

CONTRIBUTIONS TO THE SYSTEMATICS OF FLUROSILICATES  
AND FLUOROGERMANATES. II.\*

THE  $\text{Ca}_{12}\text{Al}_2(\text{SiF}_6)_4(\text{SO}_4)_3\text{F}_{16}\cdot 45\text{H}_2\text{O}$  COMPOUND

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Compound  $\text{Ca}_{12}\text{Al}_2(\text{SiF}_6)_4(\text{SO}_4)_3\text{F}_{16}\cdot 45\text{H}_2\text{O}$  was studied. A reproducible preparative method was found and the compound was characterized by both chemical analysis and by Debye-Scherrer X-ray method. It was found that the substance crystallizes with the highest probability in the cubic system. The space groups  $O^5-I 4 3$  or  $T^3-I 4 3m$  can be assumed from the absence of reflexes of  $(hk1)$  type for  $h + k + 1 = 2n + 1$ , and of  $(hk0)$  for  $h + k = 2n + 1$  and of  $(h00)$ , where  $h$  is an odd number.

Caron and Vanboeckstaël<sup>1</sup> prepared a compound of the above mentioned composition by reaction of fluorosilicic acid, calcium chloride and aluminum sulfate. Initiative of their study came from the fact of producing a insoluble compound during a reaction of hydrofluoric acid that was contaminated with sulfuric acid and of calcium aluminate glass. The exact composition of the compound was not presented.

As the authors started only from analytical data and microscopic observation, we tried to confirm existence, composition and individuality of the compound. In the crystal lattice of the compound there should be in addition to anions of  $\text{SiF}_6^{2-}$  also anions of  $\text{F}^-$  and  $\text{SO}_4^{2-}$ . It would be a more complicated type of salt than the double salts of the  $\text{A}_3(\text{XF}_6)\text{F}$  type (where X is Si or Ge), which were described in previous communication<sup>2</sup>.

#### EXPERIMENTAL

*Preparation:* 25 ml of 15% aqueous solution of  $\text{Al}_2(\text{SO}_4)_3$  was added to 50 ml of 35%  $\text{H}_2\text{SiF}_6$ . Then 500 ml of 1% aqueous solution of  $\text{CaCl}_2\cdot 6\text{H}_2\text{O}$  was being added during 2–3 minutes. White crystalline precipitate was filtered off, washed by water and by alcohol, and dried in air at room temperature.

*Analysis.* The total content of fluorine was determined by titration with 0.04M- $\text{Th}(\text{NO}_3)_4$  using alizarine as indicator. Fluorine was in preceding operation separated by distillation as fluorosilicic acid. Anion  $\text{SO}_4^{2-}$  was determined as barium sulfate, silicium as silicic acid by Hoffman-Lundell method<sup>3</sup>. Calcium was determined as oxalate and aluminum by complexometry according

\* Part I: This Journal 35, 2494 (1970).

to Paleček<sup>4</sup> using xylene blue as indicator. Water was determined by drying the sample up to a constant weight at 150°C in the presence of PbO to prevent loss of SiF<sub>4</sub>.

For Ca<sub>12</sub>Al<sub>2</sub>(SiF<sub>6</sub>)<sub>4</sub>(SO<sub>4</sub>)<sub>3</sub>F<sub>16.45</sub> H<sub>2</sub>O (2509) calculated: 4.47% Si, 30.35% F, 19.17% Ca, 11.50% SO<sub>4</sub>, 2.15% Al, 32.35% H<sub>2</sub>O; found: 4.42% Si, 30.71% F, 18.90% Ca, 11.13% SO<sub>4</sub>, 2.00% Al, 32.81% H<sub>2</sub>O.

*X-ray measurements:* Debye-Scherrer records were obtained on Mikrometa II (Chirana). Radiation CuK<sub>α</sub> = 1.548 Å, 40 kV, 21 A, exposure time 3 hours. Chamber diameter 114.7 mm, diameter of aperture 1 mm. Gelatine capillaries and Agfa-Laue photomaterial were used. Microscopic observation were performed on polarizing microscope, density was determined by pycnometric method at 26°C in xylene.

## RESULTS

It was found that the method published by Caron and Vanboeckstael<sup>1</sup> does not provide the pure substance, but the product that is contaminated with calcium fluoride. Using the method described in experimental a white crystalline material was ob-

TABLE I

Diffraction Record of Ca<sub>12</sub>Al<sub>2</sub>(SiF<sub>6</sub>)<sub>4</sub>(SO<sub>4</sub>)<sub>3</sub>F<sub>16.45</sub> H<sub>2</sub>O

<i>I</i> / <i>I</i> <sub>0</sub>	<i>d</i> , Å	<i>h k l</i>
100	9.79	2 1 1
80	5.96	4 0 0
60	5.10	3 3 2
60	4.21	4 4 0
10	3.89	6 1 1
20	3.44	4 4 4
80	3.25	5 5 2, 6 3 3, 7 2 1
30	3.00	8 0 0
60	2.86	6 5 3
50	2.68	8 4 0
80	2.57	6 6 4
30	2.36	10 1 1, 7 7 2
60	2.26	9 5 0, 9 4 3
80	2.19	11 3 0, 9 7 0
5	2.10	11 4 1, 8 7 5
5	2.04	12 1 1, 11 5 0, 11 4 3
10	1.98	12 3 1, 9 8 3
10	1.83	10 6 6
90	1.79	12 6 0, 10 8 4
5	1.76	13 4 1, 11 8 1
5	1.72	13 5 0, 13 4 3, 12 7 1
10	1.62	13 7 0, 12 7 5, 11 9 4
10	1.61	12 8 4

tained the composition of which corresponded to the composition suggested by the above mentioned authors. Also the microscopic observation confirmed that the substance crystallizes in colourless octahedric crystals which are optically isotropic. After the indexes of individual diffraction lines of Debye records had been found, and after the lattice constant  $a_0 = 25.0$  had been analytically calculated, it followed that the prepared substance has, most probably, the cubic structure. From the absence of reflexes of  $(hkl)$  type for  $h + k + l = 2n + 1$ , and of  $(hk0)$  for  $h + k = 2n + 1$  and of  $(h00)$  for odd  $h$ , it can be assumed one of the following space groups:  $O^5-I 4 3$ ,  $T_d^3-I \bar{4} 3m$ . From the pycnometric density  $\rho_{pyc} = 2.66$  the number of configuration units  $Z = 9$  follows. On the basis of these results the existence of  $Ca_{12}Al_2(SiF_6)_4(SO_4)_3F_{16} \cdot 45 H_2O$  is fully confirmed. It is also the first case of a compound of  $M_{12}^{II}M_2^{III}(AF_6)_4(XO_4)_3F_{16} \cdot 45 H_2O$  type (where  $M^{II}$  is cation of a bivalent metal,  $M^{III}$  is cation of a trivalent metal,  $A = Si$  or  $Ge$  and  $X = S$  or  $Se$ ). This type of compounds could be represented by a series of compounds containing anions  $SiF_6^{2-}$  or  $GeF_6^{2-}$ ,  $F^-$ , and  $SO_4^{2-}$  or  $SeO_4^{2-}$ .

## REFERENCES

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