On the unit cell of calcium potassium sulphate hydrate: synthetic and natural syngenite.

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Summary. The space group and unit cell of natural syngenite have been redetermined. X-ray powder photographs of natural syngenite and synthetic $CaSO_4.K_2SO_4.H_2O$ were found to be practically identical. Optical and d.t.a. data are also given.

A MATERIAL causing a dark stain to appear on the surface of a gypsum building plaster could not be satisfactorily identified using the data available in the A.S.T.M. Index (1955). Other evidence suggested that the material was produced by the interaction of dissolved potassium sulphate with the gypsum. An attempt to form the material under controlled conditions was successful, and the product proved to be syngenite. Since the two published reports on the unit cell of the mineral showed significant differences, a redetermination of the unit cell was carried out on the synthetic material and also on natural crystals.

The synthetic mineral was prepared as follows: a cake of gypsum plaster, about 5 mm. thick, was partly immersed in a shallow dish of K_2SO_4 solution at room temperature; after two weeks the slab was taken out and dried in the air. When the crusty surface was removed, the soft white core was found to be homogeneous and was identified as syngenite.

Chemical analysis by Mrs. A. J. Green gave: CaO 17·1, K_2O 28·1 (by difference), SO_3 48·6, insoluble residue 0·6 (probably gypsum and quartz, as shown by X-ray analysis of the residue), loss at 700° C. 5·6 %. This can be represented by formula $CaSO_4.0{\cdot}98K_2SO_4.1{\cdot}02H_2O$. Under a microscope the crystals appear as birefringent needles, showing straight extinction, positive elongation, $\alpha = 1{\cdot}500$, $\gamma = 1{\cdot}518$, in agreement with data for natural syngenite. Specific gravity 2·56–2·58.

Differential thermal analysis shows a larger endothermic peak at 285° C., smaller peaks at 440° and 560° C., and a medium peak at 880° C. Bodaleva and Lepeshkov (1956) recorded peaks at 265°, 430°, 560°, 880°, and 950° C.

Natural syngenite from Glückauf, Sondershausen, Thuringia (B.M. 1913,368), was kindly supplied by Dr. G. F. Claringbull.

X-ray investigation. The unit cell and space group of syngenite have been determined by single crystal methods by Laszkiewicz (1936) on a sample from Kalusz, and by Kurylenko (1954) on a sample of unknown origin; an abstract only of the latter paper has been published. Both found syngenite to be monoclinic, space group $P2_1/m–C^2_{2h}$ ($0k0$ reflections appear only when k is even), but the axial lengths differ significantly. Their results, together with those of the present investigation, are given in table I.

TABLE I. The unit cell of syngenite.

Author.	Sample.	*a.*	*b.*	*c.*	*β.*
Laszkiewicz	Single crystal	9·72	7·16	6·21 Å.*	104°
Kurylenko	Single crystal	9·55	7·13	6·00 Å.*	105°
Aruja	Synthetic, powder	9·775	7·156	6·251 Å.	104·0°
Aruja	Natural, powder	9·771	7·146	6·251 Å.	104·02°
Aruja	Natural, single crystal	9·774	7·156	6·249 Å.	133·95°

Axial ratios: X-ray method: synthetic, powder .. 1·3660 : 1 : 0·8735
Optical goniometry (Dana, 7th edn) .. 1·3691 : 1 : 0·8747

* Converted into Å. units from kX.

The present work confirms the space group found by earlier workers, but the axial lengths are found to be closer to those given by Laszkiewicz.

Oscillation and rotation photographs of single crystals of the natural mineral were taken about the *b*- and *c*-axes in a 6-cm. diameter camera, with filtered Cu-$K\alpha$ radiation. Powder photographs were taken in an 18-cm. diameter Debye-Scherrer camera (Co-radiation) as well as in a focusing camera of slightly higher resolution (Cu-radiation). The powder patterns of the synthetic and natural syngenite are practically identical. Only the difference of 0·01 Å. in the length of the *b*-axis, shown in table I, seems to exceed the limit of probable error.

The powder data for both natural and synthetic syngenite are reproduced in table II. This records substantially more lines than the card in the A.S.T.M. index (1955). Comparison with the table of $\sin^2\theta$ values given by Bodaleva and Lepeshkov (1956) is made difficult because the X-ray wavelength they used is not stated. Assuming two molecules of $K_2Ca(SO_4)_2.H_2O$ in the unit cell, the calculated density is 2·570 g./c.cm., which compares well with the measured density of the synthetic mineral, 2·56–2·58. For natural syngenite the figures are $D_{calc.} = 2·575$ and $D_{obs.} = 2·579$ (Dana, 7th edn).

TABLE II. X-ray powder data for syngenite. Camera diameter 18·4 cm., Co-$K\alpha$ radiation (λ 1·7902 Å.). The three strongest lines are italicized. Natural syngenite from Glückauf, Sondershausen, Thuringia (B.M. 1913,368). Synthetic syngenite: calcium sulphate di-hydrate slab soaked in K_2SO_4 solution. Indices calculated for a monoclinic cell with *a* 9·775, *b* 7·156, *c* 6·251 Å., β 104·0°; the relative importance of jointly contributing planes has not been assessed. Intensities for the natural mineral were obtained by a calibrated strip, and can be taken to apply to the synthetic material. *b*, broad line, *D*, doublet, resolved on focusing camera; n.m., not measured because of weakness. $\Delta = 4\sin^2\theta_{obs.} - 4\sin^2\theta_{calc.}$.

Natural.		Synthetic.			
d.	*I.*	*d.*	$4\sin^2\theta_{obs.}$	*hkl.*	$\Delta.10^4$
9·514	*62*	*9·522*	0·0353	100	−3
5·716	56	5·712	0·0982	110	0
4·748	9	4·743	0·1425	200	0
4·630	38	4·626	0·1499	011 101	+2 +2
4·499	19	4·501	0·1582	$11\bar{1}$	−2
3·951	8	3·960	0·2046	210	−5
3·884	15	3·889	0·2123	111	0
3·571	19	3·573	0·2508	020	+4
3·348	22	3·350	0·2681	201 120	+26 +1
3·157	*75*	*3·161*	0·3206	300	0
3·110	6	3·114	0·3300	$30\bar{1}$ $10\bar{2}$	+31 −2
3·035	34	3·035	0·3482	$12\bar{1}$ 211 002	+21 +21 −3
2·953	1	not obs.			
2·896	12	2·896	0·3832	310 $20\bar{2}$	0 0
2·857	*100*	*2·860*	0·3922	$11\bar{2}$ 220	−6 −7
2·823	22	2·827	0·4013	121	+12
2·789	22	2·791	0·4111	012	0
2·740	38	2·741	0·4264	$22\bar{1}$	+3
2·702	5	2·705	0·4378	102	−2
n.m.	1	2·680	0·4460	$21\bar{2}$	+2
2·511	25	2·514	0·5071	$30\bar{2}$	−3
2·447	4	2·449	0·5342	221	+3
2·408	5	2·412	0·5512	$40\bar{1}$ 311	+19 0
2·373	5	2·369	0·5708	$31\bar{2}$ 400 320	+8 +8 −2
2·353	18	2·353	0·5784	$32\bar{1}$ $12\bar{2}$	+11 −22
2·313	10	2·314	0·5984	202 022 130	−4 −5 −5
2·287	1	2·289	0·6116	$41\bar{1}$	−3
2·247	1	2·249	0·6337	410 $22\bar{2}$	+9 +1
n.m.	1	2·219	0·6512	031	+8
2·200	2	2·200	0·6625	$13\bar{1}$ 212	+34 +11
n.m.	1	2·132	0·7049	230 $40\bar{2}$	−7 +20
2·083	19	2·082	0·7391	$23\bar{1}$ 321 $10\bar{3}$	+1 +1 +2
2·045	22	2·047	0·7646	401 $20\bar{3}$ $41\bar{2}$	−3 −3 −9
1·999	6	2·001	0·7999	$42\bar{1}$ $11\bar{3}$	+2 −16
1·963	18	1·965	0·8305	411 $21\bar{3}$ 302	+30 +30 −3
1·943	15*D*	1·945	0·8482	013 231 222	+15 +14 −10
1·901	5	1·904	0·8839	330	0
1·892	10	1·892	0·8947	500 312 $13\bar{2}$	+41 +13 +12
1·872	8	1·875	0·9118	032	0
1·836	4	1·839	0·9478	$23\bar{2}$	+13
n.m.	1	1·819	0·9685	113 $50\bar{2}$	+53 −11
1·787	22	1·788	1·0027	132 040	+14 +13
n.m.	1	1·777	1·0155	421 $22\bar{3}$	+2 +2
1·759	2	1·761	1·0339	$40\bar{3}$ $51\bar{2}$ 023	+32 +17 −6
n.m.	1	1·745	1·0520	331	+1
1·728	2	1·730	1·0702	$33\bar{2}$	−5
n.m.	1	1·712	1·0933		
n.m.	1	1·696	1·1137		
n.m.	1	1·676	1·1411		
n.m.	1	1·669	1·1499		
n.m.	1	1·661	1·1617		
n.m.	1	1·591	1·2654		
n.m.	1	1·581	1·2826		
n.m.	1	1·567	1·3050		
1·556	8*b*	1·556	1·3248		
1·530	4	1·532	1·3664		
1·483	2	1·484	1·4566		
n.m.	2*b*	1·450	1·5253		
n.m.	1	1·428	1·5713		
n.m.	1	1·417	1·5957		
n.m.	1	1·397	1·6415		
1·369	5*b*	1·370	1·7068		
n.m.	2	1·351	1·7572		
n.m.	1	1·340	1·7864		
n.m.	1	1·330	1·8129		
1·321	6*b*	1·321	1·8351		
&c.		&c.			

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