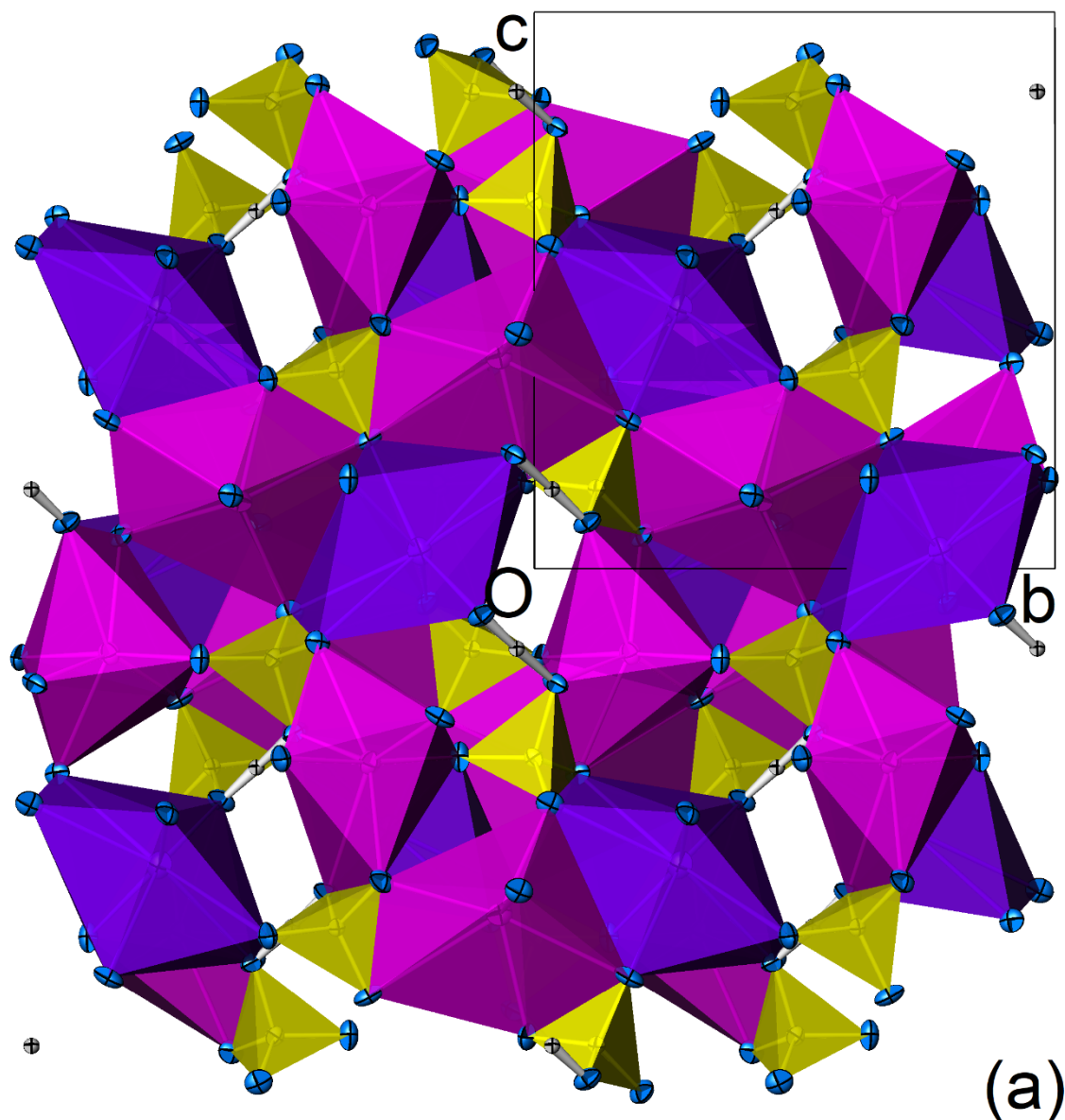


**Fig. 4.**  $SO_4$ -H- $SO_4$  dimer. Atomic displacement ellipsoids drawn at the 50% probability level.



**Fig. 5.** Crystal structure viewed along [010]. Dark violet = K atoms, magenta = Na atoms, yellow = S coordinations, blue = O atoms, grey = H atoms. One unit cell indicated. Atomic displacement ellipsoids drawn at the 50% probability level.

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**Fig. 6.** Crystal structure along [100]. Dark violet = K coordinations, magenta = Na coordinations, yellow = S coordinations, blue = O atoms, grey = H atoms. One unit cell indicated. Atomic displacement ellipsoids drawn at the 50% probability level.

### Table captions

**Table 1.** Details of the crystal, SXRD measurement and crystal structure refinement.

<b>Crystal data</b>	
Crystal formula	$\text{KNa}_2\text{H}(\text{SO}_4)_2$
Crystal system, space group	Monoclinic, $P2_1/n$
$a, b, c$ (Å)	6.9625(1), 9.9953(1), 11.0928(2)
$\beta$	105.637(2)°
$V$ (Å <sup>3</sup> )	743.40(2)

Reflections for unit cell refinement	14232, 2.773°-31.849° 2 $\theta$
Z	4
Calculated density (g cm <sup>-3</sup> )	2.4856
$\mu$ (mm <sup>-1</sup> )	1.403
Crystal description	Colourless columnar
Crystal dimensions (mm)	0.150 × 0.100 × 0.075
<b>Data collection</b>	
Temperature (K)	293
Radiation type and wavelength (Å)	X-rays, 0.71073
Absorption correction	Multi-scan
$T_{\min}$ , $T_{\max}$	0.88896, 1.00000
$\theta_{\min}$ , $\theta_{\max}$	2.79°, 31.91°
Indices range	-10 ≤ h ≤ 10, -14 ≤ k ≤ 14, -16 ≤ l ≤ 15
Measured fraction	0.98
$R_{\text{int}}$	0.0163
<b>Refinement</b>	
Reflections	2427
Observed ( $I > 3 \sigma_I$ )	2258
$R_1$ ( $I > 3 \sigma_I$ )	1.87%
$R_1$ (all)	2.04%
wR (all)	3.68%
GoF	1.878
Weighting function	$w = 1/\sqrt{[(\sigma^2)F_o + (0.016F_o)^2]}$
Parameters	122
Residual $\rho_e$ (+, -)	0.37, -0.30

**Table 2.** Chemical data (in wt.%) for kristjánite.

Constituent	Mean	Range	Stand. Dev. ( $\sigma$ )	Reference Material
Na	14.51	13.81-15.28	0.61	Blödite
K	13.11	11.43-15.07	1.18	Leonite
S	24.48	24.26-24.77	0.20	Blödite
O	43.75	41.36-47.83	2.38	Blödite
<b>Total</b>	<b>95.87</b>	92.95-99.02	2.29	

**Table 3.** Powder X-ray diffraction data ( $d$  in Å) for kristjánite. Intensities of the eight strongest diffraction maxima are in bold.

$I_{\text{meas}}$	$d_{\text{meas}}$	$d_{\text{calc}}$	$hkl$	$I_{\text{meas}}$	$d_{\text{meas}}$	$d_{\text{calc}}$	$hkl$
9	5.46	5.46	1 1 -1	4	2.175	2.176	3 0 -3
5	5.06	5.09	1 0 1				1 1 -5
13	5.00	5.00	0 2 0	21	2.162	2.163	1 3 3
4	4.71	4.71	0 1 2	8	2.125	2.126	3 1 -3
4	4.52	4.53	0 2 1	3	2.101	2.102	3 2 -1
<b>59</b>	4.37	4.37	1 1 -2			2.089	0 1 5
27	4.00	4.01	1 2 0			2.084	0 3 4
16	3.97	3.97	1 2 -1			2.078	3 0 1
<b>32</b>	3.65	3.65	0 2 2	3	2.082	2.074	1 4 2
			1 0 -3	5	2.040	2.040	3 2 0
18	3.57	3.57	1 2 1	22	2.028	2.029	2 4 -1
<b>78</b>	3.48	3.48	1 1 2			2.026	1 2 -5
		3.36	1 1 -3	13	2.023	2.024	2 3 2
			0 1 3	5	1.994	1.995	3 2 -3
<b>100</b>	3.36	3.35	2 0 0	10	1.960	1.961	3 1 -4
19	3.26	3.26	2 0 -2	10	1.918	1.919	3 2 1
			0 3 1			1.914	2 4 1
<b>76</b>	3.18	3.18	2 1 0	6	1.912	1.911	1 5 -1
23	3.10	3.10	2 1 -2	4	1.893	1.893	1 0 5
			1 3 0			1.881	1 3 4
13	2.98	2.98	1 2 2	7	1.880	1.880	2 4 -3
24	2.97	2.97	1 3 -1			1.859	2 0 4
5	2.90	2.90	0 2 3	8	1.858	1.856	3 1 2
28	2.85	2.85	2 2 -1	9	1.849	1.849	1 4 -4

			2 1 1		1.825	0 4 4	
13	2.84	2.84	1 0 3		1.822	3 3 -3	
<b>43</b>	2.83	2.83	0 3 2		1.818	1 1 -6	
		2.79	1 3 1	3	1.821	1.816	2 3 3
27	2.79	2.78	2 2 0	10	1.806	1.807	3 0 -5
9	2.75	2.75	2 1 -3	5	1.783	1.784	2 0 -6
			1 1 3	4	1.780	1.780	0 0 6
<b>38</b>	2.73	2.73	2 2 -2	7	1.763	1.763	3 3 1
27	2.67	2.67	0 0 4	4	1.752	1.753	0 1 6
10	2.65	2.65	1 1 -4	11	1.742	1.742	2 2 4
6	2.58	2.58	0 1 4	8	1.739	1.739	4 0 -2
3	2.50	2.50	0 4 0			1.715	3 3 -4
		2.471	1 2 3	9	1.713	1.713	4 1 -2
9	2.469	2.468	2 1 2			1.699	3 4 -1
			0 4 1	7	1.698	1.698	3 0 3
15	2.432	2.433	2 0 -4	3	1.689	1.690	3 4 -2
<b>23</b>	2.405	2.406	2 3 -1	5	1.645	1.646	0 6 1
		2.364	2 1 -4	5	1.595	1.595	1 1 6
15	2.362	2.363	2 3 0			1.590	0 6 2
23	2.354	2.355	0 2 4			1.589	4 2 0
5	2.332	2.334	1 4 -1	3	1.589	1.588	3 3 -5
4	2.256	2.257	3 1 -1	5	1.583	1.583	1 6 1
6	2.243	2.243	1 4 1			1.573	2 5 2
		2.223	1 4 -2	2	1.571	1.570	0 3 6
		2.222	1 1 4	4	1.537	1.537	2 2 5
		2.220	2 3 1				
5	2.219	2.216	1 0 -5				



**Table 4.** Fractional atomic coordinates and equivalent isotropic displacement parameters or isotropic displacement parameter (for H) ( $\text{\AA}^2$ ).

Site	x	y	z	$U_{\text{eq}}/U_{\text{iso}}(\text{H})$
K1	0.83569(4)	0.77976(3)	0.03181(3)	0.02503(9)
S1	0.77920(4)	0.49878(2)	0.83958(2)	0.01453(8)
S2	0.27181(3)	0.88062(2)	0.85599(2)	0.01350(8)
Na1	0.30316(7)	0.56670(5)	0.87861(4)	0.02187(14)
Na2	0.40630(7)	0.81654(5)	0.15175(4)	0.02063(14)
O1	0.41776(13)	0.79390(9)	-0.06059(8)	0.0239(2)
O2	0.65292(13)	0.53007(9)	-0.07806(8)	0.0238(3)
O3	0.69272(13)	0.68159(10)	0.23334(8)	0.0261(3)
O4	0.95573(11)	0.58344(8)	0.86794(8)	0.0210(2)
O5	0.16436(13)	0.95943(9)	0.20573(8)	0.0245(3)
O6	0.10310(13)	0.89839(9)	-0.08331(8)	0.0232(2)
O7	0.17851(13)	0.64306(8)	0.16189(9)	0.0258(3)
O8	0.65071(14)	0.98685(8)	0.15899(9)	0.0261(3)
H1	0.010(4)	0.036(3)	0.138(3)	0.093(9)

**Table 5.** The parameters of the coordination polyhedra calculated with the program IVTON (Balić Žunić and Vicković, 1996). Notes: CN = coordination number;  $\langle d \rangle$  = average bond length; bvs = bond valence sum, calculated using the exponential function of Brown & Altermatt (1985) with the parameters of Brese & O’Keeffe (1991);  $V_p$  = polyhedral volume; vd = volume distortion; asp = asphericity; ecc = eccentricity.

Cation	CN	$\langle d \rangle$ ( $\text{\AA}$ )	bvs	$V_p$ ( $\text{\AA}^3$ )	vd	asp	ecc
K1	8	2.904	1.029	37.94(3)	0.1479	0.0368	0.0260
S1	4	1.477	5.981	1.647(2)	0.0012	0	0.0455
S2	4	1.473	6.020	1.637(2)	0.0008	0	0.0281
Na1	7	2.538	1.096	22.35(2)	0.1241	0.0795	0.0997
Na2	7	2.495	1.201	22.46(2)	0.0733	0.0741	0.0978

**Table 6.** Bond valence sums (bvs) for oxygen atoms. The oxygens that participate in hydrogen bond are marked with \*.

oxygen	bvs
O1	2.09
O2	2.10
O3	2.01
O4	2.03
O5*	1.83
O6*	2.26
O7	1.99
O8	2.05

**Table 7**, The bond lengths in the coordination polyhedra of cations, hydrogen bond excluded (can be found in the text).

cation	oxygen	Sym.op. oxygen	Bond length (Å)
K1	O6	1+x, y, z	2.790(1)
	O7	1+x, y, z	2.791(1)
	O1	x, y, z	2.816(1)
	O3	x, y, z	2.855(1)
	O2	x, y, z	2.915(1)
	O4	x, y, -1+z	2.945(1)
	O8	x, y, z	2.986(1)
	O5	1+x, y, z	3.131(1)
S1	O7	1-x, 1-y, 1-z	1.449(1)
	O4	x, y, z	1.455(1)
	O2	x, y, 1+z	1.462(1)
S2	O5	$\frac{1}{2}+x, \frac{1}{2}+1-y, \frac{1}{2}+z$	1.542(1)
	O8	1-x, 2-y, 1-z	1.457(1)
	O1	x, y, 1+z	1.461(1)
Na1	O3	$-\frac{1}{2}+x, \frac{1}{2}+1-y, \frac{1}{2}+z$	1.462(1)
	O6	x, y, 1+z	1.514(1)
	O2	1-x, 1-y, 1-z	2.358(1)
	O2	x, y, 1+z	2.380(1)
	O4	-1+x, y, z	2.396(1)
	O8	$-\frac{1}{2}+x, \frac{1}{2}+1-y, \frac{1}{2}+z$	2.440(1)
Na2	O1	x, y, 1+z	2.441(1)
	O3	1-x, 1-y, 1-z	2.779(1)
	O3	$-\frac{1}{2}+x, \frac{1}{2}+1-y, \frac{1}{2}+z$	2.975(1)
	O7	x, y, z	2.373(1)
	O3	x, y, z	2.375(1)
	O1	x, y, z	2.389(1)
	O8	x, y, z	2.393(1)
	O5	x, y, z	2.404(1)
	O4	$-\frac{1}{2}+x, \frac{1}{2}+1-y, \frac{1}{2}+z$	2.535(1)

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