

## SOME EXPERIMENTS IN THE PREPARATION OF GLASS-CERAMICS

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A few compositions of glass ceramics have been developed and their improved physical and mechanical properties obtained and discussed. The experimental results show that glasses studied lend themselves especially well to be converted into glass ceramics of high quality.

### Introduction

Glass-ceramics were first introduced by Corning Glass Works in 1957 under the trade name of "Pyroceram". Glass-ceramics are products which have been melted, and fabricated as glass and later on converted by special heat treatments to a crystalline material. The crystalline ceramic material thus obtained is usually several times stronger than the parent glass and at the same time it has much smaller and more uniform crystals than ordinary ceramics.

The process of crystallization may be divided into two parts; nucleation and crystal growth. For the production of high strength glass-ceramics, a large number of very fine crystals and efficient nucleation throughout the body of the material is essential.

The present work describes the development of ceramic-like materials from molten glasses as a result of nucleation.

### Experimental

Materials of high purity are required since some types of impurity even in small concentrations, could effect the crystallization characteristics of the glass. Silica sand was washed and graded in order to reduce the iron content to a minimum. The alkaline earths such as calcium oxide and magnesium oxide were introduced in the form of limestone and magnesite.  $\text{Al}_2\text{O}_3$  is added as hydrated alumina ( $\text{Al}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$ ). Feldspar is also a source of alumina. Lithium oxide was added as  $\text{Li}_2\text{CO}_3$  and phosphate anions were introduced in the form of a metal phosphate.

*Melting.*—The batches were thoroughly mixed; they were melted between 1350-1400°C for 4-6 hr. The melts were normally cast into stainless steel rings and then annealed at 400°C.

*Conversion to Glass-Ceramics.*—The glass samples to be devitrified were heated in an electric furnace at the rate of 5°C per min to the final tempera-

ture. On completion of the run they were cooled at the natural rate of the furnace. The diameter and thickness of each sample, before and after heat treatment, were measured.

*Study of Properties.*—The following properties of the parent as well as the converted glass samples were studied by the conventional laboratory methods. The results are given in Table 2.

(i) Specific gravity was determined at room temperature by pycnometer.

(ii) Hardness was determined by Moh scale of hardness.

(iii) Thermal expansion was measured using the laboratory conventional apparatus (20-410°C in case of glass and 20-500°C for the glass-ceramics). The graphs showing the per cent expansion vs. temperature are drawn (Figs. 1 and 2). The coefficient of expansion was also calculated. The results are given in Table 2.

(iv) Softening temperature was determined by an arbitrary method using glass rods 2 to 3 mm in diameter drawn from the glass melt. The assembly was heated in an electric furnace at the rate of 100°C per hr. The temperature at which the rod started to bend by its own weight was taken as the softening temperature. The results are correct within a range of  $\pm 10^\circ\text{C}$ . Similarly the softening temperature for glass-ceramics was determined. The results are presented in Table 2.

### Results and Discussion

Six glass bodies were prepared (Table 1). The properties of prepared glass and converted glass-ceramics are given in Tables 2 and 3. A photograph of one of the glass-ceramics sample having E composition is given in Fig. 3. It may be observed that the crystal growth is brought to an end by the crystallization fronts colliding. The X-ray photographs of the glass and the converted crystalline ceramics have been obtained. As expected the X-ray photograph of glass has shown no crystals

whereas the converted glass-ceramics (Fig. 4) gives clear lines indicating the presence of crystals in the converted sample.

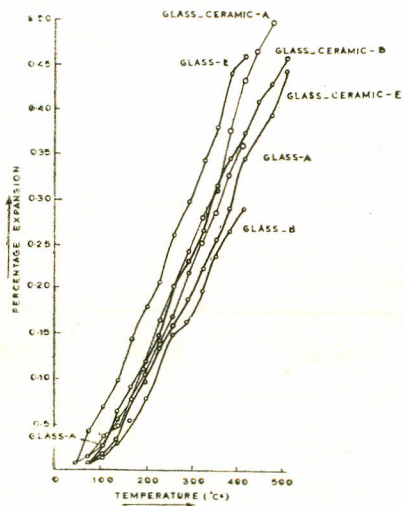


Fig. 1.—Thermal expansion curves of glass-ceramics and parent glasses.

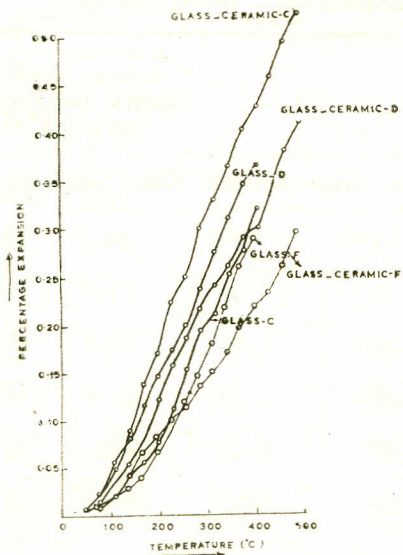


Fig. 2.—Thermal expansion curves of glass-ceramics and parent glasses.

Glass-ceramics are non-porous and their densities vary depending on the composition and crystal phases and proportions of these phases present in the material. The density of a glass-ceramic generally differs to some extent from the density of original glass. The small change in volume is usually in the region of 3% which enables glass-ceramic article to be made to accurately controlled dimension. In conventional ceramics, relatively large shrinkage (40–50% by volume)<sup>1</sup> occurs during the drying and firing operation. Consequently, control of final dimensions is more difficult for conventional ceramics than for glass-ceramics.

In a sintered high alumina ceramic the percentage closed porosity is usually 5 to 10%.<sup>2</sup> In contrast with conventional ceramic, glass-ceramics are entirely free from any type of porosity (Table 3). This complete absence of pores in glass-ceramics is responsible for high mechanical strength. Certain electrical properties may be adversely affected by the presence of pores and, of course, pores would also reduce the thermal conductivity; this may or may not be desirable, depending upon the application for which the material is to be used. In short the dense, fine texture of glass-ceramics serves to distinguish them

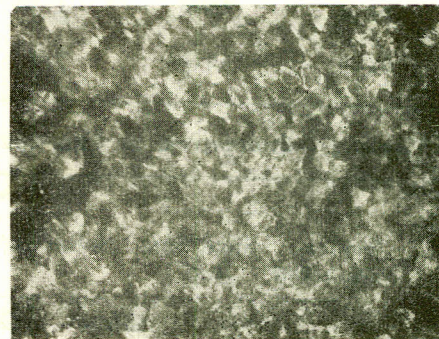


Fig. 3.—Thin section photograph of the structure of  $P_2O_5$  nucleated  $Li_2O-Al_2O_3-SiO_2$  glass-ceramics composition 'E' ( $\times 40$ ).



Fig. 4.—X-ray photograph of the structure  $Li_2O-Al_2O_3-SiO_2$  glass-ceramics composition.

from conventional ceramics and determines many of their special characteristics.

The thermal properties of the glass ceramics prepared are given in Table 2 in comparison with the thermal properties of parent glasses and ceramics. The thermal expansion curves for glasses and glass ceramics given in Figs. 1 and 2 show that parent glasses having similar thermal expansion coefficients can give rise to glass-ceramics having markedly different coefficients of expansion due to the different crystal phases. The coefficient of expansion of glass-ceramics A, B and C is greater than their respective parent glasses while in case of glass-ceramics D, E and F the coefficient of

thermal expansion has decreased compared with their respective parent glasses.

A principal objective in the development of these glass-ceramics is to match their thermal expansion coefficients with those of metals and thus to prevent stresses when a composite article is heated or cooled. Further, if a glass ceramic is required to have high thermal shock resistance, the coefficient of thermal expansion should be as low as possible to minimize strain resulting from temperature gradient within the material. Glass-ceramics are remarkable for the very wide range of thermal expansion coefficients which can be obtained.

TABLE 1.—GLASS COMPOSITION.

No.	SiO <sub>2</sub>	LiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	MgO	CaO	K <sub>2</sub> O <sub>3</sub>	P <sub>2</sub> O <sub>5</sub>
A	76.5	12.0	3.00	—	5.00	3.5	—
B	81.0	12.5	4.00	—	—	2.5	—
C	62.4	12.4	—	25.2	—	—	—
D	66.8	13.15	7.95	12.1	—	—	—
E	71.2	19.8	4.18	—	—	—	3.00
F	64.7	12.9	7.7	11.7	—	—	3.00

TABLE 2.—PROPERTIES OF PREPARED GLASS AND CORRESPONDING GLASS-CERAMICS.

Sample	Nuclea- tion temp.	Soak time (hr)	Softening temp.(°C)	Sp. gr. 25°C	Linear coeff. of thermal expansion-7 (20-410°C) <sup>10</sup>			
					Glass	Glass-ceramic	Glass	Glass-ceramic
A	720	0.5	540	920	2.404	2.65	94.7	125.2
B	750	0.5	540	970	2.321	2.41	77.6	120.00
C	700	0.5	600	930	2.431	2.65	91.8	104.2
D	700	1.0	580	945	2.481	2.503	97.1	68.1
E	675	0.5	550	960	2.38	2.45	103	94.3
F	690	1.0	615	920	2.50	2.65	80.8	59.9
Conventional ceramics (high alumina)	—	—	—	—	—	3.6-3.7	—	70-73

TABLE 3.—PROPERTIES OF PREPARED GLASS AND CORRESPONDING GLASS-CERMICS.

Sample	Crushing strength lb/in <sup>2</sup>		Water absorption		Porosity (gas permeability)		Moh's hardness	
	Glass	Glass-ceramic	Glass	Glass-ceramic	Glass	Glass-ceramic	Glass	Glass-ceramic
A	2,000	8,000	} Water-tight	}	}	} Gas-tight	} 5-7	} 7-9
B	9,000	20,000						
C	11,000	23,000						
D	4,000	12,000						
E	19,000	36,000						
F	11,000	18,000						
Conventional ceramic (high alumina)	1600—2500						7-9	

The thermal expansion characteristics of a material are particularly influenced by the crystalline phases and properties of each phase present. Thus a glass ceramic of low thermal expansion coefficient may contain beta-eucryptite, cordierite or beta-spodumene as major phases while glass-ceramics of high expansion coefficient may contain major proportion of crystals such as lithium disilicate quartz or cristobalite.<sup>3</sup>

The thermal expansion of parent glasses is  $77.6 \times 10^{-7}$  to  $103 \times 10^{-7}$  which has changed appreciably on crystallization. The thermal expansion of glasses D, E and F has decreased while for glasses A, B and C it has increased (Table 2). The lowest thermal expansion was of a crystallized glass of composition F.

The presence of crystal phases in the glass ceramic which undergo phase inversion is reflected in the shape of the thermal expansion curve. The thermal expansion curves of glass-ceramics C, F and B show a marked change of slope at a temperature in the region of 200–250°C. It has been observed that this change in slope is due to the presence of cristobalite. Further, it has also been observed that the thermal expansion characteristics of a glass-ceramic are greatly influenced by the heat treatment schedule.

Another change in physical characteristic brought about by devitrification is increase in refractoriness of the material. Although there

are a number of ways of defining this characteristic, a conventional method of comparing materials of the type under consideration is to make use of the softening temperature. The data given in Table 2 shows that the softening temperature has increased considerably on devitrification of the parent glasses. The softening temperature of the parent glasses ranges from 540–615°C whereas for glass-ceramics it changes from 910–970°C.

Factors governing the softening temperature are complex, since there are one or more crystal phases present together with a residual glass phase; this phase is probably distributed fairly uniformly between the crystals. Obviously, the proportion of glass phase present will have strong bearing on the refractoriness of the glass-ceramic and from this point of view it is desirable to limit the glass phase to the smallest possible proportion. In addition, the composition of the glass phase is of great importance and it is necessary to ensure that oxides which lower the softening point of the glass phase are present only in small proportion.

The mechanical characteristics of a material is often a major factor in determining the suitability of material for a particular application. The data given in Table 3 shows that the crushing strength (lb./in<sup>2</sup>) of glass-ceramic is greater than that of the parent glasses. The crushing strength for glass-ceramics varies from 8,000 to 36,000 lb./in<sup>2</sup> whereas for parent glasses it is 2,000 to 19,000 lb./in<sup>2</sup>. This property too depends upon the

heat treatment schedule, microcrystalline structure of glass-ceramic and the complete absence of the glass phase in the glass-ceramic.

Hardness is not a fundamental physical characteristic of a material but rather it is a complex function of a number of physical properties which are combined in differing degrees depending on the method of test. It has been found that some glass-ceramics have a hardness of about 9 in comparison with their parent glasses having a hardness of 5-7.0. It means that glass-ceramics are comparable with corundum ( $\text{Al}_2\text{O}_3$ ) with a hardness of 9 and silicon carbide with a hardness of 9-9.5.

In the literature<sup>5</sup> several glass-ceramic compositions and their properties are given. Compositions B and C were taken from the above reference and included in our investigations. In calculating the formula for the remaining four compositions, the main consideration was that of high strength and high refractoriness (softening temperature) to be obtained in the glass-ceramics by the conversion of low-melting glass compositions. Composition B gave better results than obtained previously.<sup>5</sup> Its softening temperature was  $970^\circ\text{C}$  instead of  $910^\circ\text{C}$ . This could be due to a carefully controlled crystallization process used by the present authors. The results obtained with composition C are similar to those given in the literature.<sup>5</sup> The strength of known compositions (B and C) obtained by us was 20,000 and 23,000 lb./in<sup>2</sup>, respectively. The prepared samples have the strength varying between 8,000 and 36,000 lb./in<sup>2</sup>.

Of the prepared samples, composition E is the best having a strength of 36,000 lb./in<sup>2</sup>. But

in cases where thermal expansion is important, compositions D, E and F are better than A, B, and C.

### Conclusion

Although a great progress has been made in the science and technology of glass-ceramics during the past few years, there is considerable scope for further research and developments. In this paper a preliminary study is described, many compositions were tried but a few of them were selected finally for detailed investigation. The mechanical and physical properties obtained on the converted glass-ceramics compositions clearly indicate their superiority as compared to their corresponding glass bodies. As the results found so far are encouraging, we, therefore, have a plan to investigate this problem in all its aspects—the possibility of fabricating the actual articles and their exploitation in Pakistan will be taken up later.

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### References

1. P. W. Mcmillan, *Glass Ceramics*, fourth edition (Academic Press, London and New York, 1964).
2. *Ibid.*, p. 127.
3. *Ibid.*, p. 176.
4. *Ibid.*, p. 130.
5. *Ibid.*, p. 99.