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# Preparation of Mica Glass-Ceramics by Crystallization of Fluorphlogopite-Fluormuscovite Glass

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## Abstract

Transparent and clear glasses were prepared from fluorphlogopite-fluormuscovite system mixtures. Mica crystals were precipitated in the glass by later heat treatment. The mica crystals were identified as fluorphlogopite by x-ray powder diffraction patterns. An interlocking microstructure of mica was observed at above 800°C. The density of crystallized glass increased with the increasing heat treatment temperatures. The density attained a maximum at about 900°C.

## 1. Introduction

Micas are representative sheet silicate minerals. The hydroxyl ions in natural micas can be readily replaced by fluorine ions to form fluormica. Fluormica has many useful properties in electrical insulation, thermal stability and mechanical strength (1, 2). Work on fluormica systems has been directed toward replacing suitable cations of tetrahedral or octahedral sites and growing single crystals (3, 4). Fluorphlogopite in fluormica groups readily crystallize from the melt (5). A glass can not be obtained from the melt consisting of replaced mica composition by cooling. However, Hatch et al reported that a clear glass could be produced by quenching the melt of a tetrasilic mica composition,  $\text{KMg}_{2.5}\text{Si}_4\text{O}_{10}\text{F}_2$  (6). After crystallization of the glass by heat treatment, interlocking mica flake crystals were developed in whole of the glass. The unique microstructure enables mica glass-ceramics to be machined to a close tolerance by drilling, sawing or turning. We have already reported on the preparation and properties of glass-ceramics based on lead-substituted fluorphlogopite,  $\text{K}_{(1-2n)}\text{Pb}_n\text{Mg}_3\text{AlSi}_3\text{O}_{10}\text{F}_2$  (7). The crystals of lead-substituted fluorphlogopite developed progressively with the increasing value of  $n$ . The mica glass-ceramics having composition of  $n=0.3-0.5$  could be also machined by drilling and turning.

In the present study, we describe the preparation of mica glass-ceramics based on the fluorphlogopite-fluormuscovite system. Crystal chemistry of the precipitated mica and resulting properties of the glass-ceramics are also discussed.

## 2. Experimental

Chemical composition of fluorphlogopite-fluormuscovite system can be expressed as  $\text{KMg}_{3(1-n)}\text{Al}_{2n}\text{AlSi}_3\text{O}_{10}\text{F}_2$ . Starting mixtures from  $n=0$  to 1 with an interval of 0.1 in the chemical composition were prepared from  $\text{SiO}_2$ ,  $\text{Al}_2\text{O}_3$ ,  $\text{MgO}$ ,  $\text{K}_2\text{SiF}_6$ , and  $\text{K}_2\text{CO}_3$ . After each of these mixtures was melted at  $1400^\circ$  to  $1450^\circ\text{C}$  for 30 minutes in a crucible with a lid, the melt was rapidly poured on a steel plate to produce clear glass. As-prepared glasses were subjected to a DTA to obtain the transformation temperature from amorphous to crystalline state. Crystallization of glass by heat treatment was conducted at  $500^\circ$  to  $1100^\circ\text{C}$  for 4 to 8 hours under atmosphere in an electric furnace. Crystal phases after crystallization were identified by x-ray powder diffraction patterns. The lattice constants corresponding to fluormica were calculated from (200), (003), (005) and (060) reflection lines by using silicon powders as an internal standard. Chemical composition of as-prepared glass and glass-ceramics after crystallization was analyzed by wet methods. Microstructural characterization was performed on both fractured surfaces and etched surfaces after polished by transmission electron microscope. Densities were measured by the water displacement method. Hardness was measured under a load of 500g for 30 minutes at room temperature on polished surfaces by a Vickers hardnesstesting machine. A machinability was tested by drilling and turning.

## 3. Results and Discussion

Transparent and clear glasses were obtained from  $n=0.3-0.7$  in the chemical compositions. In the compositions of  $n=0-0.2$ , the melts rapidly crystallized to be mica by cooling on a steel plate. The crystallized phase was identified as fluorphlogopite by x-ray powder diffraction patterns. Opaque glasses were also obtained from the compositions with high alumina contents ( $n=0.7$ ). Unmelted alumina was partly observed in these compositions. Within the composition range of prepared clear glasses, the following discussion is related to crystallization of the clear glass composed of  $n=0.3$  and 0.5 in chemical composition by heat treatment, and characterization of the glass-ceramics.

DTA curves for each glass are shown in Fig. 1. In a curve for  $n=0.3$ , two exothermic peaks at about  $630^\circ$  and  $850^\circ\text{C}$  indicate transformation from the amorphous to the crystalline state of the glass. According to x-ray powder diffraction analysis, the former corresponds to the crystallization of bcc chondrodite-like crystals reported by Chang et al (8), and the latter to that of fluormica. The DTA peak corresponding to the crystallization of bcc chondrodite-like crystals became smaller

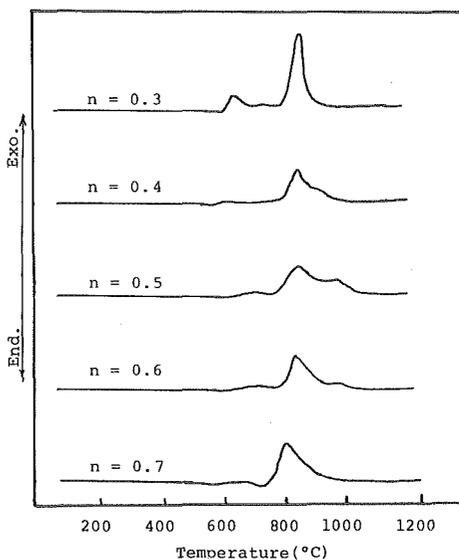


Fig. 1 DTA curves for fluorphlogopite-fluormuscovite system glasses.

with the increasing the value of  $n$ . There was only one exothermic peak at about 845° to 860°C in curve for  $n=0.5$  and 0.6. But x-ray powder diffraction patterns corresponding to bcc chondrodite-like crystals were conformably recognized in the compositions for  $n=0.5$  and 0.6. The crystallization temperature of fluormica in these compositions did not show so much change, and was much higher than that of tetrasilicic fluormica by Daniels et al (6) or lead-fluorphlogopite by the authors (7). Although the reason is not clear, it may be due to the high alumina content in the present system.

Glasses were isothermally heat-treated at 500° to 1200°C for 8 hours. In both compositions of  $n=0.3$  and 0.5, glasses after crystallization at 750° to 1200°C for 8 hours were devitrified to a white color, while that at 500° and 600°C were as yet translucent. Typical sequence of crystallization are listed with precipitated phases in Table 1. At temperatures from 600° to 750°C, only bcc chondrodite-like crystals precipitated in the glass of both compositions. But the diffraction patterns of the crystallized glass for  $n=0.3$  were sharper than that to  $n=0.5$  to show good crystallization. As the heat treatment temperatures increased, fluormica and  $MgF_2$  crystallized at 850° to 1050°C instead of bcc chondrodite-like crystals. The lowest temperatures of mica formation as detected by x-ray diffraction is about 800°C. Massive formation of mica crystals occurred after heating to 900°C, accompanied by a decrease in the x-ray intensities of all other phases. But mullite

**Table. 1** Typical sequence of crystallization by heat treatment at 8 hours

Temperature (°C)	Crystal phases		Appearance
	$n = 0.3$	$n = 0.5$	
600	bcc ch	bcc ch	translucent
700	bcc ch	bcc ch	opaque
800	ph, $MgF_2^*$	bcc ch, $MgF_2$	white
900	ph, $MgF_2$	ph, $MgF_2$	white
1000	ph, $MgF_2$	ph, $MgF_2$	white
1050	ph, $MgF_2^*$	ph, $MgF_2$ , mu*	white
1100	ph	ph, $MgF_2^*$ , mu	white
1150	ph	ph, mu	white
1200	ph	ph	white

bcc ch: bcc chondrodite( $4MgO \cdot 2SiO_2 \cdot MgF_2$ ), \*: trace, mu: mullite( $3Al_2O_3 \cdot 2SiO_2$ ), ph: fluorphlogopite.

**Table. 2** Lattice constants of synthetic fluormica

	Lattice constant			
	a (nm)	b (nm)	c (nm)	$\beta$ (°)
Present study				
$n = 0.3$	0.5354	0.9174	1.0204	101.75
$n = 0.5$	0.5315	0.9180	1.0162	100.48
Fluorphlogopite				
Kohn et al(3)	0.5299	0.9188	1.0135	99.92
McCauley et al(9)	0.5308	0.9183	1.0139	100.07
Fluormuscovite				
Matsushita (10)	0.5161	0.8970	1.0217	101.03
Yoder et al(11)	0.5208	0.8995	1.0275	101.58

phase was also recognized at 1100°C from the composition of  $n=0.5$ . Single phase of fluormica was obtained at above 1100°C for  $n=0.3$  and 1200°C for  $n=0.5$ . Accordingly, in the series of heat treatment at temperatures from 500° to 1200°C for 8 hours, fluormica crystals will be precipitated through an intermediate stage of bcc chondrodite-like crystals. X-ray diffraction patterns corresponding to fluormica became progressively sharper with increasing temperatures.

The lattice constants of fluormica for each composition calculated as 1M type crystals are listed in Table 2 with those of fluorphlogopite and fluormuscovite. The same lattice constants were recognized for both compositions. The precipitated mica in these glasses was identified as fluorphlogopite, because the lattice constants are very close to that of fluorphlogopite reported by Kohn et al (3) and McCauley et al (9) and crystallization of fluormuscovite is very difficult by solid state reactions under atmosphere (10). A glass matrix contains fluormuscovite-rich composition. Therefore, in the present system, crystals of fluorphlogopite-fluormuscovite solid solution could not be precipitated in fluormica composition glasses by heat treatment.

In the present experiments, there are possibilities of vaporization of fluorine during glass melting and crystallization of glasses. Grossman has also reported that a fluorine deficiency causes fluormica compounds to decompose to forsterite ( $Mg_2SiO_4$ ) and norbergite ( $Mg_2SiO_4 \cdot SiO_2$ ). Thus, wet chemical analyses were conducted for both as-prepared glass and glass-ceramics after crystallization. Both results were in good agreement with the composition of starting mixtures. Therefore, vaporization of fluorine can almost be ignored through the present procedures of glass making and crystallization of the glass.

Transmission electron microphotographs of a surface etched with 20% HF solution after polishing are shown in Fig. 2 and 3. For glass having a composition of  $n=0.3$ , phase separation was observed on both as-prepared glass and glass heat-treated at 500°C for 8 hours (fig. 2). Fine crystals as shown in Fig. 3 precipitated at 700°C for 8 hours. The

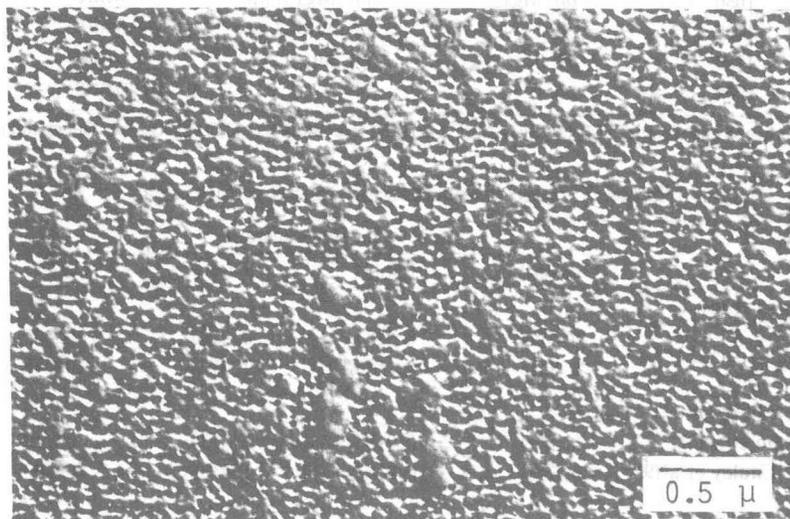
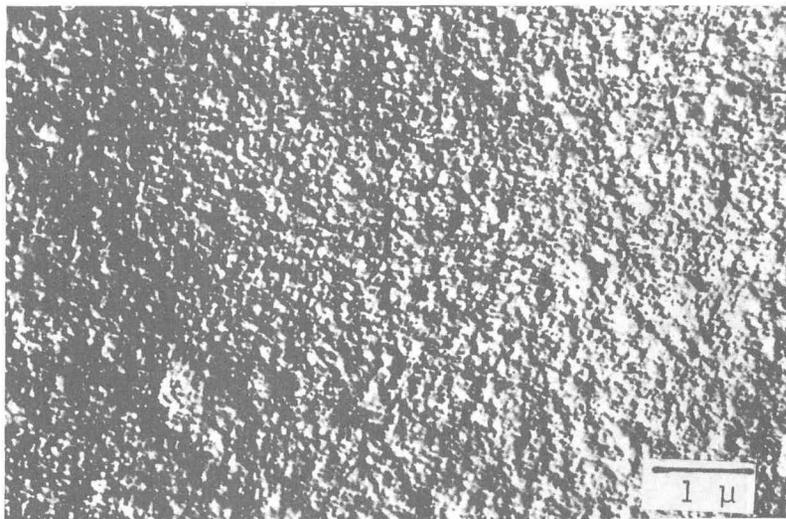
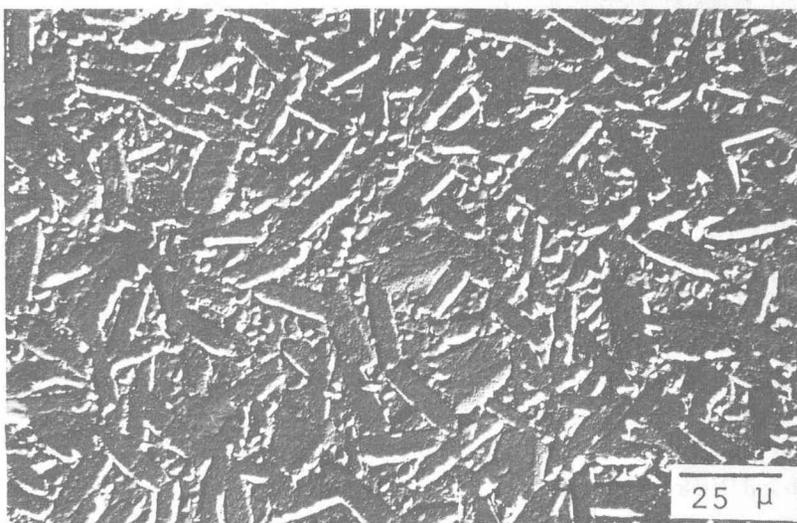


Fig. 2 TEM photograph of the glass heat-treated at 500°C for 8 hours ( $n=0.3$ ).

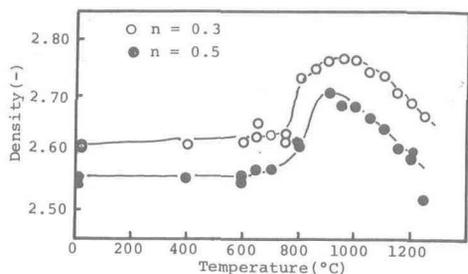
crystals will be bcc chondrodite-like crystals as expected from the results by x-ray powder diffraction analysis and DTA. An interlocking microstructure of mica flakes can be recognized at about 900°C as indicated in Fig. 4. At higher temperatures, well developed crystals showing a layer structure was observed. The crystals were larger with increasing temperatures. For example, the crystals heat-treated at 1100°C for 8 hours were about 10  $\mu\text{m}$  in length. A microstructure showed the same patterns on both compositions. The fraction of fluormica crystals in  $n=0.5$  was somewhat more than that in  $n=0.3$ , because the precipitated mica is only fluorphlogopite.



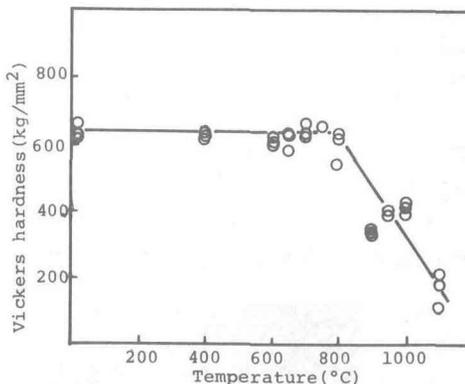
**Fig. 3** TEM photograph of the glass heat-treated at 700°C for 8 hours ( $n=0.3$ ).



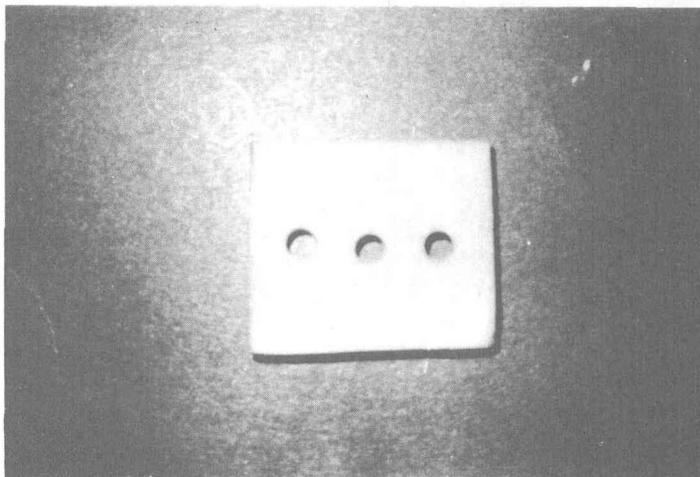
**Fig. 4** Interlocking microstructure of mica flakes in the glass-ceramics heat-treated at 900°C for 8 hours ( $n=0.5$ ).



**Fig. 5** Change in densities of the glass-ceramics.



**Fig. 6** Change in the Vickers hardness with crystallization temperatures.



**Fig. 7** Drilled fluormica glass-ceramics. The sample with  $n=0.7$  composition was heat-treated at  $1000^{\circ}\text{C}$  for 4 hours.

Densities of as-prepared glasses decrease linearly with the increasing value of  $n$ . The densities were 2.61 for  $n=0.3$  and 2.55 for  $n=0.5$ . A change in densities of glass-ceramics heat-treated at  $400^{\circ}$  to  $1200^{\circ}\text{C}$  for 8 hours are shown in Fig. 5. An increasing density was recognized at temperatures above  $750^{\circ}\text{C}$  with the precipitation of mica crystals. As the temperatures increased, the density of glass-ceramics increased, and the maximum density was obtained at about  $950^{\circ}\text{C}$  in both compositions. Densities again decreased with the increasing temperatures. The decrease in density may be attributed to the decomposition of mica and propagation of cracking into interlocking mica crystals with the growth. On the other hand, Vickers hardness for  $n=0.5$  at room temperature was constant up to  $800^{\circ}\text{C}$  and decreased with the crystallization of mica as shown in Fig. 6. For example, the values for  $n=0.5$  at room temperature were about  $630\text{ kg/cm}^2$  at  $600^{\circ}\text{C}$  and  $200\text{ kg/cm}^2$  at  $1100^{\circ}\text{C}$ . These values were similar to that for  $n=0.3$ . The decrease in hardness is also due to a development of interlocking mica flake crystals. Thermal expansion coefficients

vary from 72 to  $125 \times 10^{-7}/^{\circ}\text{C}$  at  $150^{\circ}$ – $450^{\circ}\text{C}$  in both compositions. These values became larger with the proceeding the crystallization. Generally, machinability of mica glass-ceramics increases with the development of crystallinity. Fig. 7 shows the example drilled and cut. The present fluormica glass-ceramics samples could be machined to precise tolerances with conventional tools.

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