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SYNTHETIC ASBESTOS INVESTIGATIONS, I: STUDY OF SYNTHETIC FLUOR-TREMOLITE*

J. E. COMEFORO† AND J. A. KOHN,
*U. S. Bureau of Mines, Electrotechnical Laboratory,
Norris, Tennessee.*

ABSTRACT

A study of synthetic fluor-tremolite by *x*-ray and optical methods was considered basic to research on fluor-amphiboles as potential substitutes for asbestiform minerals.

A review and critique of previous syntheses is given, together with earlier optical and *x*-ray data on both natural hydroxy- and synthetic fluor-tremolite. Optical determinations on chemically analyzed synthetic fluor-tremolite gave the following values:

$$\begin{array}{ll} \alpha = 1.581 \pm 0.001 & 2V = 86\frac{1}{2}^\circ \\ \beta = 1.593 \pm 0.002 & Z \wedge c = 21^\circ \\ \gamma = 1.602 \pm 0.002 & \text{Biaxial negative} \end{array}$$

The values were compared with those for natural hydroxy-tremolite. On an *x*-ray powder pattern of synthetic fluor-tremolite, all resolved maxima were indexed up to $76^\circ 2\theta$. The following monoclinic cell dimensions were obtained:

$$\begin{array}{l} a_0 = 9.781 \pm 0.005 \text{ \AA} \\ b_0 = 18.007 \pm 0.004 \\ c_0 = 5.267 \pm 0.006 \\ \beta = 75^\circ 29' \pm 5' \end{array}$$

A comparison was made with the values for natural hydroxy-tremolite. Goniometric measurements on well-formed single crystals of synthetic fluor-tremolite gave values in agreement with the calculated figures. Single-crystal *x*-ray patterns (rotation and Weissenberg) were made.

INTRODUCTION

In the course of research on the synthesis of asbestiform minerals, experimentation is being conducted on the crystallization of fluorine-containing amphiboles from melts. The compound fluor-tremolite ($\text{Ca}_2\text{-Mg}_5(\text{Si}_4\text{O}_{11})_2\text{F}_2$) was chosen as a logical starting point because its structure is basic to all of the monoclinic amphiboles. Thus, determination of some of its fundamental constants is necessary as a standard of compari-

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† Present address: Electronics Division, Sylvania Electric Products, Inc., Woburn, Mass.

son for other fluor-amphiboles synthesized during the course of this investigation.

In the present study, particular attention has been given to the synthesis of fluor-tremolite of a known composition, so that a meaningful determination of its x -ray and optical properties could be made.

REVIEW OF PREVIOUS RESEARCH

Ehrenberg (1) attempted to synthesize fluor-tremolite by reacting an appropriate mixture of CaF_2 , CaCO_3 , MgO , and SiO_2 in the solid state. The products formed were identified by x -rays. At 620°C . forsterite formed, and at 750° diopside was observed in addition to forsterite and fluorite. The same phases were observed at 800° , with fluor-tremolite absent in every instance. Ehrenberg came close to synthesizing fluor-tremolite, since with the same raw materials fluor-tremolite was recently prepared at this laboratory by solid-state reaction at temperatures just below the formation of a liquid phase. By crystallization from the melt, fluor-tremolite is readily obtained with these batch components, although diopside and forsterite are invariably present.

In 1935 Grigoriev (2) attempted the synthesis of a fluorine-containing hornblende, utilizing the technique previously found suitable for the synthesis of fluor-micas. The batch used approximated the empirical formula $\text{K}_2\text{CaMg}_6(\text{AlSi}_6)\text{O}_{19\frac{1}{2}}\text{F}_2$. Equilibrium conditions were not attained because of the continual loss of volatile material from the batch and also because a method of maintaining a constant temperature was lacking. The resulting product contained fluor-phlogopite, spinel, and fluorides, as well as fluor-amphibole. From the composition of the batches, the presence of these other phases is not unexpected. Intergrowth with phlogopite precluded chemical analyses.

A petrographic examination showed the synthetic hornblende crystals to be sharply bounded, with the faces (001), (010), and (110) usually well formed. The angles between the faces were as follows:

$$\begin{aligned} (010):(1\bar{1}0) &= 118^\circ \\ (\bar{1}10):(110) &= 124^\circ. \end{aligned}$$

The optical constants of the synthetic hornblende were reported as

$$\begin{array}{ll} \alpha = 1.615 & \gamma - \alpha = 0.021 \\ \beta = 1.623 & 2V = 70 - 90^\circ \\ \gamma = 1.636 & \text{Optic plane} = (010) \end{array}$$

After showing that amphiboles may be synthesized from fluorine-containing silicate melts, Grigoriev, working with Isküll (3), investigated the feasibility of synthesizing amphiboles by melting natural amphiboles to which a fluoride had been added. A hornblende represented by the

formula $(\text{Na, K, Ca})_{2.9}(\text{Mg, Fe}^{++}, \text{Fe}^{+++}, \text{Al, Ti})_5(\text{Al, Si})_8\text{O}_{22}(\text{OH, F})_{1.98}$ was fused both with and without an addition of CaF_2 . All fusions were made in graphite crucibles at approximately 1350°C . As expected, the fluoride-free melt failed to yield an amphibole; it consisted almost entirely of pyroxene crystals. The melts to which 5% CaF_2 was added resulted in crystallization of an amphibole. Most of the iron originally present was reduced to the metallic state. Unfortunately, no chemical analysis of the reaction product was made.

The optical properties of the regenerated, colorless amphibole were reported as follows:

$$\begin{array}{ll} \alpha = 1.586 \pm 0.003 & \gamma - \alpha = 0.017 \\ \beta = 1.590 \pm 0.003 & 2V = 55 - 60^\circ \\ \gamma = 1.603 \pm 0.003 & Z \wedge c = 17^\circ \end{array}$$

The regenerated amphibole gave an x -ray powder pattern similar to the natural material used; no indexing was made.

The dependence of the optical properties of amphiboles on their chemical composition was investigated by Grigoriev (4), using synthetic fluor-amphiboles whose compositions were readily controllable. Four batches composed of CaF_2 , MgO , and SiO_2 were compounded in the proportions required for tremolite. To these were added 1, 3, 5, and 10% alumina and the batches melted in carbon crucibles at approximately 1400°C . A microscopic examination indicated amphibole to be the only crystalline phase present. No mention was made of any glassy phase. Recent research in the authors' laboratory with similar batches has always resulted in the crystallization of some diopside and free silica, a small amount of glass, and occasionally, with higher alumina contents, anorthite. As the materials were not especially volatile, Grigoriev did not make a chemical analysis of the final products. This is unfortunate, as the optical data presented would be more significant if the exact compositions of the fluor-amphiboles were known. However, Grigoriev's results show that an increase in Al_2O_3 causes a decrease in α , γ , $\gamma - \alpha$, and the extinction angle.

In the early thirties Lüdke (5) began research on the synthesis of asbestos. Lüdke's process was a type of pneumatolytic technique in which mixtures of alkalis, alkaline earth compounds, silica, and fluorides were heated in an air stream at temperatures below the decomposition temperature of the synthetic amphibole. Undoubtedly, Lüdke's experimentation and small-scale production represent the most extensive effort to date on the synthesis of amphiboles. The severe shortage of asbestos in Germany during World War II gave impetus to his work, and many attempts were made to utilize the amphibole as a substitute for asbestos. In every test, however, the synthetic amphibole was inferior to the nat-

ural material. In spite of technical improvements in his process, the quality of the synthetic amphibole asbestos was not improved. The fibers were comparatively brittle and insufficiently resistant to chemical attack, the later primarily due to the high alkali content.

The synthetic amphiboles prepared by the Lüdke process contained both hydroxyl and fluorine and consequently differed from those synthesized by Grigoriev and later investigators. Analyses show that Lüdke's products were comparatively high in sodium, probably similar to richterite and eckermannite in composition.

The index of refraction of one of his synthetic amphiboles was "very close to 1.60," and the extinction angle was 18–19°. *X*-ray powder patterns were similar to those for natural hornblendes, but a detailed indexing was not made.

Bowen and Schairer (6) have synthesized fluor-amphiboles by heating pyroxenes with an addition of a small amount of NaF in evacuated silica tubes. The quantity of amphibole produced was too small to permit a chemical analysis. Inasmuch as the original material was a pure clinostatite in one case and a glass of the composition FeSiO_3 in the other, the composition of the amphibole synthesized from each of these two end members must have been close to $\text{Mg}_7(\text{Si}_4\text{O}_{11})_2\text{F}_2$, and $\text{Fe}_7(\text{Si}_4\text{O}_{11})_2\text{F}_2$, respectively. As NaF was added, however, it is reasonable to assume the presence of some sodium in their products. Such a possibility was acknowledged by the investigators in their report, and recent work at this laboratory makes the assumption probable.

Recent work by Van Valkenburg and Pike (7) has indicated that fluor-tremolite melts incongruently, with forsterite the primary phase. The liquidus temperature was determined as 1350° C., with tremolite forming near 1145°. The exact determination was difficult owing to a tendency for defluorination of the melt.

EXPERIMENTAL PROCEDURES

In the first experiments, specially machined crucibles of approximately 30 cc. capacity with screw-on graphite covers were employed. The charge was melted by heating to 1400° C., maintained at the maximum temperature at least 30 minutes, and then cooled to 1200° C. within 2 hours. The resulting product consisted of acicular crystals of fluor-tremolite, some as long as several millimeters, associated with small amounts of diopside, tridymite, CaF_2 , and MgF_2 . By this simple method the actual synthesis of fluor-tremolite is readily accomplished. However, for the purpose of this research, single crystals suitable for *x*-ray study and goniometric measurements were required. No such crystals were obtained in the experiments with 20 to 30-gram batches.

It was soon apparent that the manner in which the desired components

were added had a definite effect on the fusion temperature and also, particularly when the reaction was confined to the solid state, on the resulting crystalline phases, although in all instances the major crystalline product was fluor-tremolite. In the initial experiments, natural wollastonite, MgF_2 , MgO , and finely ground quartz were proportioned to yield fluor-tremolite ($\text{Ca}_2\text{Mg}_5(\text{Si}_4\text{O}_{11})_2\text{F}_2$). These raw materials melted below 1400°C . The same ultimate composition when prepared from CaF_2 , CaCO_3 , MgO , and finely ground quartz required a temperature in excess of 1450° for melting.

In an attempt to grow larger crystals, batches as large as 20 pounds were crystallized in carbon crucibles, which were in turn sealed into large SiC crucibles and soaked at 1450°C . for 4 to 8 hours in an electric furnace. The rate of cooling of the furnace was varied from 4° to 100° per hour to 1100°C ., at which temperature the power was turned off. In

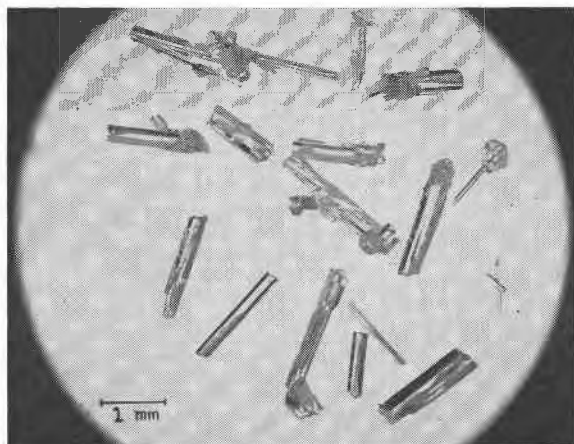


FIG. 1. Photograph of synthetic fluor-tremolite crystals (9 \times).

every experiment but one the general character of the resulting fluor-tremolite crystals was similar and unfavorable, regardless of the size of the batch or the rate of cooling (providing the cooling was slow enough to permit crystallization).

In the one crystallization which yielded an abundance of single crystals of remarkable clarity and distinct crystal form, the maximum temperature (1450°C .) was maintained for 4 hours and then lowered at a rate of 5°C . per hour to 1100° . The single crystals (up to 4 mm.) of fluor-tremolite were found in the lower portion of the reaction product, having crystallized from a liquid phase.

Some of these crystals were separated from the mass by hand sorting for α -ray and optical studies. A few selected crystals, shown in Fig. 1, were used for goniometric measurements. A portion of the crystallized

product was beneficiated by heavy liquid media to obtain a sample of fluor-tremolite pure enough to justify a chemical analysis. Tetrabromoethane and methylene iodide (adjusted to 2.95 and 3.10 gm/cc., respectively) were used to remove a small amount of glass, tridymite, diopside, and CaF_2 . The separation effectively removed these impurities, although some MgF_2 attached to fluor-tremolite crystals persisted. The amount of MgF_2 remaining was determined by petrographic analysis to be less than 3%.

RESULTS

(1) Chemical Composition

The beneficiated synthetic fluor-tremolite sample was examined optically and found to consist of more than 95% fluor-tremolite, with a small amount (2–3%) of MgF_2 . This sample was chemically analyzed, and the results are given in Table 1.

TABLE 1. CHEMICAL ANALYSIS OF SYNTHETIC FLUOR-TREMOLITE (PER CENT)*

Constituent	Theoretical Composition	Actual Composition	Corrected Composition†
SiO_2	58.88	56.86	58.56
MgO	24.69	26.61	25.45
Fe_2O_3	0.00	0.06	0.06
CaO	13.74	12.76	13.14
Na_2O	0.00	0.10	0.10
F^-	4.65	6.30	4.65
$\text{O}=\text{F}$	-1.96	-2.65	-1.96
	100.00	100.04	100.00

* Analysts: H. R. Shell, R. L. Craig; Sample 3838, dried at 110° C.

† On assumption that fluor-tremolite and MgF_2 are sole phases present; using 22 oxygen and 2 fluorine anions as basis, composition of synthetic fluor-tremolite calculated from analysis as $\text{Na}_{0.03}\text{Ca}_{1.91}\text{Mg}_{5.15}(\text{Si}_{3.98}\text{O}_{11})_2\text{F}_2$, indicating 2.9% MgF_2 . Slight excess of Mg^{++} attributed to small amount (<1.0%) of an isotropic phase, probably glass.

From the corrected analysis, the chemical composition of the synthetic fluor-tremolite is seen to approximate closely that of the theoretical composition, $\text{Ca}_2\text{Mg}_5(\text{Si}_4\text{O}_{11})_2\text{F}_2$.

(2) Optical Properties

The optical constants of selected single crystals of synthetic fluor-tremolite were measured at 23° C. with a petrographic microscope, using the oil immersion technique and monochromatic sodium (D) light. The

results are compared with those of two natural hydroxy-tremolites (8), (9) in Table 2.

For comparison, the indices of refraction of a fluor-tremolite similarly synthesized by Van Valkenburg and Pike (10) are given as $\alpha=1.58$ and $\gamma=1.61$, while "the extinction angle as measured parallel to the elongation is about 16° ". This is in close agreement with the present results.

The synthetic fluor-tremolite crystals obtained by Van Valkenburg and Pike, although acicular, appeared quite brittle. This observation was

TABLE 2. TREMOLITE OPTICAL CONSTANTS*

	Synthetic Fluor-tremolite	Natural Hydroxy- tremolite (8)	Natural Hydroxy- tremolite (9)†
α	$1.581 \pm 0.001 \dagger$	1.599	1.602
β	1.593 ± 0.002	1.613	1.618
γ	1.602 ± 0.002	1.625	1.631
$Z \wedge c$	21°	18°	16°
2V	$86\frac{1}{2}^\circ \dagger$	88°	$82^\circ \pm 2^\circ$
Optical character	Biaxial negative	Biaxial negative	Biaxial negative

* Determinations on fluor-tremolite made by M. V. Denny.

† α and 2V determined by means of a 5-axis universal stage, using sodium (D) light.

‡ Analysis by Allen and Clement (reference (9), p. 414) shows presence of 1.21% Al_2O_3 and 0.6% alkali, plus small amounts of other impurities.

confirmed by the present authors. It is possible that the brittleness may be due to the comparatively large cross-sectional area of the synthetic fluor-tremolite crystals in relation to the natural asbestiform material.

(3) X-Ray Data

The authors were able to find but scant information on the indexing of x -ray patterns of synthetic fluor-amphibole. The few x -ray investigations conducted apparently have been limited to comparing the location and intensities of the powder pattern maxima with those of a natural amphibole.

The most detailed x -ray data available on synthetic fluor-amphiboles are those given by Comeforo and Eitel (11), although no cell dimensions are reported. In the present study, accurate unit cell dimensions have been determined, and the x -ray pattern has been extended by a calculation of all Miller indices permissible by the space group symmetry of the tremolite structure ($C2/m$) up to $76^\circ 2\theta$. Every resolved peak in this range on a powder pattern has been indexed (see Table 3).

All powder-pattern maxima were determined with a Philips high-angle x -ray diffractometer, using unfiltered Cu radiation. The unit cell dimen-

TABLE 3. X-RAY DIFFRACTION DATA (POWDER) FOR SYNTHETIC FLUOR-TREMOLITE
(SPACE GROUP $C2/m$)

hkl	2θ obs.	2θ calc.*	$\Delta 2\theta$	Meas. Int.
020	9.80°	9.815°	+0.015°	9
110	10.555	10.545	-0.01	>>100
130	17.465	17.48	+0.015	7
11 $\bar{1}$	18.255	18.235	-0.02	5
200	18.72	18.725	+0.005	6
040	19.705	19.705	0	12
220	21.195	21.185	-0.01	25
13 $\bar{1}$	22.98	23.00	+0.02	3
131 } 041 }	26.37	{ 26.38 } { 26.385 }	—	6
240	27.315	27.315	0	23
310	28.72	28.69	-0.03	>100
15 $\bar{1}$ } 221 }	30.44	{ 30.43 } { 30.44 }	—	8
330	32.025	32.01	-0.015	26
33 $\bar{1}$	32.92	32.935	+0.015	3
151	33.12	33.14	+0.02	9
061	34.65	34.655	+0.005	2
20 $\bar{2}$	35.51	35.53	+0.02	2
350	37.88	37.87	-0.01	4
35 $\bar{1}$	38.68	38.675	-0.005	5
42 $\bar{1}$	39.00	38.99	-0.01	5
17 $\bar{1}$	39.28	39.27	-0.01	3
31 $\bar{2}$	39.79	39.77	-0.02	1
171	41.45	41.455	+0.005	1
261	41.84	41.835	-0.005	4
202	44.36	44.34	-0.02	1
351	45.03	45.025	-0.005	4
370	45.43	45.445	+0.015	5
510	48.29	48.28	-0.01	5
242	48.935	48.95	+0.015	7
530	50.485	50.495	+0.01	4
461	55.835	55.835	0	18
480	56.365	56.355	-0.01	3
1·11·0	57.045	57.045	0	2
600	58.43	58.43	0	4
15 $\bar{3}$	58.57	58.57	0	1
570 } 35 $\bar{3}$ }	60.66	{ 60.675 } { 60.685 }	—	2
0·12·0	61.755	61.77	+0.015	8

TABLE 3—Continued

<i>hkl</i>	2θ obs.	2θ calc.*	$\Delta 2\theta$	Meas. Int.
551 } 482 }	61.93	{ 61.94 } { 61.96 }	—	2
3·11·0	64.005	64.02	+0.015	2
66 $\bar{1}$	65.165	65.16	-0.005	6
512	68.91	68.92	+0.01	4
710	69.63	69.615	-0.015	2
263	70.695	70.69	-0.005	1
114	72.39	72.41	+0.02	2
224 } 751 }	72.49	{ 72.495 } { 72.505 }	—	2
2·12·2	73.325	73.33	+0.005	1

* Using $\lambda_{\text{CuK}\alpha_1} = 1.54050 \text{ \AA}$.

sions were obtained by employing a fixed-time counting operation in conjunction with this instrument. The region surrounding a maximum was manually scanned down-scale, with intensity counts being made at decrements of $0.01^\circ 2\theta$. The scanning operation was repeated five times in each case, the values then being averaged and plotted against 2θ . The position of a maximum was read from a curve drawn through the plotted points. The instrumental setting used was the following: scale factor, 4-32 (depending on peak height); multiplier, 1.0 (thus the counting rate ranged from 200 to 1600 counts per second, full scale); time constant, 4 seconds; Geiger overvoltage, 300 volts; divergence slit, 1° ; receiving slit, 0.003 inch; scatter slit, 1° .

The powder diffraction measurements were made using $-200 +325$ mesh powder, packed in the normal rectangular aluminum holder supplied with the instrument. For calibration purposes, appropriate peaks on a silicon standard compact (also supplied with the instrument) were determined before and after each fluor-tremolite reading, and the proper correction was applied. Such corrections, obtained by comparison with Parrish's (12) data for silicon, ranged from $+0.005^\circ$ to $+0.012^\circ$. Thus, a value of 2θ to the third decimal place (the last place being somewhat uncertain) was determined for each of the maxima involved in the evaluation of the cell dimensions. The four peaks used in this determination were $600\alpha_1$, $0\cdot12\cdot0\alpha_1$, $461\alpha_1$, and $661\alpha_1$. The 2θ positions determined for these peaks and the resulting cell dimensions are given in Table 4, together with the calculated density.

Table 5 compares the unit cell dimensions obtained for synthetic

TABLE 4. MONOCLINIC CELL DIMENSIONS OF SYNTHETIC FLUOR-TREMOLITE

Peak	Determined 2θ	Cell Dimensions (Angstroms)
600 α_1 *	58.431°	$d_{100} = 9.469 \pm 0.002$; $a_0 = 9.781 \pm 0.005$
0.12-0 α_1	61.769°	$d_{010} = 18.007 \pm 0.004$; $b_0 = 18.007 \pm 0.004$
461 α_1	55.834°	$d_{001} = 5.099 \pm 0.004$; $c_0 = 5.267 \pm 0.006$ $\beta = 75^\circ 29' \pm 5' = 75.48 \pm 0.08^\circ$ Calculated density = 3.021 ± 0.006 gm./cm. ³ †
66T α_1	65.161°	

* $\lambda\text{CuK}\alpha_1$ taken as 1.54050 Å.

† This compares with the measured density of 3.023 ± 0.006 gm./cm.³ at 20° C., as determined pycnometrically by M. V. Denny.

fluor-tremolite with Warren's (13) data on natural hydroxy-tremolite. It is interesting to note that substitution of fluoride for hydroxyl causes virtually no change in the a and c dimensions; b_0 increases slightly (1+%) while β increases by 1.5° (2%).

TABLE 5. TREMOLITE CELL DIMENSION COMPARISON

	Warren	Comeforo and Kohn	Increase
a_0	9.78 Å	9.781 Å	—
b_0	17.8	18.007	1+%
c_0	5.26	5.267	—
β	73°58'	75°29'	2%

The determination of the observed 2θ values listed in Table 3 was made using a chart operation with the Philips unit. The instrument setting was the same, except that the scale factor was constant at 16 (giving a counting rate of 800 counts per second, full scale). Additionally, the scanning speed was $\frac{1}{4}^\circ$ per minute and the chart scale $\frac{1}{2}$ inch per degree. With the aid of a binocular microscope (low power), the positions of the maxima were read to 0.005° 2θ (0.0025 inch on the chart). Following the method of Donnay and Donnay (14), the reading was “. . . taken at the mid-point of the peak width at approximately two-thirds of the peak height, an empirically determined value, which minimizes the interference of the α_2 peak and the effect of the detailed shape of the graph.”

A chart was obtained, using the silicon standard compact, both before and after the analysis of fluor-tremolite. The corrections applied, forming a smooth-curve variation with 2θ , ranged from +0.035° to +0.06°. Referring to Table 3, listing only resolved peaks or doublets warranting

mention, only one peak (310), which "ran off the chart," shows a deviation ($\Delta 2\theta$) of more than 0.02° . For all intents and purposes, the total of the positive deviations cancels that of the negative deviations, an additional fact speaking for the accuracy of the cell dimensions used in the calculations.

Single-crystal x -ray exposures (rotation and Weissenberg) were made both as a check on crystal quality and as a means for comparing intensity maxima and thus making an unambiguous indexing of certain peaks. Rotation, zero-, first-, and second-level exposures were obtained with rotation about the c axis. The rotation film yielded an identity period (c_0) of 5.3 \AA , which, upon applying the calculated β of $75^\circ 29'$, led to a d_{001} value of 5.1 \AA . The zero-level Weissenberg film yielded directly 18.0 \AA and 9.5 \AA for d_{010} and d_{100} , respectively.

A check on the unit cell dimensions obtained from the x -ray powder pattern was sought by measuring on the optical goniometer the best synthetic fluor-tremolite crystals available (see Fig. 1). Six crystals were measured. All but one showed good to excellent unit prism faces. Front and side pinacoids were poorly developed but occasionally measurable. One crystal, twinned on (100), was found to be definitely terminated, the twinning giving rise to two basal pinacoids as the terminating faces. Indications of terminal faces were seen on another crystal, but these were too faint to measure. Several of the crystals examined showed indications of modified prism faces.

The interfacial angle (100) \wedge (110) was determined, using 10 measurements on 5 different crystals. The readings ranged from $27^\circ 33'$ to $27^\circ 44'$, averaging $27^\circ 39'$. The theoretical value, based on the ratio $d_{100}:d_{010}$ is $27^\circ 44'$ ($\Delta = 5'$). The twinned crystal mentioned above permitted two direct measurements of β . The observed values were $75^\circ 11'$ and $75^\circ 32'$, averaging $75^\circ 22'$. The calculated value for β is $75^\circ 29'$ ($\Delta = 7'$). The agreement in these cases is considered good.

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The writers are indebted to Prof. Wilhelm Eitel, whose earlier work on the indexing of tremolites served as a starting point for the present investigation. Dr. Eitel also placed at our disposal translations of several of the articles discussed. Dr. R. A. Hatch made available data on the reactivity of fluor-silicate batches, offered helpful suggestions for the synthesis of single crystals of fluor-tremolite, and critically reviewed the manuscript. We are grateful to M. V. Denny for the optical and density determinations and to H. R. Shell and R. L. Craig for the chemical analyses. Mrs. G. M. Huff performed much of the calculating required for indexing the x -ray patterns.

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