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Kartini Tjokroatmodjo

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A STUDY OF CRYSTALLIZATION OF SYNTHETIC FLUOR-GLAUCOPHANE COMPOSITIONS

By

KARTINI TJOKROATMODJO, 1936-

A

THESIS

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Approved by

D. E. Day (Advisor)

Robert E. Moore

Wm. H. Webb

A. Legsdin

ABSTRACT

The ability to form a stable glass and the crystallization properties of four compositions close to that of glaucophane, $Na_2Mg_3Al_2Si_8O_{22}(OH)_2$, have been studied. Three glasses were compared with a fourth glass containing no fluorine. The crystallization products of all four glasses were examined between the temperature range 600 - 1200°C. The crystallization products of the three fluorine containing glasses were similar, consisting of mica below 1000°C and of mica, fluor-glaucophane, enstatite and forsterite above 1000°C. In the fluorine free glass, enstatite was the only crystalline phase present below 1000°C, however, forsterite and enstatite were both present in samples crystallized above 1000°C. It is concluded that, although the fluor-glaucophane compositions could be used to study orientation effects in glass fibers, these compositions are not ideally suited for such a study since it was never possible to crystallize fluor-glaucophane from these compositions without the accompanying crystallization of mica, enstatite, and forsterite.

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I. INTRODUCTION

A. STATEMENT OF THE PROBLEM

In many respects inorganic glasses can be considered as polymers of silicon, boron, phosphorous, or other glass forming atoms connected by oxygen atoms. This concept suggests that glasses of certain compositions may contain linear chains and/or more complicated spatial configurations.

If it is assumed that linear chains are present in certain melts from which a glass is made, then it should be possible to orient the chains into a more or less regular pattern. Since the bonding between the chains is expected to be considerably weaker than the bonding within the chains, the orientation of these configurations should have a significant influence upon the properties of a glass. The properties of thin glass fibers, 5 - 20 microns in diameter, would be expected to be particularly sensitive to any orientation effects within the fiber.

The literature reveals conflicting opinions regarding oriented structures in glass fibers. Obviously, not all glasses need contain some type of orientable configuration. It becomes necessary, therefore, to have some knowledge of the structure of the melt from which the fiber is obtained. In other cases, some type of linear chain may be present in the melt, but the forming conditions may not be conducive to orienting the chains. These two factors, the lack of basic information pertaining to the structure of a melt and inappropriate forming conditions, could account for the differences in opinion regarding oriented structures in glass fibers.

In a recent study of meta-silicate melts having the composition $CaMgSi_2O_6$ (diopside) and $LiAlSi_2O_6$ (spodumene), De Wys$^{(1)}$ reported the presence of silicon-oxygen chains and found that these chains could be oriented under certain conditions. By controlled nucleation and crystallization of these melts he was able to vary the length of the chains. The importance of the controlled nucleation and crystallization raises the question, therefore, as to whether the structure of a melt would be the same regardless of the manner in which it is prepared. In other words, would the structure of a $CaMgSi_2O_6$ melt be the same if it is prepared from the various oxides CaO, MgO, SiO_2 as that obtained from melting diopside?

In order to answer this question it was considered appropriate to study a silicate melt of such a composition that when crystallized the crystalline material would be known to contain silicon-oxygen chains. This requirement limits the melts which can be studied to those having a composition corresponding to the pyroxenes, single chain silicates, or amphiboles, double chain silicates. In addition, the melt should be reasonably fluid at 1400 - 1600°C, the melting temperatures, and should form a stable glass.

Glaucophane, a naturally occurring amphibole of the composition $Na_2Mg_3Al_2(Si_4O_{11})_2(OH)_2$, was selected for study since this material was believed to fulfill most of the stated requirements. Since the hydroxyl ions cannot be retained in the melt at the melting temperatures, it was necessary to substitute fluorine ions for the hydroxyl ions. This problem was designed, therefore, to determine (1) whether a melt of the fluor-glaucophane composition would form a stable glass and had satisfactory forming characteristics, (2) the crystallization characteristics of the glass, and (3) whether this composition could be used in subsequent experiments for studying the orientation of chains in glass fibers.

B. LITERATURE REVIEW

1. Orientation in Glass Fibers

The presence of oriented structures in fine glass fibers has been demonstrated by Banerjee(2) and by Goldstein and Davies(3) with X-ray diffraction techniques. Banerjee(2) used this technique to study the influence of small additions (0.20 - 0.75%) of Au, Pt, and Ag-halides on the X-ray diffraction patterns of B_2O_3 glass fibers.

The degree and nature of crystallization in relation to the aging period of the glass samples was also studied. He found that the small additions of Au, Pt, and Ag-halides in B_2O_3 glass tended to show orientation of the crystals in the fibers, with the orientation becoming more prominent during the aging period. However, no orientation was found in borax, pure B_2O_3, or fused silica glass. Since oriented crystallization of the glass proceeded from the surface inward, Banerjee concluded that the chemical and physical nature of the surface is quite different from the interior.

Goldstein and Davies(3) reported the existence of oriented chains in B_2O_3 and $NaPO_3$ glass fibers, but they found no evidence of an oriented structure in silicate glass fibers. They suggest that Banerjee's failure to observe orientation in pure B_2O_3 fibers was accidental and caused by uncontrollable factors.

Among the studies which reported an absence of any orientation is that of Otto and Preston(4). In an investigation of the contraction of heat-treated alumino-borosilicate glass fibers, they observed a very similar contraction of the fibers in both the transverse and longitudinal directions. They interpreted the isotropic contraction of the glass fibers as indicating an absence of orientation. Strength tests, in both torsion and tension, also failed to show evidence of an oriented flaw strucutre on the surface of the fibers. This conclusion was based on the theory of Inglis(5), which states that a longitudinal orientation of the flaws, i.e., parallel to the axis, will not affect the longitudinal tensile strength. Since very similar contractions and equal strengths were observed in all directions, Otto and Preston concluded that the high strength of fibers is not due to an oriented molecular structure or to an oriented flaw structure, but must arise from other factors.

Further evidence against the orientation of chains in glass fibers was reported by Brannan(6). He investigated the elastic properties of alumino-borosilicate glass fibers from which he calculated Poisson's ratio. This work was based on the assumption that if there is any orientation of bonds, these bonds will be destroyed by heat-treating the glass fibers. Brannan found that Poisson's ratio was the same for as-formed fibers and fibers subjected to heat-treatment for periods of 2 1/2 hours at 510°C. He concluded, therefore, that elastic properties lend no support to the view that strong bonds are preferentially oriented in fine glass fibers.

2. Structural Studies

a. Silicates Containing Chains

The basic structural configuration in naturally occurring silicates is the SiO_4^{4-} group in which the silicon ion is located at the center of a tetrahedron formed by the four oxygen ions. Depending upon the number of shared oxygen ions at the corners, these tetrahedra can be joined to form single chains, double chains, sheet structures, or three dimensional frameworks. The two types of chain structures are described below.

(1) Single bonded chains, which are characteristic of the pyroxenes, are shown in Figure 1 and have the general formula $[SiO_3]_\infty$. Each SiO_3 unit has two negative charges which are balanced by cations located along the chains.

(2) Double bonded chains are characteristic of the amphibole minerals and are formed by combining two $[SiO_3]$ chains as shown in Figure 2. The basic repeating unit in the double chain is the $[Si_4O_{11}]_\infty$ group which has six negative charges. The negative charge on this group is again balanced by neighboring cations.

b. Silicates with Sheet Structures

Another silicate structure of importance to this study is the sheet structure or the two-dimensional network. In this type of structure three of the four tetrahedral corners of each SiO_4 tetrahedron are linked to adjoining SiO_4 tetrahedrons to form a continuous two-dimensional network. The composition of the sheet can be represented as $[Si_2O_5]_\infty$ where each $[Si_2O_5]$ group has two free

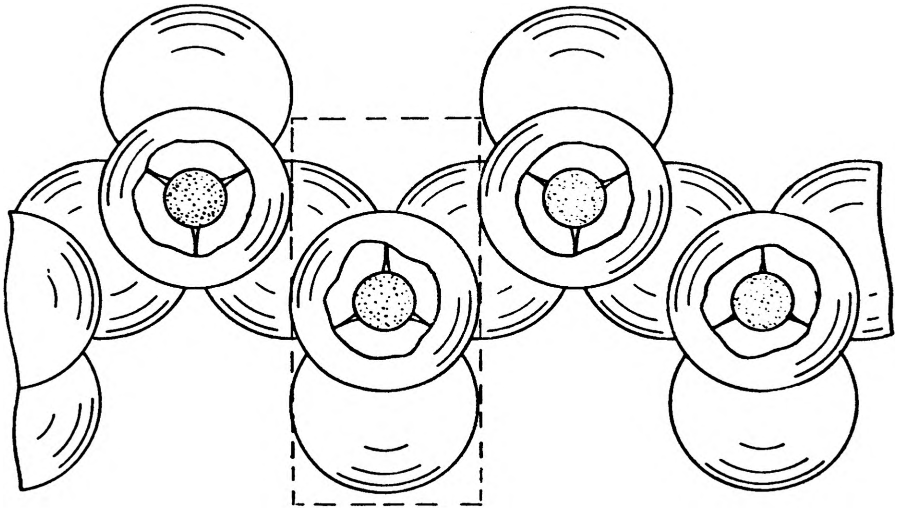

Figure 1. Pyroxene (meta-silicate) unit, $(SiO_3)^{2-}$.

(After Hauth$^{(7)}$)

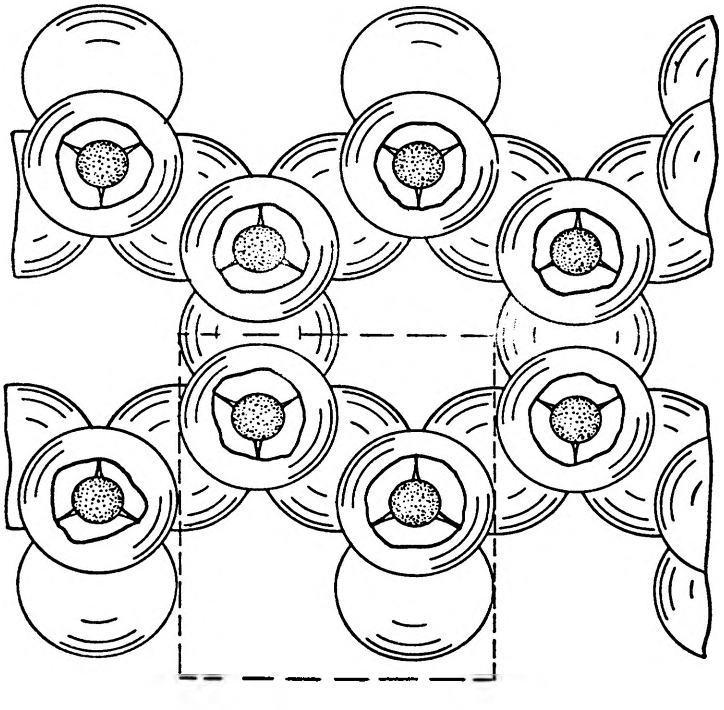

Figure 2. Amphibole unit, $(Si_4O_{11})^{6-}$.

(After Hauth$^{(7)}$)

negative charges as shown in Figure 3. These sheets may be associated singly with a layer of octahedrally coordinated cations as in kaolinite, $(OH)_4Al_2(Si_2O_5)$, or two silica sheets may be joined by a non-silica sheet as in pyrophyllite, $(OH)_2Al_2(Si_2O_5)_2$. Only the latter example will be discussed since it will show a possible relationship with the results of this study.

Minerals which have the same basic structural configuration as that of pyrophyllite are the montmorillonites, the illites, and the micas. The basic structure of these minerals is presented in Figure 4. The general formula for this class of minerals as proposed by Hoffman, Endell, and Wilm(8) is $(K, Na)_x(Al, Mg, Fe)_2(Al_xSi_{4-x})O_{16}$. In this three layer structure, cleavage takes place between the sheets, breaking the weak oxygen - to - oxygen bonds.

The structural difference between these minerals is a result of the extensive substitution of the cations in the octahedral and/or the tetrahedral positions. In pyrophyllite no substitution occurs in either position. The tetrahedral substitution in the other minerals may be represented by the formula (Al_xSi_{4-x}). In the montmorillonites the substitution of aluminum in the tetrahedral positions occurs only to a limited extent with $x < 0.25$. The general formula for the minerals of the montmorillonite group may be written as $(OH)_2(Al, Mg, Fe)_2(Si_2O_5)_2$ where the parent mineral, montmorillonite, has the octahedral positions filled predominantly with aluminum ions. In the illites $x = 0.25$ to 0.75. The illites may be considered to be intermediate between the montmorillonites and the micas. In the micas $x > 0.75$ and the charge deficiency created by the substitution of

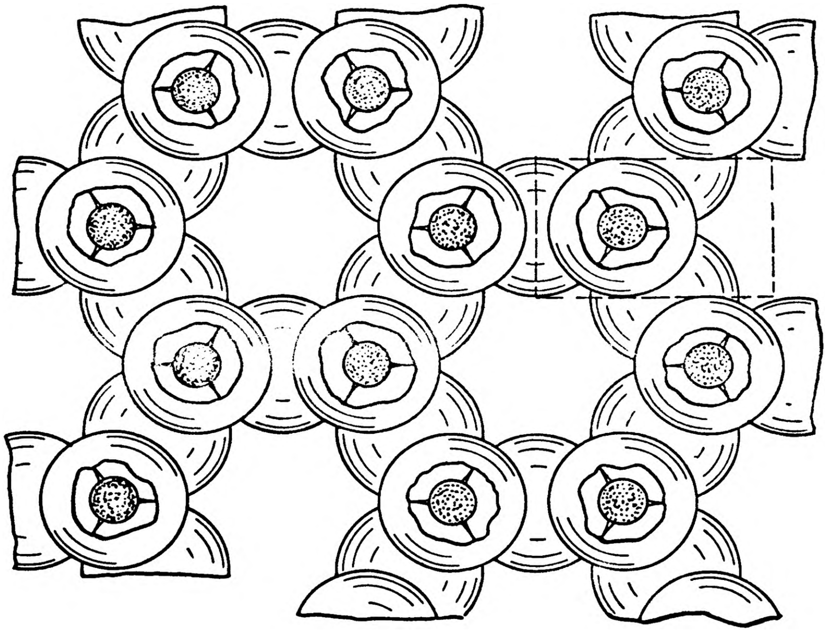

Figure 3. Silica layer unit, $(Si_2O_5)^{2-}$. (After Hauth(7))

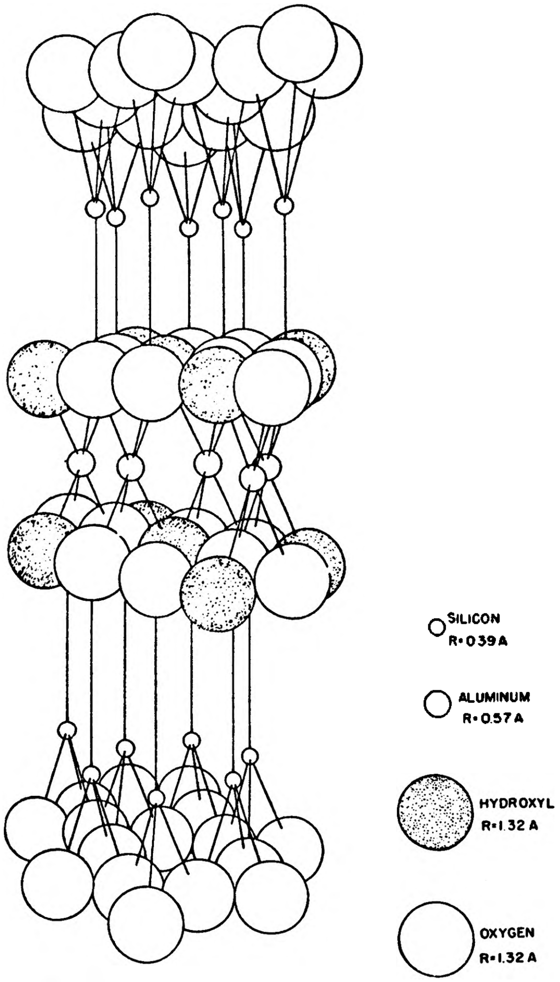

Figure 4. The three-layer sheet structure of Pyrophyllite, $(OH)_2Al_2(Si_2O_5)_2$, perspective, exploded in c direction

(After Hauth(7))

aluminum for silicon in the tetrahedral sites is balanced by cations such as K^+, Na^+ or Ca^{++}. These cations have a coordination number of approximately twelve. The cations K^+, Na^+ and Ca^{2+} are bonded to neighboring oxygen ions situated in the sheets above and below the cations. These relatively weak bonds hold the sheets together and are responsible for the large, thin flakes so characteristic of the micas.

c. Structure of Glaucophane

Glaucophane is a member of the amphibole group. It belongs to the monoclinic system and is characterized by the following parameters: (1) axial angle β+ 104°, (2) lattice dimensions of $a \simeq 9.7$(A°); $b \simeq 17.7$(A°); $c \simeq 5.3$(A°), and (3) space group: C 2/m.

According to Sundius' Classification discussed by Eitel(21), glaucophane may be derived from tremolite, $Ca_2Mg_5(Si_8O_{22})(OH)_2$, which has been considered to be the typical structure of the monoclinic amphiboles. Glaucophane is derived from the tremolite structure, Figure 5, by substituting two Na^+ ions for the two Ca^{2+} ions. This substitution creates a positive charge deficiency which is restored by substituting two Al^{3+} ions for two of the Mg^{2+} ions in tremolite. These two substitutions combine to give the composition of glaucophane, $Na_2Mg_3Al_2(Si_8O_{22})$ $(OH)_2$.

In glaucophane the double chains repeat along their length at intervals of approximately 5.3 A°, thus defining the c parameter of the unit cell. The double chains are then bonded to each other laterally by the Mg^{2+} ions to form a unit cell. This unit cell is in turn linked back to back by larger cations such as Ca^{2+}, Na^+, and K^+. The Na^+ ions occupy the eight-fold coordination sites while

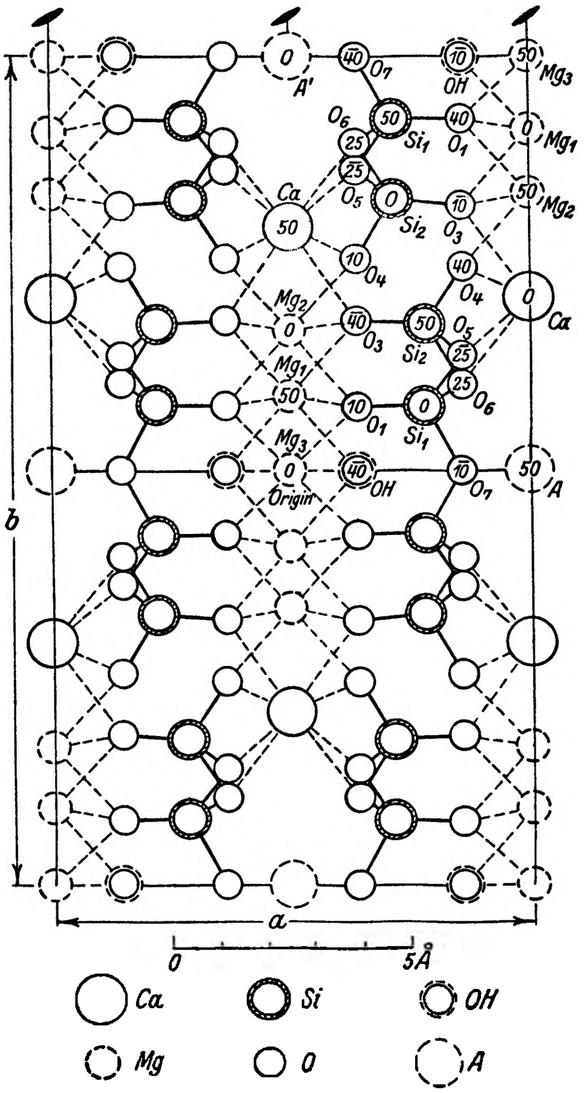

Figure 5. Projection of Tremolite Structure on (001). In Glaucophane, the positions occupied by Ca^{2+} ions are filled with Na^+ ions.

(After Warren(9))

the Mg^{2+} and the Al^{3+} ions are in six-fold coordination sites. The hydroxyl ions are bonded to the magnesium ions, with each hydroxyl ion being shared between three magnesium ions. In synthetic amphiboles the hydroxyl ions may be replaced partially or totally by fluorine.

3. Synthesis of Amphiboles & Pyroxenes

Numerous attempts have been made to produce synthetic amphibole minerals by several different techniques. This research becomes very extensive after Ludke's(10) work on synthesizing amphiboles as a potential substitute for asbestos. He used a pneumatolytic technique in which alkalies, alkaline earth compounds, silica and fluorides were heated in an air stream at temperatures below the decomposition temperature of the synthetic amphibole.

Ehrenberg(11) synthesized fluor-tremolite by the solid state reaction of an appropriate mixture of CaF_2, $CaCO_3$, MgO, and SiO_2. Tremolite was obtained when the mixture was reacted at temperatures just below the formation of a liquid phase, although diopside and forsterite were invariably present. A fluor-tremolite was obtained by recrystallization from the melt.

Gregoriev's(12) method of synthesizing amphiboles was of particular interest to the present investigation. He found that amphiboles can be synthesized at normal pressure from melts in which fluorine replaces the hydroxyl normally present in the natural amphiboles. He concluded, however, that only pyroxenes would crystallize from melts obtained by melting natural amphiboles without fluorine additions.

Comeforo and Kohn(13) used a similar technique in which (1) the batch was melted by heating to 1400°C (2) maintained at the melting temperature for 4 - 8 hours, and (3) cooled to 1100°C within 3 - 8 hours, whereupon, the furnace was turned off and allowed to cool to room temperature. Sealed graphite crucibles were used to prevent the loss of fluorine from the melt. To eliminate the presence of carbonates, hydroxides, or other compounds that decompose with the liberation of gases, certain components were initially reacted to form stable anhydrous non-volatile materials such as $Na_2MgSi_3O_8$ (as glass) and $CaSiO_3$. The resulting crystalline phases consisted primarily of brittle, acicular crystals of fluor-amphiboles (at least 80%).

II. EXPERIMENTAL PROCEDURE

A. SAMPLE PREPARATION

Reagent grade chemicals were used to prepare four different glasses, the compositions of which are given in Table I. Composition A corresponds to synthetic fluor-glaucophane, $Na_2Mg_3Al_2(Si_8O_{22})F_2$, whereas composition B and C contain an excess of fluorine. The excess fluorine was introduced into the batches by substituting MgF_2 for the MgO. Composition D, which contains no fluorine, was prepared for purpose of comparison.

After thorough mixing the batches were placed in kyanite crucibles and melted in a gas fired furnace at 1500°C. Glasses A, B, and C were held at 1500°C for approximately 30 minutes, whereupon the glasses were immediately quenched in water. The total melting time was about two hours. A similar procedure was followed for composition D, with the exception that it was held at 1500°C for three hours before quenching in water.

Table I. Composition of Experimental Glasses, Weight Percent.

	A	B	C	D
Na_2O	7.9%	7.8%	7.7%	8.1%
Al_2O_3	13.0	12.8	12.6	15.75
MgO	10.3	7.6	5.0	13.35
MgF_2	7.9	11.7	15.4	-
SiO_2	61.0	60.1	59.4	62.8

After each glass had been dried and crushed, the -8 to +50 mesh material was separated and used for the subsequent crystallization experiments.

Since the loss of fluorine from the glasses during melting was inevitable, the quenched glasses were analyzed to determine the final fluorine content. The initial and final fluorine contents of glasses A, B, and C are given in Table II.

Table II. Flourine content of glasses
A, B, and C. Before and after
Melting, Weight Percent.

initial			final		
A	B	C	A	B	C
4.8%	7.15%	9.4%	2.79%	3.54%	5.54%

B. HEAT TREATMENT

Samples of each glass were heat-treated in an electric furnace at various temperatures ranging from 600°C to 1200°C. After the furnace had reached the desired temperature, platinum foil containers filled with the crushed glass (-8 to +50 mesh) were placed in the furnace for the desired period of time. When the required time had elapsed, the platinum containers were removed from the furnace and the glass samples allowed to cool to room temperature. The heat-treated samples were then divided into two portions. One portion was ground to -200 mesh for X-ray diffraction, while the second unground portion was used for optical property measurements.

C. IDENTIFICATION OF CRYSTALLIZED PRODUCTS

The crystallized material in each heat-treated sample was identified by X-ray diffraction using Ni - filtered Cu-K_α radiation. In addition, the refractive index and the general crystal habit of each heat-treated sample were determined with a petrographic microscope.

Since no previous X-ray data could be found for glaucophane, it was necessary to examine samples of naturally occurring glaucophane. Two different samples of natural glaucophane were obtained from the Geology Departments at the Missouri School of Mines and Metallurgy and at the University of Missouri, Columbia. The X-ray diffraction patterns for the two samples were identical. The X-ray data for these samples are given in Table III, which shows a comparison between the data for glaucophane and that for fluor-tremolite and fluor-richterite, $Na_2CaMg_5(Si_8O_{22})(F_2)$. The X-ray data for fluor-richterite, also called soda-tremolite, have been included since a comparison of this compound with fluor-tremolite and glaucophane reveals many similarities.

TABLE III. X-Ray Data of Synthetic Fluor-Tremolite, Fluor-Richterite and Natural Glaucophane

	d(A°)			I/Io		
hkl	Tremolite* (obs.)	**Richterite**** (calc.)	Glaucophane (obs.)	Tremolite	Richterite	Glaucophane
110	8.41	8.4	8.2	100	100	100
040	4.468	4.489	4.45	12	10	9
220	4.261	4.205	4.0	25	4	13
131	3.9458	3.859	3.78	3	4	9
131	3.4682	3.38	3.375	6	10	9
240	3.357	3.265	3.2	23	60	26
310	3.206	3.124	3.055	100	100	100
330	2.905	2.803	2.9	26	76	26
331	2.8346	2.721	2.74	3	9	12
151	2.8194	2.70	2.68	9	20	22
061	2.7094	2.582	2.58	2	7	9
202	2.6522	2.524	2.52	2	6	10
350	2.509	2.387	2.387	4	11	12
171	2.4332	2.207	2.281	3	7	8
261	2.3094	2.159	2.150	4	8	8
202	2.2034	2.048	2.056	1	3	5
510	2.0636	1.8920	1.865	4	29	8
1.11.0	1.8359	1.609	1.603	2	10	18

* Taken from American Mineralogist 39, 1954, pp. 544.
**Taken from American Mineralogist 40, 1955, pp. 415.

III. RESULTS AND DISCUSSION

A. CRYSTALLIZATION OF GLASSES A, B, C, AND D.

At 1500°C all four glasses were fluid and easily quenched. Composition A, B, and D quenched to a clear glass, whereas composition C was slightly opaque. The glass remaining in the crucible for composition A, B, and C became opaque on cooling because of the fluorine-induced instantaneous crystallization. The degree of opacity was directly related to the fluorine content, being least for composition A and greatest for composition C. Composition D, which was free of fluorine, did not exhibit instantaneous crystallization and remained clear.

The behavior of fluorine as a catalyst for crystallization is illustrated by temperatures necessary to initiate crystallization as shown in Table IV. It is apparent that the fluorine-containing glasses commenced to crystallize at 700°C, whereas a temperature of 900°C was necessary to initiate crystallization in the fluorine-free glass, composition D.

An examination of the X-ray diffraction patterns for the glasses containing fluorine, revealed that a mica phase was the only crystalline material present in the samples heat-treated below 1000°C. The results of the various heat-treatments are tabulated in Table IV, where the differences in crystallization characteristics of the compositions with and without fluorine are apparent. In the case of glass D which contained no fluorine, enstatite ($MgSiO_3$) was the only crystalline phase present below 1000°C and no mica was observed.

TABLE IV. Crystalline Phases Identified in Heat-Treated Glasses.

Temperatures (°C)	Time (hours)	GLASS			
		A	B	C	D
600	1	glass	glass	glass	glass
	4	"	"	"	"
700	1	"	"	"	"
	4	mica + glass	mica + glass	mica + glass	"
800	4	"	"	"	"
900	4	"	"	"	enstatite + glass
	8	"	"	"	"
	24	"	"	"	"
1000	4	"	"	"	"
	24	mica + glaucophane + forsterite + glass	mica + glaucophane + forsterite + glass	mica + glass	"
1100	4	enstatite + glass	mica + glaucophane + glass	mica + glass	"
	12	forsterite + enstatite + glass	glaucophane + enstatite + glass	mica + glaucophane + glass	"
	24	forsterite + glass + enstatite	forsterite + glass + enstatite	glaucophane + forsterite + glass	enstatite + glass + forsterite

When the glasses containing fluorine (A, B, and C) were heat-treated above 1000°C, the phases crystallizing from these glasses were no longer identical. The results summarized in Table IV show that glaucophane was one of the phases crystallizing in glasses B and C. On the other hand, the phases crystallizing above 1000°C for glasses A and D are similar, consisting of forsterite, Mg_2SiO_4, and enstatite. However, the major crystalline phase in glass A was forsterite, whereas that in glass D was enstatite. This similarity between glasses A and D is most probably related to the fluorine content, since glass D contains no fluorine and glass A contains only 2.79%. Likewise, the similar fluorine contents for glasses B and C are reflected in the nearly identical crystallization behavior.

The composition of glass D corresponds to the composition of glaucophane, except that in this glass all of the hydroxyl ions in naturally occurring glaucophane have been replaced by oxygen ions. The presence of enstatite, a pyroxene, in glass D is not considered unusual. It is improbable that an amphibole could crystallize from this glass since the amphibole compounds require either hydroxyl or fluorine ions. Previous studies on the crystallization behavior of amphibole melts have reported the crystallization of a pyroxene compound. In a study of the crystallization tendencies of hornblende compositions, Gregoriev(12) concluded that a pyroxene would crystallize if a natural amphibole was remelted with no fluorine addition.

The crystallization of mica in glasses A, B, and C heat-treated below 1000°C is in agreement with the results reported by Comeforo, Eitel and Shell(14) and Doelter(15). Doelter, in a study of artificial mica, concluded that fusion of alumina-bearing amphibole with NaF and MgF_2 result in the crystallization of a magnesium mica. Similarly, Comeforo, Eitel, and Shell state that compositions containing alumina and sodium tend to promote the crystallization of a sodium fluor-mica, $(Na, K)_2Mg_6(F)_4Si_6Al_2O_{20}$.

It should be noted that the exact composition of the mica phase observed in glasses A, B, and C has not been completely determined. A comparison of the X-ray diffraction patterns for the mica phase in these glasses with all of the patterns published previously for the different micas always revealed some dissimilarities. Sodium fluor-phlogopite mica, $Na_2Mg_6(Si_6Al_2O_{20})(F)_4$, has been observed in melts of similar composition by Comeforo, Eitel and Shell. However, no X-ray data have been published for a synthetic sodium fluor-phlogopite mica. The X-ray data for the mica phase in glasses A, B, and C have been compared with published data for a synthetic potassium fluor-phlogopite mica, but the agreement is not good.

Tentatively, the mica in glasses A, B, and C is believed to have a composition close to that of paragonite mica, $Na_2Al_4(Si_6Al_2O_{20})(OH)_4$. Since no X-ray data are available for a synthetic fluor-paragonite mica, it has only been possible to compare the data for the mica in glasses A, B, and C with that published for naturally occurring paragonite mica. This comparison also shows a lack of agreement. However, this lack of agreement could result from the total replacement of the hydroxyl ions and from a partial replacement of the Al^{3+} ions in natural paragonite with fluorine ions and Mg^{2+} ions, respectively, in the synthetic mica.

Another difficulty encountered in the identification of the crystallization products in glasses B and C was the detection of glaucophane. Reference to the X-ray data, Table III, shows that glaucophane has only two strong diffraction lines at 8.2(A°) and 3.055(A°), with the remaining lines being relatively weak. The identification of glaucophane in these glasses, therefore, was based upon the two strongest lines. The weaker diffraction lines for glaucophane were never observed in any of the glasses studied.

The partially crystallized samples of each composition were also examined with a petrographic microscope to determine the general appearance of the crystals and the refractive index of the remaining glass. Only a small change in the refractive index of the remaining glass was observed as the various crystalline phases separated from the host glass. The refractive index varied between 1.50 - 1.52, 1.49 - 1.51, 1.48 - 1.50, and 1.52 - 1.54 for compositions A, B, C and D, respectively. From the relative magnitudes of the refractive index it is apparent that fluorine tends to lower the refractive index.

Rather pronounced changes were observed in the appearance of the crystals. At lower temperatures very small crystals separated from the glass, which later grew to an acicular shape. At higher temperatures, 1100°C, a very large number of large fibrous crystals were observed.

B. INVESTIGATION OF GLASS B

Since the preliminary crystallization experiments on all three of the fluorine-containing glasses indicated that glass B was the composition most likely to crystallize to significant amounts of glaucophane, it was decided to explore that temperature range over which the crystallization of glaucophane was likely to occur. A pronounced change in the crystallization products of glass B was observed for the two samples heat-treated at 900°C - 24 hours and 1100°C - 24 hours; mica being in the former with forsterite and a small amount of enstatite being in the latter. The appearance of forsterite and enstatite and the disappearance of the mica at 1100°C suggested that fluorine was being liberated at these temperatures with the subsequent decomposition of the mica. Since the crystallization of glaucophane was also detected in this temperature range, additional samples of glass B were given several heat-treatments to determine whether the quantity of glaucophane crystallized could be increased.

The selection of the additional heat-treatments was influenced by the observation that below 1000°C mica crystallized from the glass, while at higher temperatures, 1100 - 1200°C, enstatite and forsterite crystallized. This change in the crystallization products was considered important since in mica the SiO_4 tetrahedra form infinite two dimensional sheets, whereas, enstatite contains single chains of the formula $[SiO_3]_\infty$ and forsterite contains isolated SiO_4 tetrahedra. It should be recalled that glaucophane contains double chains of the type $[Si_4O_{11}]_\infty$ and this structural configuration can be considered as being intermediate between the infinite sheet structures in mica and the single chains and isolated tetrahedra in enstatite and forsterite, respectively. The assumption that the formation of glaucophane could be related to the disappearance of the mica was supported further by the preliminary crystallization experiments, wherein glaucophane had only been detected in a few samples heat-treated close to the upper temperature limit for the mica, Table IV.

The first heat-treatment shown in Table V consisted of holding glass B at 1050°C for periods of time from 4 to 24 hours. This heat-treatment resulted in an increased quantity of glaucophane in addition to the mica and forsterite present. In the second heat-treatment, samples of glass B were given a preliminary heat-treatment at 600°C for 4 hours followed by an additional heat-treatment at 1050°C. Glaucophane was also present in these samples and appeared to be forming at the expense of the mica.

The third heat-treatment in Table V consisted of crystallizing the mica phase at 800°C and then heat-treating the partially crystallized samples at 1050°C. This procedure also resulted in an increased amount of glaucophane, but this was accompanied by an apparent increase in the amount of forsterite at longer times. Unfortunately, glaucophane was never obtained as the only crystalline phase, since mica and forsterite were also present. However, the concept that larger amounts of glaucophane could be formed if the SiO_4 tetrahedra were initially joined into the continuous sheet structure of the mica appears to have been realized.

TABLE V. Selected Heat Treatments and Crystalline Products for Glass B.

NO.	Temperatures (°C)	Time (hrs.)	Sample B
1	1050	4	mica (>) + glaucophane (<) + forsterite (<) + glass
		12	mica + glaucophane + forsterite + glass
		24	mica (<<) + glaucophane (>) + forsterite (>) + glass
2	600 followed by	4	glass only
	1050	4	mica (>>) + glaucophane (<<) + glass
		12	mica + glaucophane (>) + forsterite + glass
		24	mica (<<) + glaucophane + forsterite (>>) + glass
3	800 followed by	4	mica (>>) + glass
	1050	12	mica + glaucophane + forsterite + glass
		24	mica (<) + glaucophane (>>) + forsterite (>) + glass
		48	mica (<<) + glaucophane + forsterite (>) + glass
4	1200	4	forsterite (>>) + glass
		12	forsterite (>) + enstatite + glass

A complicating factor associated with the crystallization of glass B at higher temperatures was the continuous loss of fluorine. While it was felt that the formation of glaucophane could be enhanced by crystallizing the mica at 800°C, where the loss of fluorine was low, and then raising the temperature to increase the fluorine loss and decompose the mica, this procedure was never completely successful.

The partial success of this procedure is undoubtedly related to the sudden increase in weight loss for glass B at 1000 - 1050°C as shown in Table VI. It is apparent from the losses shown in Table VI that the decomposition of the mica at 1050°C is directly related to the increase loss in fluorine. The loss of fluorine at 1050°C indicates, therefore, that forsterite will invariably be present at and above this temperature. The weight loss of the fluorine-free composition, glass D, was 0.2% after 24 hours at 1050°C.

TABLE VI. Weight Loss on Heating Composition B for 24 Hours at the Temperatures Indicated.

Temperature (°C)	Weight Loss (%)
600	0.06
750	0.26
850	0.75
925	0.85
1000	1.23
1050	3.83
1100	3.53

IV. SUMMARY

This investigation is considered to be the first attempt to synthesize fluor-glaucophane from a melt at normal pressure. The procedure followed was to prepare three glasses of varying fluorine content which were then crystallized over the temperature range 600 - 1200°C. The crystallization products of the fluorine containing glasses were also compared to the crystallization products of a fourth fluorine-free glass which had been crystallized at the same temperature.

All four compositions were found to be sufficiently fluid at a melting temperature of 1500°C and formed a stable clear glass when quenched in water. The general properties of the melt such as viscosity and surface tension indicated that glass fibers could be drawn from melts without difficulty.

The crystallization characteristics of these compositions were studied since one of the purposes of this investigation was to determine whether a fluor-glaucophane composition could be used for studying orientation effects in glass fibers. While the glasses studied in this investigation could be used in such a study, they have one disadvantage; namely, the crystallization of fluor-glaucophane composition was always accompanied by the crystallization of mica, enstatite, and forsterite. Consequently, when the crystallized glasses are remelted, as would be done in a study of orientation in fibers, the melt would contain several different types of silicon-oxygen configurations. In other words, it is possible that remnants of the sheet structure from the mica, single chains from the enstatite, and isolated SiO_4 tetrahedra from the forsterite could all exist in the melt from which the fibers would be drawn. Since the orientation of chain structures in glass fibers is not well established, the presence of several different structural configurations would be an undesirable complication.

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VITA

Kartini Tjokroatmodjo was born in Solo, Indonesia, on August 10, 1936. After receiving her elementary education at the Public Elementary Grade School, she attended the Junior and Senior High School at Jogjakarta and graduated in June, 1955.

In August of 1955, she enrolled in Chemical Engineering at the University of Gadjah Mada at Jogjakarta, and received her Bachelor of Science Degree in May, 1960.

After graduation she worked with the Java Glass Company and the Java Enamel Company at Djakarta for two years. In 1963, under the sponsorship of the National Research of Science of Indonesia at Djakarta, she continued her study in Ceramic Engineering with a scholarship granted from the Agency for International Development. She entered the Graduate School of the University of Missouri at Rolla in January, 1963.