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Crystallization of a Tetrasilicic Fluormica Glass

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The crystallization of a tetrasilicic synthetic mica glass of nominal composition $K_2Mg_5Si_8O_{20}F_4$ was investigated at selected temperatures from 560° to 1150°C using DTA, density measurements, electron microscopy, and X-ray diffraction techniques. Crystallization is shown to occur in 2 stages. (1) Initial structural ordering occurs at $\approx 600^\circ\text{C}$, as indicated by a strongly exothermic reaction, an increase in density, and the appearance of X-ray diffraction lines. (This transformation temperature is related to fluorine content.) (2) The crystal morphology of the glass-ceramic changes at 900° to 1150°C. A mechanism is proposed for the transformation from amorphous to crystalline structure in this synthetic mica system.

I. Introduction

FLUORINE micas can be used for electrical insulation because they exhibit an unusual combination of good dielectric and mechanical strength and thermal stability. These compounds, commonly called fluormicas, are structural analogs of natural micas in which fluorine ions replace hydroxyl ions. The original work on fluormica systems was directed toward developing suitable substitutes for the strategic natural minerals muscovite and phlogopite. However, as the properties of the synthetic materials became evident, fluorine micas were considered a new and unique class of materials. Shell and Ivey¹ have thoroughly reviewed and documented the extensive literature on the fluormicas.

Although most synthetic mica compounds readily crystallize when the melt is cooled, Hatch *et al.*² reported that a tetrasilicic fluormica, $K_2Mg_5Si_8O_{20}F_4$, exhibited a tendency toward glass formation when severely quenched. Tuzzeo³ developed a process for forming this composition by conventional glass-ceramic fabrication techniques. Subsequently, Schumacher⁴ and Ainsworth⁵ reported the dielectric and mechanical properties, respectively, of the same mica glass-ceramic composition. The results of these investigations indicate that, although $K_2Mg_5Si_8O_{20}F_4$ melts near 1200°C, a dramatic structural transformation occurs at $\approx 600^\circ\text{C}$ when the quenched glass is heated. This transformation is especially evident as sharp discontinuities in measurements of the dynamic elastic modulus, mechanical damping, and thermal expansion.

Chen⁶ reported that a synthetic mica glass crystallizes in 2 stages, wherein the appearance of mica crystals is preceded by the formation of an intermediate pseudocrystalline phase. Chen did not report the exact composition of the mica glass studied, indicating only that it was near fluorphlogopite ($K_2Mg_6Al_2Si_6O_{20}F_4$) and contained B_2O_3 , which appeared to facilitate melting. Grossman⁷ has described the phase development and dependence of mechanical properties on microstructure for tetrasilicic fluormica glass-ceramics from the system K_2O - MgF_2 - MgO - SiO_2 ; these glass-ceramics exhibit easy machinability. This worker reported a 2-stage crystallization mechanism for materials which are near the theoretical tetrasilicic composition, $K_2Mg_5Si_8O_{20}F_4$, but are ≈ 25 mol% deficient in fluorine.

In the present study, the structural transformations encountered during the crystallization of a tetrasilicic fluormica glass are characterized. This glass, from the quaternary system K_2O - MgF_2 - MgO - SiO_2 , is also near the theoretical $K_2Mg_5Si_8O_{20}F_4$ composition but contains a slight excess of F.

II. Crystal Chemistry

Several classification systems based on molecular composition and crystal structure have been proposed for mica compounds. One of the most general structural formulas is that given by Pauling:⁸ $KX_nY_4O_{10}(OH,F)_2$, where $2 \leq n \leq 3$, X represents cations of coordination number 6 and Y cations of coordination number 4, chiefly

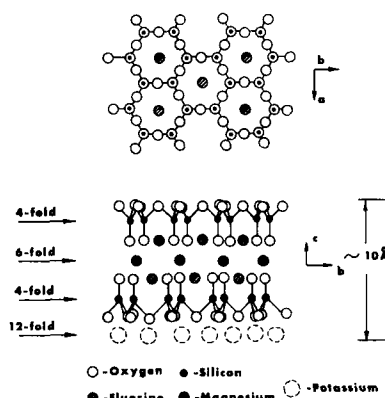


Fig. 1. Schematic of tetrasilicic fluormica ($K_2Mg_5Si_8O_{20}F_4$) structure.

Si^{4+} and Al^{3+} . Applying this formula to synthetic fluormica compounds yields a general formula $ZX_nY_4O_{10}F_2$, where Z denotes a cation of coordination number 12, usually K (as noted by Pauling), but possibly Ca or Na. Winchell⁹ classified micas into 2 systems, heptaphyllite and octaphyllite, indicating either 7 or 8 cations for every 10 oxygen atoms in the structure, corresponding to the cation content when Pauling's subscript n reaches the extreme values.

The structure of the tetrasilicic synthetic mica $K_2Mg_5Si_8O_{20}F_4$ is shown schematically in Fig. 1. Basically it consists of 2 sheets of SiO_4 tetrahedra with their vertices pointing inward. These tetrahedra are linked in one plane by sharing the 3 O atoms which form the base of each tetrahedron, each anion being shared by 2 tetrahedra. Continuous extension of this linkage creates a hexagonal network within each tetrahedrally coordinated plane. The 2 tetrahedral sheets are strongly bonded together by Mg ions which are in 6-fold or octahedral coordination. The F ions, although lying in the plane of the apical O ions, are bonded to the Mg cations only. Thus the anions forming the octahedral site are 2 F ions and 4 O ions. The K ions, in 12-fold coordination, bond adjacent double sheets together. The cleavage plane characteristic of mica minerals lies between sets of double sheets.

The cations in tetrahedral coordination are usually either Si or a combination of Si and Al. Micas containing only Si in the tetrahedral sites are called tetrasilicic; those containing an average Si:Al ratio of 3:1 in 4-fold coordination, trisilicic; and those with equal numbers of Si and Al in YO_4 coordination, disilicic.

The octahedral sites formed by the 2 F and 4 O ions are occupied by cations having ionic radii of 0.6 to 0.9 Å, most commonly Mg^{2+} , Al^{3+} , Mn^{2+} , Mn^{3+} , Ti^{4+} , and Li^+ . Two distinct groups of mica compounds (as determined by the number of filled octahedral positions) are known, i.e. those having $2/3$ of the available sites filled (dioctahedral) and those having all octahedral positions filled (trioctahedral). These groups correspond to Winchell's heptaphyllite and octaphyllite series.⁹

The structural formula for mica may be doubled to give $Z_2X_{2n}Y_8O_{20}F_4$. As noted by Shell and Ivey,¹ the doubled formula is the actual unit cell of the structure, indicating 2 tetrahedral sheets/layer of mica; when the doubled formula is used, as in the present discussion, subscript fractions are avoided for many substituted fluormicas.

Although the present fluormica, $K_2Mg_5Si_8O_{20}F_4$, is tetrasilicic, it is neither an octaphyllite nor a heptaphyllite and has no known

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Table I. Compositions of Tetrasilic Mica Glass-Ceramics Studied

Constituent	Amount in batch (wt%)		Analysis of batch II
	I	II	
K ₂ O	11.48	11.18	9.88
MgO	14.74	9.57	14.84
MgF ₂	15.19	22.19	19.28
SiO ₂	58.59	57.06	56.00

natural mica analog. Seifert and Schreyer,¹⁰ who synthesized K₂Mg₅Si₈O₂₀(OH)₄ by hydrothermal techniques, emphasize the theoretical importance of this compound for the crystal chemistry of the entire mica system. With ⁵/₆ of the available octahedral sites filled, the phase represents a member intermediate between the dioctahedral and trioctahedral series, which have generally been considered as independent groups.

Both the nature and quantity of the cations in octahedral sites are important in the tetrasilic system. When the tetrahedral layers are filled with Si ions only, i.e. free of Al³⁺, and the octahedral sites are either filled with Mg²⁺ or ²/₃ filled with Me³⁺ ions, the layers are neutral, no K⁺ is needed, and the material is a clay. In natural micas, Al replaces Si in the tetrahedral layer, and electrical neutrality is maintained by K⁺ ions joining the layers together. These micas are unique because the charge on the layers results from Mg²⁺ vacancies and not from the usual Al=Si interaction.

A meager amount of physical property data for K₂Mg₅Si₈O₂₀F₄ has been reported. In addition to the data already cited, Alley and Shell¹¹ gave the melting point of K₂Mg₅Si₈O_{19.75}F_{4.5} as 1176°C, and Shell and Ivey¹ listed its unit cell dimensions *a* = 5.22 Å, *b* = 9.16 Å, and *c* = 10.05 Å, with a β value of 95° and a calculated density of 2.835 g/cm³ for K₂Mg₅Si₈O₂₀F₄ formed by solid-state reaction at 1000°C.

III. Experimental Procedure

(1) Sample Preparation

The glasses studied (Table I) were prepared from K₂SiF₆,* K₂CO₃,[†] MgO,[‡] and SiO₂.[§] Composition I represents the stoichiometric K₂Mg₅Si₈O₂₀F₄ formula and composition II the same formula with 50 mol% excess F. Glasses were melted at 1400°C in covered high-SiO₂ fireclay crucibles and pressed between stainless steel plates into small disks. Analytical samples were selected from a given melt according to their density, as measured with a glass densitometer[§] using the settling method. Samples of glass II having a density of 2.525 ± 0.005 g/cm³ were selected for subsequent analyses, since preliminary studies indicated that this value was associated with consistently high F content and absence of crystallinity. Samples were heat-treated isothermally in an electric furnace under an air atmosphere at selected temperatures from 560° to 1150°C.

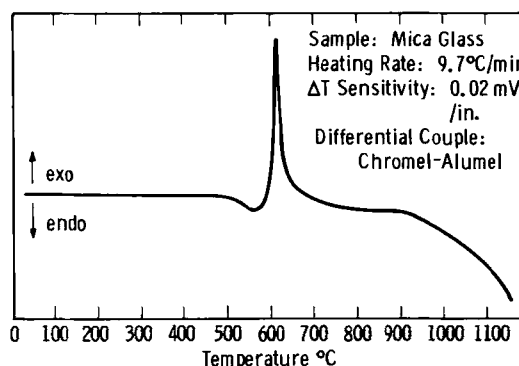
(2) Sample Analyses

Samples of both heat-treated and as-quenched glasses of ~200-mesh particle size were subjected to DTA^{*} using a Pt microsample holder on a ring-type Chromel-Alumel differential thermocouple at 10°C/min in air. Both Al₂O₃ and previously transformed glass were used as the reference standard; the latter gave a better match of thermal properties, thereby yielding a straighter baseline. A constant sample and reference weight (10 mg) was used for each DTA determination. The density of solid heat-treated samples was measured using the settling technique. Powder samples were analyzed by X-ray diffraction using the Debye-Scherrer camera technique with CuKα radiation, an Ni filter, and a 3-h exposure time. Microstructural characterization included electron microscopy^{||} of Pt-preshadowed carbon replicas of unetched fracture surfaces and SEM^{**} examination of Cr-coated etched fracture surfaces.

IV. Results and Discussion

(1) Chemistry

A primary concern in the present investigation was volatilization of F₂ during glassmelting. Previous studies have shown that an F

**Fig. 2. DTA thermogram for tetrasilic fluormica glass.**

deficiency causes fluormica compounds to decompose to forsterite (Mg₂SiO₄) and norbergite (Mg₂SiO₄·MgF₂).¹ Grossman⁷ has reported that enstatite (MgSiO₃) develops at ≈980°C in the crystallization of a tetrasilic mica glass-ceramic of gross composition near K₂Mg₅Si₈O_{20.5}F_{3.0}, i.e. ≈25 mol% deficient in F. Early melting trials using glass I, corresponding to stoichiometric K₂Mg₅Si₈O₂₀F₄, yielded F losses considered excessive for this study. Therefore, glass II, with 50 mol% excess F, was used in most of the work reported herein. Wet chemical analysis^{††} of as-melted glass II (Table I) indicates a residual F content corresponding to an approximate tetrasilic composition K₂Mg₅Si₈O_{19.75}F_{4.5}, i.e. 12.5 mol% excess F. The following discussion pertains to glass II, except where otherwise noted.

(2) DTA

A typical DTA thermogram obtained when the quenched mica glass was reheated from room temperature is shown in Fig. 2. The large exotherm at ≈600°C is indicative of the energy released in the initial stage of the transformation from amorphous to crystalline structure in this system. No thermal changes were encountered on cooling below the melting point. Thermograms of specimens subjected to prior isothermal treatments from 560° to 640°C show a decrease in exothermic peak intensity with increasing time along any given isotherm (Fig. 3). These results indicate that the transformation is irreversible and essentially complete after 4 h at 600°C and only 30 min at 640°C.

Fluorine content profoundly influences the temperature position of the exotherm. This behavior became apparent early in the investigation when identical experimental conditions (sample weight, reference weight, particle size, and heating rate) resulted in varied exothermic peak temperatures for samples from different melts. Chemical analyses of the bulk glass revealed that these samples contained various amounts of F.^{‡‡} These data indicate that the position of the exotherm occurs at progressively lower temperatures as the F content of the bulk glass increases.

(3) Density Measurements

Density measurements on isothermally heat-treated specimens (Fig. 4) indicate that the transformation approaches a limiting value after short times of heat treatment at 580°, 600°, and 620°C. Densification does not occur rapidly at 560°C; however, as the heat-treatment temperature increases, the time required to attain the limiting density diminishes rapidly. The starting density of 2.525

*Cities Service Company Industrial Chemicals Marketing Dept., Atlanta, GA.

†Reagent grade, Fisher Scientific Co., Pittsburgh, PA.

‡Ground fused, General Electric Co., Schenectady, NY.

§AGR density comparator, American Glass Research, Inc., Butler, PA.

||R. L. Stone model KAH thermal analyzer, Columbia Scientific Industries Corp., Austin, TX.

**Model JEM-7 100-kV electron microscope, Japan Electron Optics Co., Ltd., Tokyo, Japan.

††Cambridge Stereoscan scanning electron microscope, Kent-Cambridge Scientific, Inc., Morton Grove, IL.

‡‡Spectrochemical Laboratories, Inc., Pittsburgh, PA.

Exothermic peaks occurred (±5°C) at 658°, 650°, 652°, 648°, 639°, 636°, and 608°C when the F content was (in wt%) 8.73, 8.85, 8.86, 9.89, 10.30, 10.30, and 10.80, respectively. The F content of stoichiometric K₂Mg₅Si₈O₂₀F₄ is 9.26 wt%; thus, these values include both F-rich and F-deficient compositions.

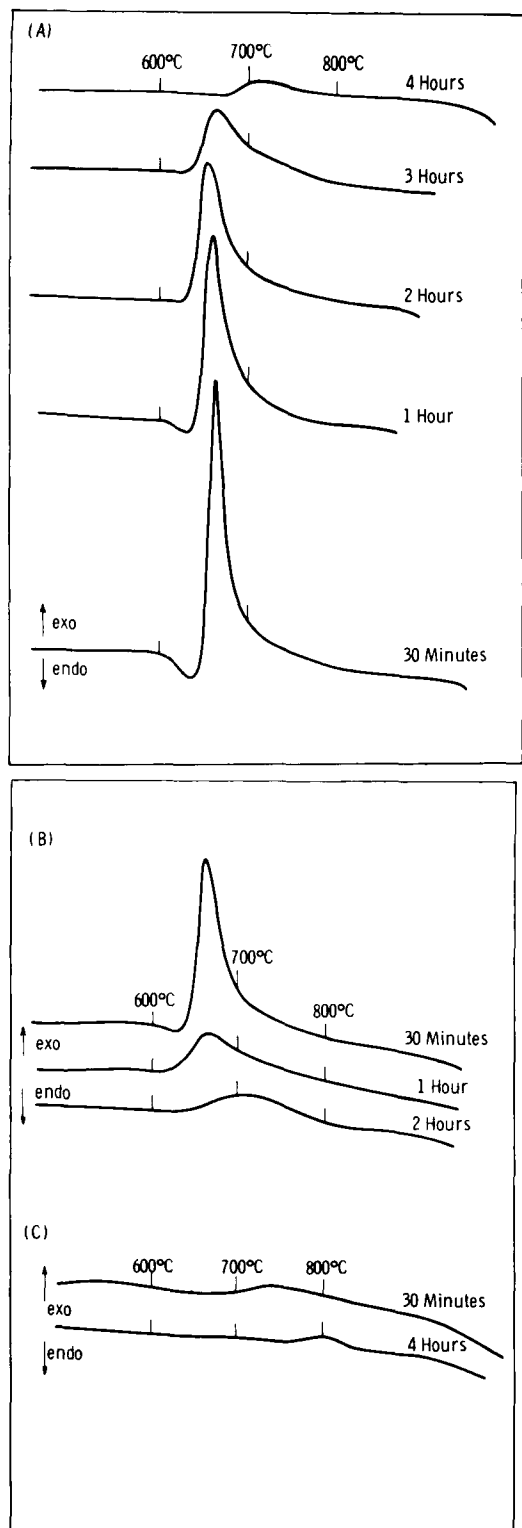


Fig. 3. DTA thermograms for tetrasilic fluormica glass isothermally treated at (A) 600°, (B) 620°, and (C) 640°C.

g/cm^3 is that for the quenched amorphous mica glass corresponding to composition II.

The density changes exhibited by specimens isothermally heat-treated at temperatures in the crystal-growth range for this system are shown in Fig. 4(B). A limiting or maximum value is reached after 1 h at 1125° and 1150°C, whereas at 1070° and 1100°C the density appeared to increase at lower rates with increasing time. At 1150°C, the highest temperature used for crystallization, the decrease in density after 1 h might indicate the onset of decomposition and loss of F. The apparently anomalous density values for short times at 1070° and 1100°C are believed to reflect an incubation

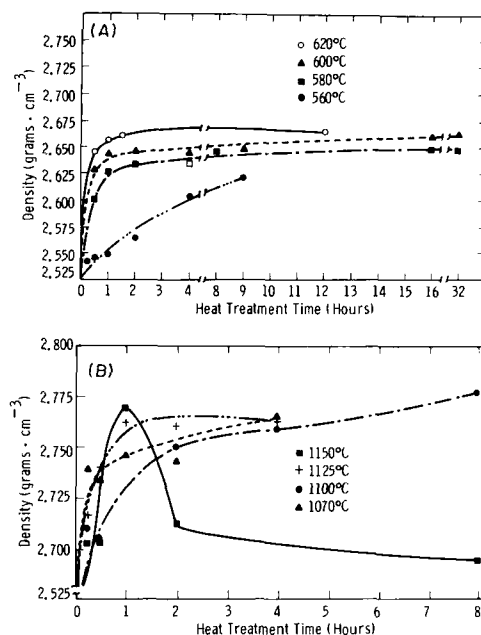


Fig. 4. Isothermal density changes for tetrasilic fluormica glass in (A) low-temperature region and (B) high-temperature region.

phenomenon resulting from the rapid rise in temperature through the initial transformation region experienced by these specimens during isothermal heat treatment.

(4) X-Ray Diffraction

X-ray diffraction measurements showed that the transformation indicated by DTA and density changes is associated with the development of a distinct crystalline phase. The X-ray powder film patterns presented in Fig. 5 depict the development of this phase. The as-quenched glass exhibits only a classical amorphous halo pattern. A crystalline phase initially appears at 560°C after a 9-h isothermal treatment. The diffraction lines appearing under these conditions correspond to the major lines of a crystalline tetrasilic fluormica pattern (Fig. 5(K)). For all thermal treatments studied from 560°C for 9 h to 700°C for 16 h, essentially the same diffraction pattern was obtained. Selected examples of these patterns (Fig. 5(B)–(F)) are characterized by broad diffuse lines, indicating a small constant crystal size with no appreciable crystal growth.

In the series of thermal treatments conducted from 800° to 1150°C, the X-ray diffraction lines became progressively sharper and more distinct as the temperature increased (Fig. 5(G)–(J)). Again, comparing these patterns to that of the standard tetrasilic fluormica material (Fig. 5(K)), it is evident that this behavior is associated with a more completely developed polycrystalline fluormica phase.

(5) Microstructure

The electron micrographs shown in Fig. 6 show the microstructural development in this tetrasilic fluormica system associated with the structural changes described. The as-quenched material (Fig. 6(A)) exhibits no evidence of structural ordering. However, after only 15 min at 560°C, there is definite evidence of particle development or phase separation in the form of a coarsening structure. Although this ordering occurs before X-ray diffraction lines appear, it does correspond to the density increase observed during the 560°C isothermal treatment. The coarsened microstructure, which prevails throughout the group of specimens treated at 560°C, consists of particles $\approx 1000 \text{ \AA}$ in diameter (Fig. 6(B)).

The microstructure just described remains constant through all thermal treatments studied up to 800°C for 64 h; the structure resulting from this treatment (Fig. 6(C)) consists of irregularly shaped particles on the order of a few thousand angstroms in size. Blocky mica-like particles with distinct grain boundaries initially appeared at 900°C after 32 h. Under such conditions the longest

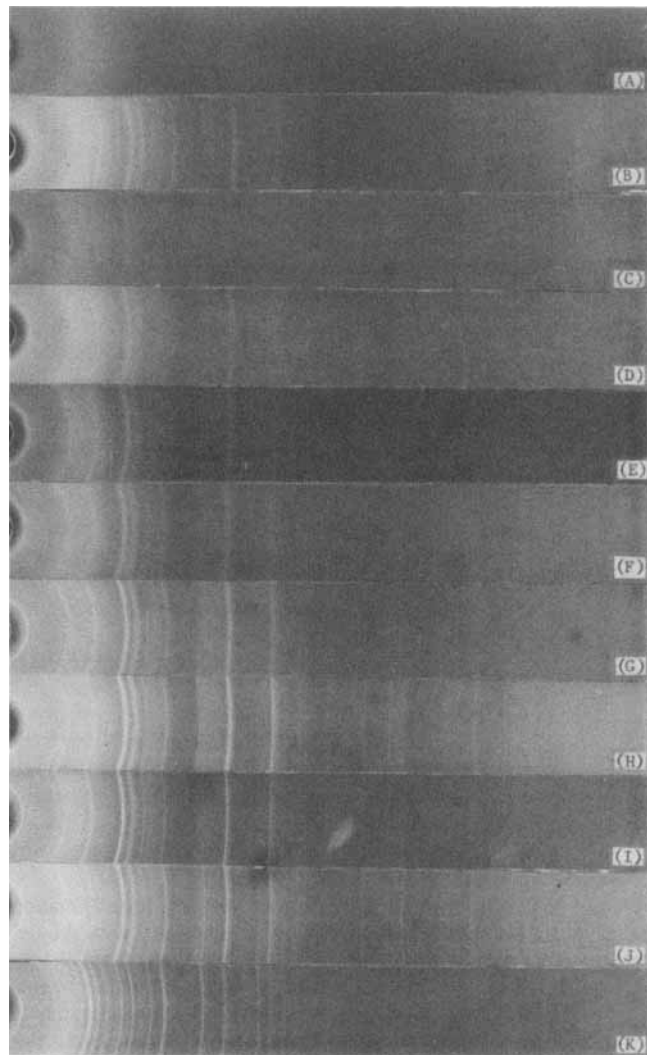


Fig. 5. X-ray diffraction patterns of tetrasilic mica glass-ceramic after selected thermal treatments. (A) As-quenched, (B) 560°C for 9 h, (C) 580°C for 30 min, (D) 600°C for 30 min, (E) 620°C for 30 min, (F) 620°C for 12 h, (G) 800°C for 64 h, (H) 900°C for 32 h, (I) 1000°C for 8 h, (J) 1150°C for 30 min, and (K) mica standard.

dimension of the mica particles measures a few microns; these particles are dispersed within a matrix of the previously developed diffuse particles (Fig. 6(D)). When the mica phase crystallizes at

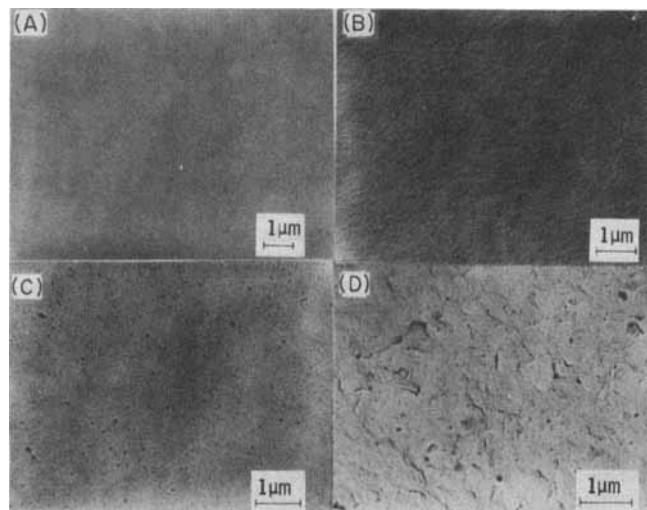


Fig. 6. Electron micrographs of tetrasilic fluormica glass (A) as-quenched and (B) heat-treated at 560°C for 2 h, (C) 800°C for 64 h, and (D) 900°C for 32 h.

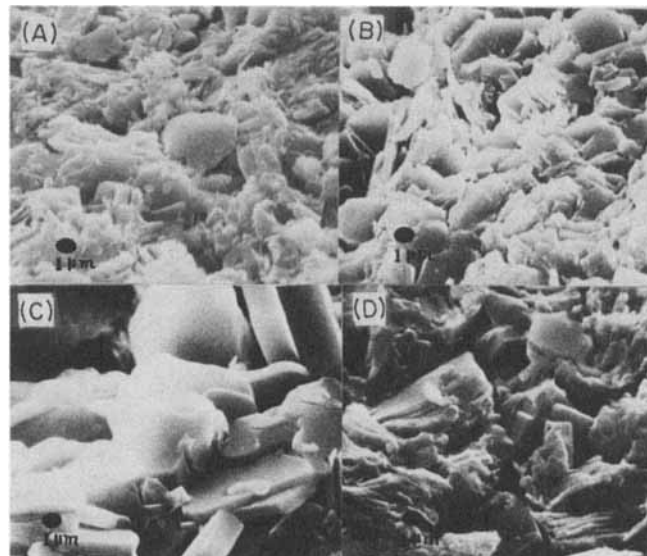


Fig. 7. Scanning electron micrographs of tetrasilic fluormica isothermally treated at 1150°C for (A) 15 min, (B) 1 h, (C) 2 h, and (D) 8 h.

higher temperatures, it rapidly undergoes more extensive development (Fig. 7).

The crystallization of the present mica glass thus proceeds from the amorphous structure through an intermediate irregularly shaped phase to a distinctly tabular plate-like mica phase. This phenomenon appears to be somewhat similar to the mechanism reported by Chen,⁶ wherein a fluorphlogopite composition, $K_2Mg_6Al_2Si_6O_{20}F_4$ with B_2O_3 additions, was shown to crystallize by a 2-stage process. An irregularly shaped intermediate "pseudocrystalline" phase, which appeared to be stable from 700° to 850°, was followed by the formation of fluorphlogopite at 1000°C. The major diffraction lines of the intermediate phase matched the pattern for fluorphlogopite at temperatures from 720° to 850°C. The crystalline mica phase appeared to develop at the interface between the intermediate phase and the glass phase.

Grossman,⁷ who also reported the development of a synthetic fluormica from a glass in a 2-stage process, studied $K_2Mg_5Si_8O_{20}F_4$ tetrasilic mica slightly deficient in F. He reported a fine-scale phase separation which led to the crystallization of quasi-spherical mica grains at temperatures as low as 625°C. At $\geq 940^\circ\text{C}$, the mica grains recrystallized by grouping into larger booklets $\approx 0.2 \mu\text{m}$ in size.

The behavior reported by Grossman⁷ most closely resembles that observed in the present study, except that the present structural transformations initiated at temperatures $\approx 60^\circ\text{C}$ lower. The present DTA results indicate that increasing the F content in this system lowers the transformation temperature. The difference in the temperatures of transformation can thus be attributed to the different F contents involved in the respective studies; Grossman's work involved a composition near $K_2Mg_5Si_8O_{20.5}F_{3.0}$, whereas the present one is near $K_2Mg_5Si_8O_{19.75}F_{4.5}$.

V. Proposed Crystallization Mechanism

Considering the experimental observations just discussed, a mechanism is proposed for crystallization of a mica glass of nominal composition $K_2Mg_5Si_8O_{20}F_4$. The amorphous material, as-quenched from above the melting range, most probably contains Mg and K ions distributed interstitially throughout an Si-O-F network structure. The F ion could readily occupy O sites in the network, since its ionic radius is 1.33 Å (compared with 1.32 Å for O). As correctly noted by Buerger¹² in a description of the structural nature of the mineralizer action of F, when an O atom at the corner of an SiO_2 tetrahedron is replaced by a univalent ion such as F, the substitution removes a possible network bridge.

Thermal excitation produced when the quenched structure is heated to $\approx 580^\circ\text{C}$ could induce movement of F ions from positions

in the network structure to more energetically favorable positions, e.g. those forming the apices of octahedral sites around the Mg ions. Such disengagement of F from positions in the network structure could account for the drastic volume shrinkage. Subsequent formation of the Mg-F bond would then result in the evolution of heat observed in this temperature region. The effect of F content on the exothermic peak position in DTA results indicates that F facilitates the transformation. As F moves into the ordered positions, it would function much like a nucleation catalyst, partially forming the octahedra which then form the central portion of the synthetic mica unit cell.

Layton and Herczog¹³ reported that heterogeneities in a quenched glass in the system Na₂O-Nb₂O₅-SiO₂ are transformed to a pseudocrystalline form through thermal excitation. In this system crystallization initiates at 680°C and is very rapid; the final stage of crystallization is described as slow because larger diffusion distances are involved. A similar mechanism appears likely in the K₂Mg₅Si₈O₂₀F₄ glass.

The results of heat treatments at temperatures just above that of the initial transformation (600°C) suggest that the development of crystalline structure is limited by certain factors. The broad low-intensity X-ray diffraction lines of these specimens (treated at <800°C) indicate the presence of relatively small particles. Duke *et al.*¹⁴ observed similar diffraction lines in the early stages of crystallization of a nepheline glass-ceramic body. They interpreted this behavior as an indication of a crystalline particle size of <1000 Å. Thus, the consistently broad, low-intensity diffraction lines observed from 580° to 625°C can be associated with a static crystalline particle size of <1000 Å.

This limit to crystal growth could result from a relatively immobile species failing to assume its preferred crystalline site. Assuming that the tetrahedral network ordered during heat treatment in

this 600°C region (as indicated by X-ray diffraction patterns) and that the F and Mg ions are in or near their correct lattice positions, the only remaining species would be the K ions. Thus, higher temperature (a more open structure) would favor the movement of K ions to preferred lattice sites. Since K ions bond adjacent mica layers to one another, this high-temperature mobility can be correlated to the change of crystal habit and the development of complete crystallinity at ≥900°C.

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Hydration of 3CaO·Al₂O₃ and 3CaO·Al₂O₃+Gypsum With and Without CaCl₂

AUD TRAETTEBERG* and P. E. GRATTAN-BELLEW

Materials Section, Division of Building Research, Ottawa, Ontario, Canada

Paste samples of tricalcium aluminate alone, with CaCl₂, with gypsum, and with gypsum and CaCl₂ were hydrated for up to 6 months and the hydration products characterized by SEM, XRD, and DTA. Tricalcium aluminate hydrated initially to a hexagonal hydroaluminate phase which then changed to the cubic form; the transformation rate depended on the size and shape of the sample and on temperature. The addition of CaCl₂ to tricalcium aluminate resulted in the formation of 3CaO·Al₂O₃·CaCl₂·10H₂O and 4CaO·Al₂O₃·13H₂O, or a solid solution of the two. The chloride retarded the formation of the cubic phase 3CaO·Al₂O₃·6H₂O; the addition of gypsum resulted in the formation of monosulfoaluminate with a minor amount of ettringite. When chloride was added to tricalcium aluminate and gypsum, more ettringite was formed, although 3CaO·Al₂O₃·CaSO₄·12H₂O and 3CaO·Al₂O₃·CaCl₂·10H₂O were the main hydration products.

I. Introduction

THE hydration of C₃A[‡] with and without CaCl₂ and CaSO₄·2H₂O (gypsum) has been extensively studied.¹⁻¹⁸ Because the addition of a small percentage of CaCl₂ to portland cement accelerates its rate of hardening, it is of interest to examine the influence of this admixture on the hydration of C₃A and C₃A+gypsum.

Previous work has defined the general sequence of formation of products in the hydration of C₃A, C₃A+CaCl₂, C₃A+gypsum, and C₃A+gypsum+CaCl₂, but the various combinations of reactants have been studied by different workers using different experi-

mental techniques and different proportions of the phases under study.

The work now reported was designed to carry out a uniform series of hydrations using the same conditions for each, so that variations resulting from differences in experimental technique would be eliminated and the effects of additives on the hydration of C₃A more firmly established.

II. Experimental Procedure

(1) Materials

Materials used were C₃A[‡] (61.6 CaO, 37.8 Al₂O₃, 0.5 MgO, 0.5 insolubles, and 0.1% Na₂O; surface area was 0.58 m²/g measured with a surface area pore volume analyzer,[§] with N₂ as adsorbate); gypsum, CaSO₄·2H₂O[¶]; calcium chloride, CaCl₂·6H₂O[¶]; and deionized decarbonated water.

(2) Preparation of Pastes

Pastes were prepared by mixing 1.5 g of solid with 1.5 ml H₂O or CaCl₂ solution. A w/s ratio of 1.0 was selected, although this is

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†C=CaO, A=Al₂O₃, H=H₂O, and w/s=water/solid ratio by weight.

‡Tetrachem International, San Diego, CA.

§Numinco Orr, Model MIC No. 103, Numec, Apollo, PA.

¶Certified reagent, Fisher Scientific Co., Pittsburgh, PA.