

## SYNTHETIC FIBROUS FLUORAMPHIBOLES AND THEIR PROPERTIES

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### ABSTRACT

Asbestiform fluoramphiboles with isomorphous substitutions of cations both in *A*, *M*(4) and *M*(1-3) positions have been synthesized by heating the fluorsilicate mixtures at 900-1100°C under atmospheric pressure.

Chemical, optical and X-ray data showed that monoclinic synthetic fluoramphiboles in which  $Mg^{2+}$  is partly substituted by  $Ni^{2+}$ ,  $Co^{2+}$ ,  $Zn^{2+}$ ,  $Cd^{2+}$  and  $Fe^{2+}$  can be referred to the richterite series. Isomorphous substitution  $Fe^{3+}$  for  $Mg^{2+}$  gives the Mg-fluorarfvedsonite, but substitution  $Cr^{3+}$  for  $Mg^{2+}$  gives intermediate member of the richterite-arfvedsonite fluoramphibole. There is a distinct tendency for increasing refractive indexes with increasing electronegativity of the substitute atom. The analysis of unit cell dimensions showed that the *M*(4) and *M*(2) are most probable structure positions for cation substitution of the fluorrichterite series under study.

Some of the physical and chemical properties of the fluoramphiboles were measured. The temperature ranges of the fluoramphibole decomposition are established to be 100-150° higher than those of the hydroxyamphiboles of the analogous compositions. Synthetic fibrous fluoramphiboles are nonhygroscopic and are stable in acid and alkali media.

### INTRODUCTION

The synthesis of fibrous amphiboles of an asbestos type is of great importance for solving a number of problems in geochemistry, mineralogy and physical chemistry of silicates. Production of artificial asbestos minerals is also aimed at the development of new commercial materials. Therefore the whole problem merits the attention of both engineers and scientists (Lüdke 1944; Comeforo and Kohn, 1954; Saito and Ogasawara, 1959; Gibbs *et al.*, 1962, Espig, 1962; Fedoseev *et al.*, 1966a). The present paper reports the synthesis of fibrous fluoramphiboles together with some of their physical and chemical properties.

### EXPERIMENTAL

Fibrous fluoramphiboles were synthesized by heating the initial mixtures of chemically pure reagents at 900-1100°C under atmospheric pressure. The initial composition of the mixture was that of the theoretical formula of the amphibole synthesized but with a definite fluorine excess. Fluxes in the form of a salt (such as NaCl; LiCl; NaCl+Na<sub>2</sub>CO<sub>3</sub>; NaCl+NaF) bearing a eutectic relationship with the fluoramphibole in the range 700-1000°C were introduced into the batch. The fluxes amounted to 20 percent of the weight of the major components. Tightly-closed platinum and ceramic crucibles were used to minimize the extent of fluoride volatilization. The batches were heated for 2 to 3 hours in an electric

<sup>1</sup> Deceased, June 14, 1968.

furnace to the temperature of the synthesis and maintained for 30–48 hours at this temperature, then the furnace was turned off.

The resulting products consist of an entangled, fibrous mass containing up to 80–90 percent fluoramphibole fibres, with impurities of quartz, fluorides, and minerals of the humite group. A brush of fibers of similar composition of up to 15–20 mm long and 1–2  $\mu\text{m}$  thick grows on the surface of this mass (Fig. 1). The length of the fibers in the bulk of the synthesized products is up to 1 mm, and the thickness is 0.1–2  $\mu\text{m}$ .

Studies of the conditions of formation of fluoramphiboles showed that the morphology of the crystals and the phase compositions of the products obtained are mainly affected by temperature and time of synthesis, and by the compositions of the initial batches (Fedoseev *et al.*, 1966b). The compositions of the fluoramphiboles under study were chosen considering isomorphic substitutions of cations in  $M(4)$  and  $M(1-3)$  positions. The synthesis of fibrous fluoramphiboles was carried out in order to study relations among composition, structure and properties of these minerals. Needle-like or fibrous crystals of the surface "brush" were used to identify the fluoramphiboles obtained and to study their properties. The materials for the experiments were selected under the binocular microscope.

Chemical analyses of the minerals synthesized were carried out by the microchemical method (Kalinina *et al.*, 1961). The results of the analyses and the chemical formula derived from them are given in Table 1.

Table 2 presents optical data obtained by using the immersion technique.

To calculate the unit cell dimensions of the synthesized fluoramphiboles, reflection roentgenograms  $hk0$  of separate fibers, as well as X-ray powder diagrams, were used. X-ray photographs were obtained using filtered Fe-radiation with a 114.6 mm Debye camera. The  $a \cdot \sin \beta$  value (reflections 600,800) and the  $b$  parameter (reflection 0.10.0, 0.12.0) were determined on the basis of the reflection roentgenograms  $hk0$ . The angle  $\beta$  and the parameter  $c$  (reflection 202,  $\bar{2}02$ ) were calculated according to the X-ray powder diffraction data, and also the  $a \cdot \sin \beta$  and  $b$  values were checked. X-ray data are summarized in Table 3.

#### RELATION OF STRUCTURAL AND OPTICAL PROPERTIES TO SITE OCCUPANCY

The chemical analysis, the optical and X-ray studies of the fluoramphiboles synthesized (Tables 1, 2, 3) show that NaMg-fluoramphibole is an analog to richterite. The fluoramphiboles in which  $\text{Mg}^{2+}$  is substituted by  $\text{Ni}^{2+}$ ,  $\text{Co}^{2+}$ ,  $\text{Zn}^{2+}$ ,  $\text{Mn}^{2+}$ ,  $\text{Cd}^{2+}$  and  $\text{Fe}^{2+}$  can be also referred to the richterite series. Isomorphous substitution of  $\text{Mg}^{2+}$  by  $\text{Fe}^{3+}$  leads to the formation of Mg-fluorarfvedsonite. By its chemical composition, a fluoramphibole containing  $\text{Cr}^{3+}$  occupies an intermediate position between arfvedsonite and richterite. Replacement of  $\text{Na}^+$  by  $\text{Li}^+$  causes the development of orthorhombic fluoramphibole.

The optical data summarized in Table 2 show that the substitution of hydroxyl for fluorine is accompanied by a considerable decrease in the refractive indexes of these minerals compared with the hydroxyl-amphiboles (Fedoseev *et al.*, 1968).

Some conclusions on the influence on the optical constants of the substitute atom can be seen in the richterite group, where one  $\text{Mg}^{2+}$  is substituted by  $\text{Mn}^{2+}$ ,  $\text{Cd}^{2+}$ ,  $\text{Zn}^{2+}$ ,  $\text{Co}^{2+}$ ,  $\text{Fe}^{2+}$ ,  $\text{Ni}^{2+}$ .

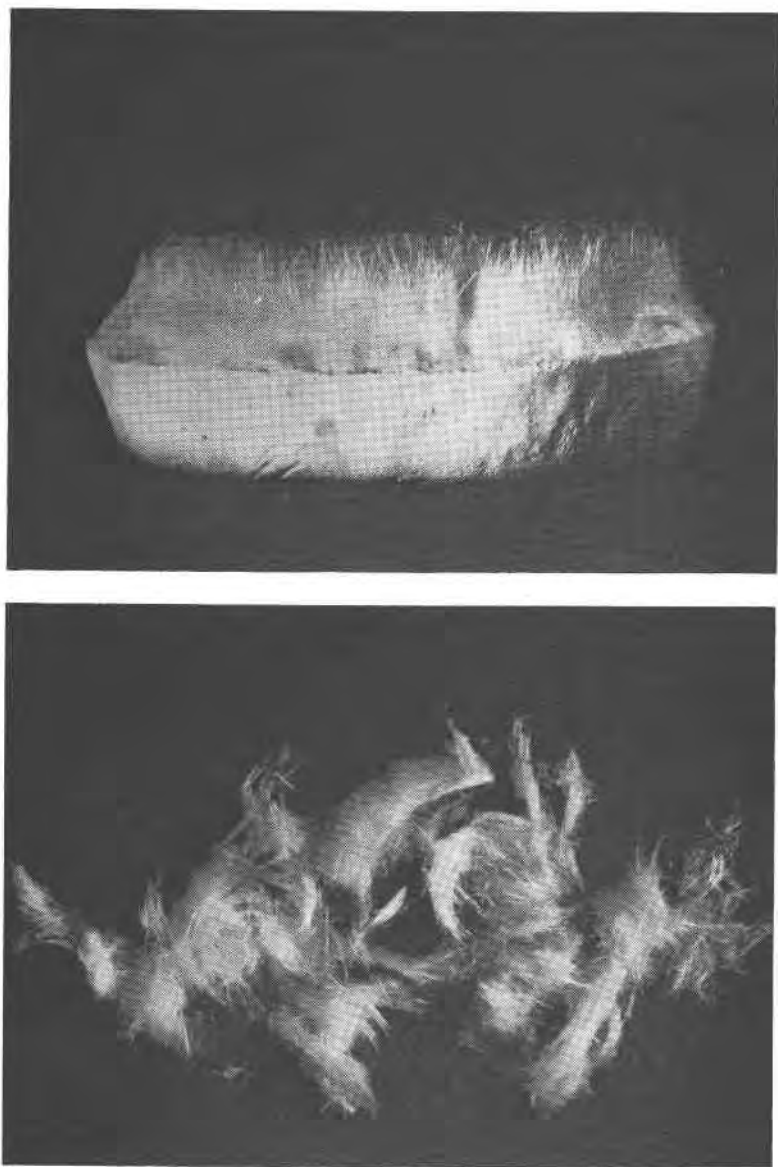


FIG. 1. Synthetic asbestos. Top: General view of the synthesis products, 0.8X.  
Bottom: Fiber crystals, 0.7X.

As seen from Figure 2, there is a distinct tendency for increasing refractive indices with increasing electronegativity of the substitute atom, that is, with the strengthening of the Me—O bond covalence. High values

TABLE 1. CHEMICAL ANALYSES AND CRYSTAL-CHEMICAL FORMULA FOR SYNTHETIC FLUORAMPHIBOLES

Component	Component content in weight percent										
	1	2	3	4	5	6	7	8	9	10	11
SiO <sub>2</sub>	59.17	57.11	57.42	53.10	56.02	56.13	57.61	56.54	58.22	55.97	61.70
Al <sub>2</sub> O <sub>3</sub>	—	—	—	—	—	—	—	—	—	0.22	—
Cr <sub>2</sub> O <sub>3</sub>	—	—	5.02	—	—	—	—	—	—	—	—
Fe <sub>2</sub> O <sub>3</sub>	0.23	—	—	—	—	—	4.40	—	—	9.09	0.36
FeO	—	—	—	—	—	—	2.97	—	—	—	—
MnO	—	7.57	—	—	—	—	—	—	—	—	—
CuO	—	—	—	—	—	—	—	—	4.44	—	—
ZnO	—	—	—	—	12.58	—	—	—	—	—	—
NiO	—	—	—	—	—	—	—	9.56	—	—	—
CoO	—	—	—	—	—	10.09	—	—	—	—	—
MgO	29.07	25.23	24.09	21.06	21.44	23.66	25.43	23.83	27.27	21.55	29.90
CaO	—	—	—	0.11	—	—	—	—	—	0.67	0.40
CdO	—	—	—	15.70	—	—	—	—	—	—	—
Na <sub>2</sub> O	8.09	6.79	10.06	7.65	7.28	7.54	7.59	7.72	7.45	9.55	—
Li <sub>2</sub> O	—	—	—	—	—	—	—	—	—	—	4.01
F <sup>+</sup>	4.90	4.11	4.83	4.18	3.92	3.82	4.22	3.92	4.10	3.85	4.62
Cl <sup>+</sup>	—	0.31	0.21	0.46	—	0.13	0.29	0.33	0.05	0.73	0.46
Loss	0.52	0.59	—	0.30	0.31	—	—	—	0.22	—	0.54
Sum	101.98	101.71	101.63	102.56	101.55	101.37	102.51	101.90	101.75	101.63	101.99
O <sup>2-</sup> -F <sup>+</sup> -Cl <sup>-</sup>	2.06	1.86	2.08	1.95	1.65	1.64	1.85	1.73	1.74	1.78	2.13
Total	99.92	99.85	99.55	100.61	99.90	99.73	100.66	100.17	100.01	99.85	99.86

<sup>a</sup> Needle-like or fibrous crystals of the surface "brush" were used for chemical analyses.

<sup>b</sup> Analyses by M. M. Piryutko, N. E. Kalinina and K. G. Gileva.

1. Mg-fluorrichterite Na<sub>2.12</sub>Mg<sub>5.88</sub>Fe<sup>3+</sup><sub>0.01</sub>(Si<sub>8</sub>O<sub>21.88</sub>)F<sub>2.09</sub>
2. Mn-fluorrichterite Na<sub>1.84</sub>Mg<sub>5.26</sub>Mn<sup>2+</sup><sub>0.89</sub>(Si<sub>8</sub>O<sub>22</sub>)(O<sub>0.11</sub>F<sub>1.82</sub>Cl<sub>0.07</sub>)
3. Na-Cr-Mg-fluoramphibole Na<sub>2.68</sub>Mg<sub>4.94</sub>Cr<sup>3+</sup><sub>0.84</sub>(Si<sub>7.92</sub>O<sub>21.86</sub>)(F<sub>2.1</sub>Cl<sub>0.04</sub>)
4. Cd-fluorrichterite Na<sub>2.23</sub>Ca<sub>0.01</sub>Cd<sub>1.16</sub>Mg<sub>4.77</sub>(Si<sub>8.00</sub>O<sub>21.89</sub>)(F<sub>1.69</sub>Cl<sub>0.11</sub>)
5. Zn-fluorrichterite Na<sub>2.01</sub>Mg<sub>4.86</sub>Zn<sub>1.33</sub>(Si<sub>8</sub>O<sub>22</sub>)(F<sub>1.78</sub>O<sub>0.01</sub>)
6. Co-fluorrichterite Na<sub>2.08</sub>Mg<sub>5.0</sub>Co<sup>2+</sup><sub>1.14</sub>(Si<sub>7.98</sub>O<sub>22</sub>)(O<sub>0.26</sub>F<sub>1.7</sub>Cl<sub>0.04</sub>)
7. Fe-fluorrichterite Na<sub>2</sub>Mg<sub>5.20</sub>Fe<sup>3+</sup><sub>0.34</sub>(Si<sub>7.92</sub>O<sub>22</sub>)(O<sub>0.10</sub>F<sub>1.84</sub>Cl<sub>0.06</sub>)
8. Ni-fluorrichterite Na<sub>2.12</sub>Mg<sub>5.0</sub>Ni<sup>2+</sup><sub>1.07</sub>(Si<sub>7.99</sub>O<sub>22</sub>)(O<sub>0.22</sub>F<sub>1.74</sub>Cl<sub>0.04</sub>)
9. Cu-fluorrichterite Na<sub>1.98</sub>Mg<sub>5.88</sub>Cu<sup>2+</sup><sub>0.46</sub>(Si<sub>8</sub>O<sub>22</sub>)(O<sub>0.13</sub>F<sub>1.79</sub>Cl<sub>0.01</sub>)
10. Mg-fluorarfvedsonite Na<sub>2.58</sub>Ca<sub>0.1</sub>Mg<sub>4.49</sub>Fe<sup>3+</sup><sub>0.97</sub>(Si<sub>7.84</sub>Al<sub>0.08</sub>O<sub>22</sub>)(O<sub>0.10</sub>F<sub>1.7</sub>Cl<sub>0.2</sub>)
11. Li<sub>2.09</sub>Ca<sub>0.06</sub>Mg<sub>5.77</sub>Fe<sup>3+</sup><sub>0.08</sub>(Si<sub>8</sub>O<sub>21.94</sub>)(F<sub>1.89</sub>O<sub>0.10</sub>)

of the refractive indexes are observed for fluoramphibole containing transition metals with  $d^5$  and  $d^{10}$  electron configurations (Cr, Mn, Cd, Zn, Fe).

The question of cation site occupancy is of great importance in studying the relations of composition to structure. Several authors showed that the occupancy of structural sites has different effects on lattice parameters of the amphiboles (Whittaker, 1960; Colville *et al.*, 1966; Ginzburg *et al.*, 1961). As seen from Table 3, the entry of larger cations into a definite structural position leads to a regular increase in unit-cell dimensions. Comparison of the lattice parameters allows one to draw some conclusions concerning the most probable cation site occupancies in synthetic fluoramphiboles of the richterite series.

TABLE 2. OPTICAL CHARACTERISTICS OF SYNTHETIC FLUORAMPHIBOLE<sup>a</sup>

Number of samples	$\gamma$	$\beta$	$\alpha$	$c/\lambda Z$	$\gamma - \alpha$
1	1.596	1.589	1.577	12°	0.019
2	1.610	1.603	1.589	16°	0.021
3	1.618	1.608	1.594	20°	0.024
4	1.620	1.612	1.600	23°	0.020
5	1.612	1.604	1.592	20°	0.020
6	1.616	1.607	1.598	17°	0.018
7	1.615	1.604	1.597	18°	0.018
8	1.618	1.605	1.597	16°	0.021
9	1.618	1.597	1.590	25°	0.028
10	1.630	1.623	1.618	20° <sup>b</sup>	0.012
11	1.598	1.589	1.578	0°	0.020

<sup>a</sup> Determinative accuracy of  $\gamma$ ,  $\beta$ ,  $\alpha$  is  $\pm 0.002$

<sup>b</sup> Value of  $C/\lambda y$  is given.

Substitution of  $Mg^{2+}$  by  $Ni^{2+}$  does not affect lattice parameters because the radii of the  $Mg^{2+}$  and  $Ni^{2+}$  ions are equal.

Substitution of  $Mg^{2+}$  by  $Co^{2+}$  and  $Zn^{2+}$  having larger ionic radii causes an increase in the angle  $\beta$ , the lattice parameters  $b$  and  $a \cdot \sin \beta$ . In the series of synthetic fluoramphiboles under study all tetrahedral positions are occupied by silicon. An increase in the angle  $\beta$ ,  $b$  and  $a \cdot \sin \beta$  therefore suggests entry of  $Co^{2+}$  and  $Zn^{2+}$  into  $M(4)$  and  $M(2)$  sites.

In Ghose's (1961) opinion, an increase of the bond covalence in the  $M(4)$  and  $M(2)$  positions leads to the stabilization of the structure. The presence of  $Ni^{2+}$ ,  $Co^{2+}$ ,  $Zn^{2+}$  in the  $M(4)$  and  $M(2)$  site is also possible from the view point of their higher electronegativity in comparison with that of  $Mg^{2+}$ .

The greatest increase in the angle  $\beta$  and  $b$  is observed on the substitution of  $Mg^{2+}$  by the larger cations  $Mn^{2+}$  and  $Cd^{2+}$ . Therefore the most possible occupants of the  $M(4)$  site are  $Mn^{2+}$  and  $Cd^{2+}$ . The argument for this assumption is that even the maximum metal-oxygen distance 2.2 Å in the  $M(1)$ ,  $M(2)$  and  $M(3)$  positions is insufficient for  $Mn^{2+}$  and  $Cd^{2+}$  occupancy (Ghose, 1961; Zussman, 1955).

As seen from Figure 3 and Table 3, the proposed variation of cation distribution in fluorrichterite agrees well with Whittaker's conclusions on the interrelationships between the angle  $\beta$  and both the average radius of the cation in the  $M(4)$  position and the value of  $a \cdot \sin \beta$ .

TABLE 3. UNIT CELL DIMENSIONS AND DATA ON CATION DISTRIBUTION IN THE STRUCTURE OF FLUORAMPHIBOLES<sup>a</sup>

Number of samples	Theoretical formula of the amphibole investigated	Unit cell dimensions, Å <sup>b</sup>						Probable distribution of cations in structural positions					
		a	a·sin β	b	c	c·sin β	β	VÅ <sup>3</sup>	A	M(4)	M(2)	M(1) + M(3)	Si(1)
													Si(2)
1	Na <sub>2</sub> Mg <sub>6</sub> (Si <sub>8</sub> O <sub>22</sub> )F <sub>2</sub>	9.92	9.42	17.92	5.26	4.99	108°24'	888	Na	Na, Mg	Mg	Mg	Si
8	Na <sub>2</sub> Mg <sub>5</sub> Ni <sup>2+</sup> (Si <sub>8</sub> O <sub>22</sub> )F <sub>2</sub>	9.92	9.41	17.91	5.26	4.99	108°27'	886	Na	Na, Mg, Ni	Mg	Mg	Si
9	Na <sub>2</sub> Mg <sub>5</sub> Ca <sup>2+</sup> (Si <sub>8</sub> O <sub>22</sub> )F <sub>2</sub>	9.88	9.42	17.92	5.26	4.99	108°28'	888	—	—	—	—	—
6	Na <sub>2</sub> Mg <sub>5</sub> Co <sup>2+</sup> (Si <sub>8</sub> O <sub>22</sub> )F <sub>2</sub>	9.93	9.43	17.96	5.26	4.99	108°15'	891	Na	Na, Mg, Co	Mg	Mg	Si
5	Na <sub>2</sub> Mg <sub>5</sub> Zn <sup>2+</sup> (Si <sub>8</sub> O <sub>22</sub> )F <sub>2</sub>	9.94	9.45	17.98	5.26	5.00	108°10'	894	Na	Na, Mg, Zn	Mg	Mg	Si
2	Na <sub>2</sub> Mg <sub>5</sub> Mn <sup>2+</sup> (Si <sub>8</sub> O <sub>22</sub> )F <sub>2</sub>	9.95	9.46	17.94	5.26	5.00	108°09'	892	Na	Na, Mn	Mg	Mg	Si
4	Na <sub>2</sub> Mg <sub>5</sub> Cr <sup>3+</sup> (Si <sub>8</sub> O <sub>22</sub> )F <sub>2</sub>	9.90	9.47	17.97	5.26	5.01	107°32'	892	Na	Na, Cd	Mg	Mg	Si
3	Na <sub>2</sub> Mg <sub>5</sub> Cr <sup>3+</sup> (Si <sub>8</sub> O <sub>22</sub> )F <sub>2</sub>	9.69	9.44	17.86	5.28	5.03	107°49'	893	—	—	—	—	—
10	Na <sub>2</sub> Mg <sub>4</sub> F <sup>2+</sup> (Si <sub>8</sub> O <sub>22</sub> )F <sub>2</sub>	9.73	9.47	17.87	5.27	5.02	107°42'	892	—	—	—	—	—
11	LiMg <sub>5.5</sub> (Si <sub>8</sub> O <sub>22</sub> )F <sub>2</sub>	9.24	—	17.88	5.25	—	90°00'	869	—	—	—	—	—

<sup>a</sup> The space groups of monoclinic fluoramphiboles are *I2/m*; of Li-fluoramphibole is *Pmm*(?).  
<sup>b</sup> Determinative errors for parameters *a*, *b*, *c* are  $\leq \pm 0.01$  Å, those of the angle  $\beta + 5'$ ,  $V \pm 2$  Å<sup>3</sup>.

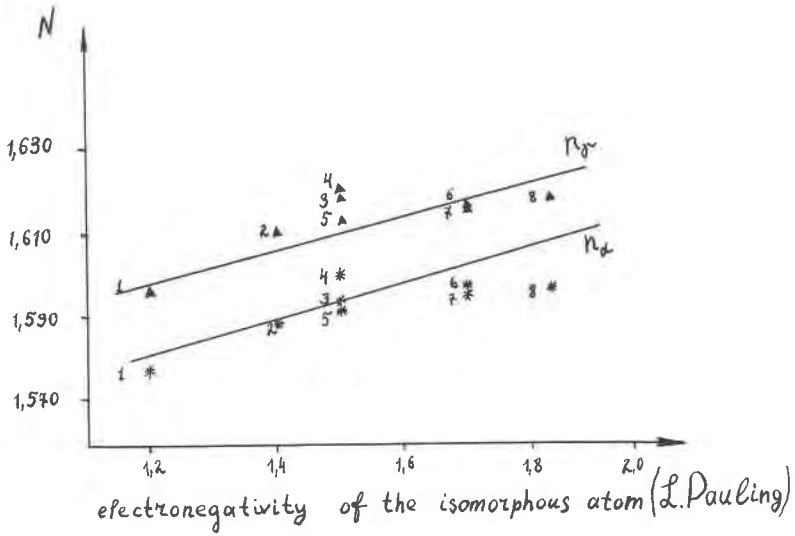


FIG. 2. Dependence of refractive indices of fluoramphiboles upon electronegativity of the isomorphous atoms (numbering of points correspond to Table 1).

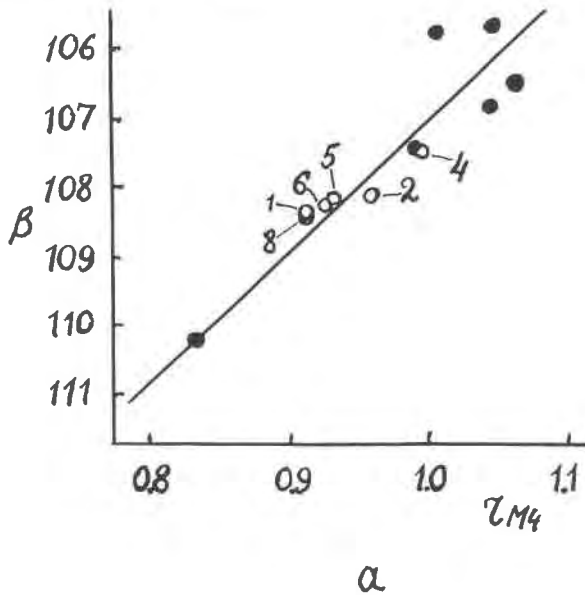


FIG. 3. Dependence of the angle  $\beta$  upon the average cation radius in the  $M(4)$  position (numbering of points correspond to Table 1). Open circles: data of the authors; filled circles: Whittaker's data.

## THERMAL, MECHANICAL AND CHEMICAL PROPERTIES

In the present study, investigations of some of the physical and physico-chemical properties of the fluoramphiboles synthesized were also carried out (Table 4).

The heating behavior of fluoramphiboles was studied by DTA and TGA. The products of heating were examined by X-ray diffraction and optically. These investigations showed that, when heated, the decomposition of the synthetic fluoramphiboles proceeds according to the scheme of the natural amphiboles: fluorine is liberated first, the mineral structure then fails, and finally melting of the disintegration products takes place. The products of fluoramphibole decomposition are a mixture of amorphous and crystalline phases (orthosilicates, pyroxenes, minerals of the humite group). Thermal stability of fluoramphiboles depends upon their chemical composition. The temperature ranges of the fluoramphibole decomposition are established to be 100–150°C higher and the decomposition rates are 5–8 orders lower than those of the natural amphiboles of the analogous compositions. This is due to the fact that the energy of

TABLE 4. PHYSICAL AND PHYSICO-CHEMICAL PROPERTIES OF SYNTHETIC FIBER FLUORAMPHIBOLES

Physical and physico-chemical properties	Fluoramphiboles investigated										
	1	2	3	4	5	6	7	8	9	10	11
Density (g. cm <sup>-3</sup> )											
Picnom.	2.95	3.55	3.24	3.48	3.29	—	—	—	3.03	—	3.00
X-ray	3.02	3.08	3.05	3.34	3.14	3.14	—	3.15	3.06	3.09	3.00
Temperature region of decomposition (°C)	950–1000	990–1050	1040–1070	970–1030	—	940–1000	840–910	960–1000	910–970	940–1000	860–900
Temperature region of melting (°C)	1170–1190	1100–1160	1160–1190	1170–1210	—	1050–1100	1010–1040	1070–1110	1090–1125	1000–1060	1090–1100
Maximum value for tensile strength (kg/mm <sup>2</sup> )	210	—	400	—	—	364	—	250	—	366	220
Weight losses (wt.%)											
HCl	3.0	15.5	11.3	—	—	8.8	—	9.1	—	8.4	33.5
KOH	0.8	4.9	4.0	—	—	1.1	—	0.7	—	1.5	3.8
Increase in weight (wt.%)											
Water vapor	0.13	0.59	0.08	0.07	—	0.14	—	0.01	0.08	—	1.9
Ethyl alcohol vapor	1.60	2.42	0.00	0.19	—	0.00	—	0.00	0.50	—	5.87



breaking the chemical bond for Mg—OH ( $56 \pm 5$  kcal/mol) is significantly lower than that for the Mg—F bond ( $120 \pm 20$  kcal/mol).

Mechanical strength of fluoramphibole fibers was investigated by the methods used in the study of whiskers (Nadgornyi, 1961). All samples were tested for tensile strength at the constant deformation rate of 12  $\mu\text{m}/\text{min}$ . The values of the strength and the diagrams for tensile strength ( $\delta$ - $\epsilon$ ) of the fibers of various diameters were determined. The data obtained show that synthetic fluoramphiboles are distinguished by high values of strength, almost of the same order as those for silicon, copper and iron whiskers (Gordon, 1959; Kushnir *et al.*, 1961). The highest values of the strength are observed for the fluoramphibole fibers of less than 3  $\mu\text{m}$  diameter (Table 4).

The diagrams for tensile strength at a strain close to breaking show no changes in deformation. A cleavage splitting is observed at the point of rupture for the fibers of all diameters.

Chemical resistance of fluoramphiboles was determined by weight losses of the samples after 4 hours boiling in HCl ( $d = 1.19$  g/cm<sup>3</sup>) and in 25 weight percent KOH solution. Adsorption properties of synthetic fluoramphiboles are characterized by an increase in the sample weight after 24 hours at 20°C in the atmosphere of 98 percent relative moisture or in ethyl alcohol. Referring to Table 4, listing the results of these studies, shows that synthetic fluoramphiboles are stable in acid and alkali media and are nonhygroscopic.

Studies on the electrical properties of synthetic fluoramphiboles revealed high dielectric constants for these minerals. Their electric resistivity is several orders higher than that of natural asbestos.

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