

Review

Some Glass-Ceramics for Special Applications

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Manufacturing process and characteristics of various glass-ceramics utilized as thermal shock resistant materials and as exterior/interior wall panels of buildings and for solidification of high level radioactive wastes are described.

KEY WORDS: Low-expansion glass-ceramics/ Transparent glass-ceramics/ Surface nucleation/ Glass-ceramic panel products/ Use of glass-ceramics for solidifying radioactive wastes/

1. INTRODUCTION

More than 200 years ago, M. Reaumur (1683–1757) reported that glasses can be converted into porcelain-like materials.¹⁾ By embedding ordinary soda-lime glass bottles in a mixture of gypsum and sand powders placed in a pot and firing in a potter's kiln, he obtained porcelain-like objects. In its process, crystallization always started from the original surfaces, and fibrous crystals grew inward perpendicular to the surfaces. The crystallized objects obtained were weak and brittle, because the thermal expansion coefficient of the precipitated crystals was higher than that of the remaining glass matrix, which during cooling resulted in tensile stresses in the crystal phase of the porcelain-like objects.

A method of conversion of glasses into crystalline glass-ceramics with high mechanical strength was first invented by S. D. Stookey,³⁾ and announced by Corning Glass Works in 1957. This process using TiO_2 as the nucleating agent gave rise to worldwide interest in the science and technology of glass.

In 1961, M. Tashiro and M. Wada developed a method of conversion of glasses into crystalline glass-ceramics with low thermal expansion coefficients using ZrO_2 as nucleating agent and reported the properties of the products.³⁾ Based on their fundamental researches, the applied researches were carried out in the authors' laboratory to develop the method of producing low-expansion glass-ceramics with high thermal shock resistance, and in 1962 the white opaque glass-ceramics of this type were first produced in our plant, being introduced as cooking wares in the domestic market. By altering the heat-treatment schedule for crystallization but using the same chemical composition as that used for the opaque type,⁴⁾ the transparent low-expansion glass-ceramics were produced in 1965, which have found a wide range of industrial applications such as heat-resistant transparent firescreens.

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The research for developing new glass-ceramic building materials using some special nucleating agents was started in the authors' laboratory in 1968. The products first developed for the use of interiors and exteriors of modernistic buildings did not appeal to architects because of their ceramic-tile-like appearance. Therefore, a new idea to develop glass-ceramics closer in appearance to natural stones was proposed. In 1971, our research group discovered the principle of manufacturing a new glass-ceramic,^{5,6)} utilizing surface nucleation without use of special nucleating agents. From 1974, the glass-ceramic building materials of this type have been produced on a commercial scale.

High level radioactive wastes (HLW) are generated at the reprocessing plant of the spent fuel. The first demonstration of solidification of fully active HLW by the use of glass was performed in France in 1978, using a low melting borosilicate glass. On the basis of years' experience in investigating glass-ceramics, our research group started a new project in 1977, concerning with solidifying high-level waste by the glass-ceramic process. In general, the internal temperature of the solidified glass in a canister (stainless steel container) rises up to *ca.* 600°C, being held there for a considerable period of time. The glass-ceramics excel the ordinary borosilicate glass as the solidified materials, because the thermal stability and mechanical strength of the former are generally higher than those of the latter.⁷⁾

The present review is mainly concerned with the results of a series of our research works on the glass-ceramics mentioned above, especially on their manufacturing processes and properties.

II. LOW-EXPANSION GLASS-CERAMICS

Manufacturing process

Glass-ceramics with low-thermal expansion coefficients are derived from the glass in the Li_2O (low)- Al_2O_3 (high)- SiO_2 system, especially in a region near the spodumene ($\text{Li}_2\text{O}\cdot\text{Al}_2\text{O}_3\cdot 4\text{SiO}_2$) composition. The typical glass composition (nominal) selected is 67.0 SiO_2 , 22.0 Al_2O_3 , 4.0 Li_2O , 0.5 MgO , 2.4 ZrO_2 , 1.8 TiO_2 , 1.3 P_2O_5 , 1.0 ($\text{Na}_2\text{O} + \text{K}_2\text{O}$) by Wt. per cent, in which ZrO_2 and TiO_2 are added as nucleating agents and P_2O_5 is used to increase solubility of ZrO_2 in the molten glass.³⁾

The glass is melted at *ca.* 1700°C in a tank furnace, and then formed into various shapes by rolling, blowing, drawing or pressing operations. After annealing and additional processing such as cutting, the glass articles produced are converted into crystalline products in a tunnel kiln, by the heat-treatments first for nucleation at 750°C for 2 h and then for crystal growth at higher temperatures for 1 h. When the heat-treatment is completed at 900°C and at 1150°C, the transparent glass-ceramic having zero in expansion coefficient and the white opaque glass-ceramic having $11 \times 10^{-7}/^\circ\text{C}$ in expansion coefficient are obtained, respectively. The transparent glass-ceramic consists mainly of crystalline particles of beta quartz solid solution (ss), *ca.* 0.07 μ in diameter, and the white opaque glass-ceramic consists of crystalline particles of beta spodumene ss, *ca.* 1.0 μ in diameter. For both products, the remaining glassy

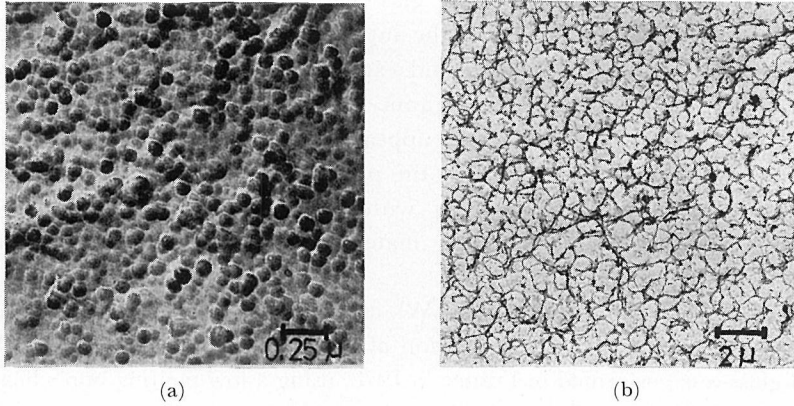


Fig. 1. Electron micrographs of low-expansion glass-ceramics.

- a) Transparent glass-ceramic (β quartz ss)
- b) White opaque glass-ceramic (β spodumene ss)

phase is less than 5 wt. %. Figure 1 indicates the electron micrographs of the textures of the two types of glass-ceramics.

Properties and usage of low-expansion glass-ceramics

The transparent glass-ceramic produced has extremely high thermal shock resistance because its thermal expansion coefficient is essentially zero in the range from room temperature to 800°C. Although its maximum service temperature is limited to 740°C for continuous use, it can withstand quenching from 800 to 0°C. High transmittance in the wavelength covering visible and infrared region (Fig. 2) facilitates its application to window panels (firescreens) of heating equipment. Compared with ordinary heat-resistant glasses, it has higher values in hardness, bending and impact strengths (Table I). As seen from Fig. 3, the bending strength increases with in-

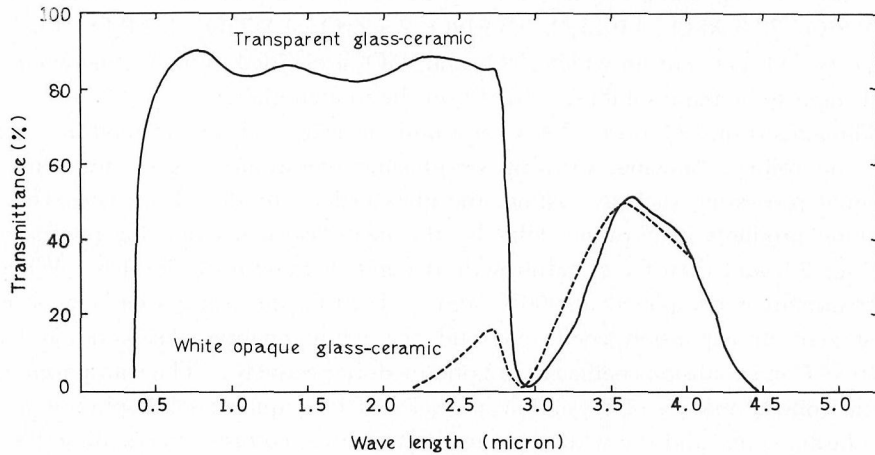


Fig. 2. Transmittance of low-expansion glass-ceramics. (5 mm in thickness)

Glass-Ceramics for Special Applications

Table I. Characteristics of low-expansion glass-ceramics

	Transparent glass-ceramic	White opaque glass-ceramic	Heat-resistant glass
Thermal exp. coeff. $\times 10^{-7}/^{\circ}\text{C}$ 30-380°C	-3	9	31
30-800°C	-1	11	—
Specific heat 25°C, Cal/g	0.19	0.20	0.17
Thermal conductivity 25°C, Kcal/m. h. °C	1.18	1.30	0.94
Max. service temp. °C	740	1100	510
Thermal shock resistance ΔT , °C, $100 \times 100 \times 3$ plate	800	600	180
Specific gravity g/cm ₃	2.51	2.50	2.23
Bending strength Kg/cm ² , Rod 5 ϕ \times 50	1000	1500	400-700
Vickers' hardness Kg/mm ² , 100 gr load	790	815	740
Young's modulus 25°C, $\times 10^5$ Kg/cm ²	8.0	8.0	7.0
Acid resistance mg/cm ² , 5% HCl, 90°C, 24 h	0.03	0.01	0.03
Alkali resistance mg/cm ² , 5% Na ₂ CO ₃ , 90°C, 24 h	0.08	0.06	0.02
Resistivity 200°C, ohm-cm	2.8×10^7	1.0×10^8	1.0×10^8
Dielectric constant 25°C, 10^6 Hz	8.4	6.6	4.6
$\tan \delta$ 25°C, 10^6 Hz, $\times 10^{-4}$	120	29	46

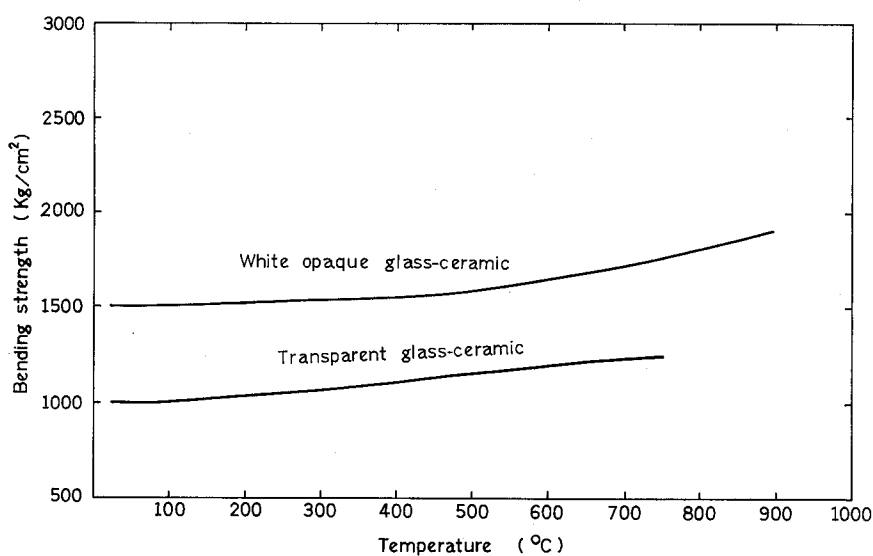


Fig. 3. Temperature dependence on bending strength of low-expansion glass-ceramics.

creasing temperature up to 750°C, which makes this material applicable to various industrial uses.

The white opaque type has an excellent thermal shock resistance because of its low thermal expansion coefficient ($11 \times 10^{-7}/^{\circ}\text{C}$), about one-third the value of ordinary heat resistant glasses, and also of its high thermal endurance as seen from the value of the maximum service temperature, 1100°C, for its continuous use (Table I). The white opaque type excels the transparent type in mechanical properties such as bending and impact strengths (Table I).

The white opaque type is used not only as ordinary cooking waves but now also as trays and shelves for microwave ovens, because it has a fairly low electrical loss at the frequency of 2.45 GHz specified for the microwave ovens (Fig. 4), beside its excellent thermal shock resistance. The transparent type has found a wide application to the industrial usages, such as fire screens for heating equipment, heat-resistant window panels for furnaces, high pressure and heat resistant transparent containers, and block gauges for calibration of high precision instruments.

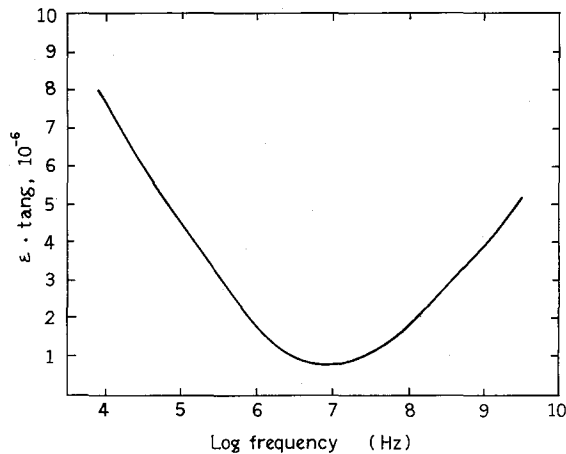


Fig. 4. High frequency loss of white opaque glass-ceramic (25°C).

III. GLASS-CERAMIC BUILDING MATERIAL

Manufacturing process of glass-ceramic panel

Silica, feldspar, calcium carbonate, zinc oxide, barium carbonate *etc.* are used as raw materials. Table II shows composition and physical properties of the mother glass of the glass-ceramic building materials. The glass is melted at 1500°C in a tank furnace, and the molten glass is poured into water to form glass grains, 1 to 7 mm in diameter. The glass grains are spread over the bottom surface of the refractory moulds to form a panel, *e.g.* 1000 × 1300 × 30 mm in size and heated up to 1100°C in a tunnel kiln. During heating, the glass grains sinter together at *ca.* 850°C to form a non-porous panel. When the temperature of the panel reaches *ca.* 950°C, numerous

Glass-Ceramics for Special Applications

Table II. Composition and properties of the mother glass of glass-ceramic panel

Composition (wt.%)	
SiO ₂	59.0
Al ₂ O ₃	7.0
B ₂ O ₃	1.0
CaO	17.0
ZnO	6.5
BaO	4.0
Na ₂ O	3.0
K ₂ O	2.0
Sb ₂ O ₃	0.5
total	100.0
Thermal exp. coeff. 30–380°C, × 10 ⁻⁷ /°C	74.0
Density, g/cm ³	2.78
Dilatometric softening point (°C)	691

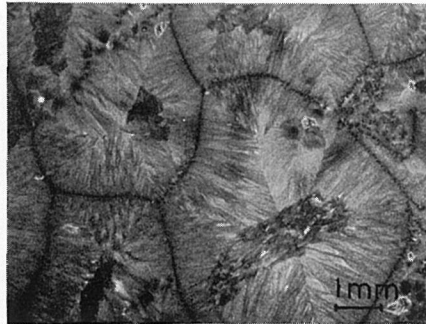


Fig. 5. Photograph of thin section of glass-ceramic panel.

needle-like crystals start growing inward from the boundaries of the glass grains in the panel (Fig. 5). By the following heat treatment at 1100°C for 1 h, panels initially consisted of many glass grains are converted into the glass-ceramic with 40% crystallinity, and the phase is mainly beta-wollastonite (CaO·SiO₂). After cooling to room temperature, the top surfaces of the crystallized panels are lapped and polished to develop the stone-like texture having needle-like crystals with different orientations. Glossy panels thus obtained are cut into pieces of the standard dimensions. Curved panels are manufactured by reheating the flat panels set in the curved heat-resistant metal frames: 60 wt % of the glass matrix still remaining in the products facilitates their bending during reheating.

Properties of glass-ceramic panel

The mechanical, thermal and chemical properties of the glass-ceramic panels produced are given in Table III, in comparison with those of the marble and granite.

Table III. Properties of glass-ceramic panel and natural stones

	Glass-ceramic panel	Marble	Granite
Specific gravity g/cm ³	2.7	2.7	2.7
Bending strength Kg/cm ²	510	170	150
Compressive strength ton/cm ²	1.2-5.6	0.9-2.3	0.6-3.0
Charpy impact strength Kg·cm/cm ²	2.5	2.1	2.0
Young's modulus × 10 ⁵ Kg/cm ²	5.2	2.8-8.4	4.3-6.1
Mohs' hardness	6.5	3-5	5.5
Specific heat cal/g, 50°C	0.19	0.19	0.19
Thermal exp. coeff. 30-380°C, × 10 ⁻⁷ /°C	62	80-260	50-150
Thermal conductivity Kcal/m. h. °C	1.4	1.9-2.0	1.8-2.1
Water absorption rate %	0.00	0.30	0.35
Acid resistance, 1% H ₂ SO ₄ wt.loss%, 25°C, 650 h	0.08	10.3	1.0
Alkali resistance, 1% NaOH wt.loss%, 25°C, 650 h	0.05	0.30	0.10
Freezing resistance ^{a)} wt.loss%	0.028	0.23	0.25

a) Weight loss of the sample of 10×10×25 mm after 25 thermal cycle between 25°C for 2 days and -20°C for 4 h.

The glass-ceramic panel excels the marble and granite panels in bending and impact strengths as well as in chemical resistance.

As the thermal expansion coefficient of the crystal phase in the glass-ceramic panel is lower than that of the remaining glassy phase, the compressive stresses develops in the crystalline phase, which suppresses the cleavages occurring easily in the crystal grains, thus increasing effectively the thermal shock resistance of the products.

Figure 6 shows the bending strengths of the glass-ceramic specimens, 15×10×60 mm, measured after each of their thermal shock tests; the abscissa indicates the differences in temperature from the furnace temperature to the temperature of water into which the specimens taken out from the furnace were dropped. The data obtained with natural stones under the same conditions are also shown by comparison in Fig. 6.

Figure 7 shows the fracture patterns of the various materials, formed when a steel ball, 535 g, was dropped on the surface of their specimens of which sizes are shown in Fig. 7. The fracture patterns formed in the specimens of the glass-ceramic building material (a) and of the marble (b) are different from those of the low-expansion glass-ceramic (c) and of the available opal glass (d). The former two, (a) and (b), have the interlocked texture of large crystals, 0.4~3 mm in length, which arrests the propagation of the cracks. The latter two, (c) and (d), contain comparatively round

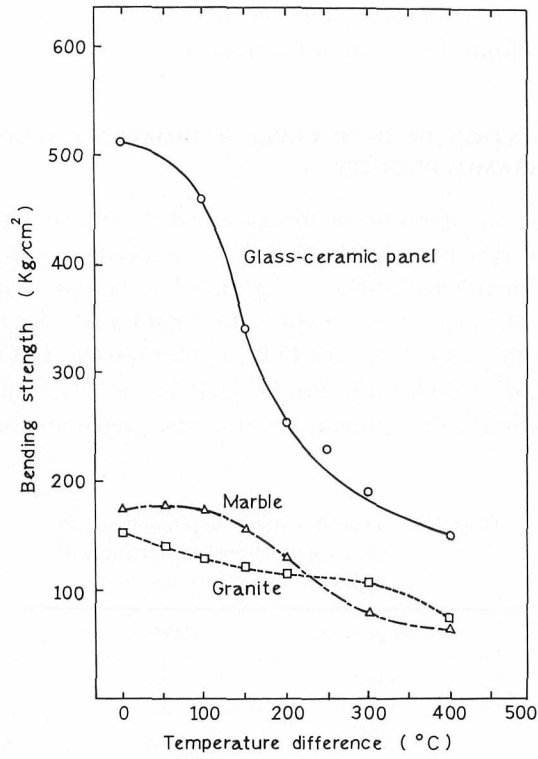


Fig. 6. Bending strength of glass-ceramic panel, marble and granite vs. temperature difference in thermal shock.

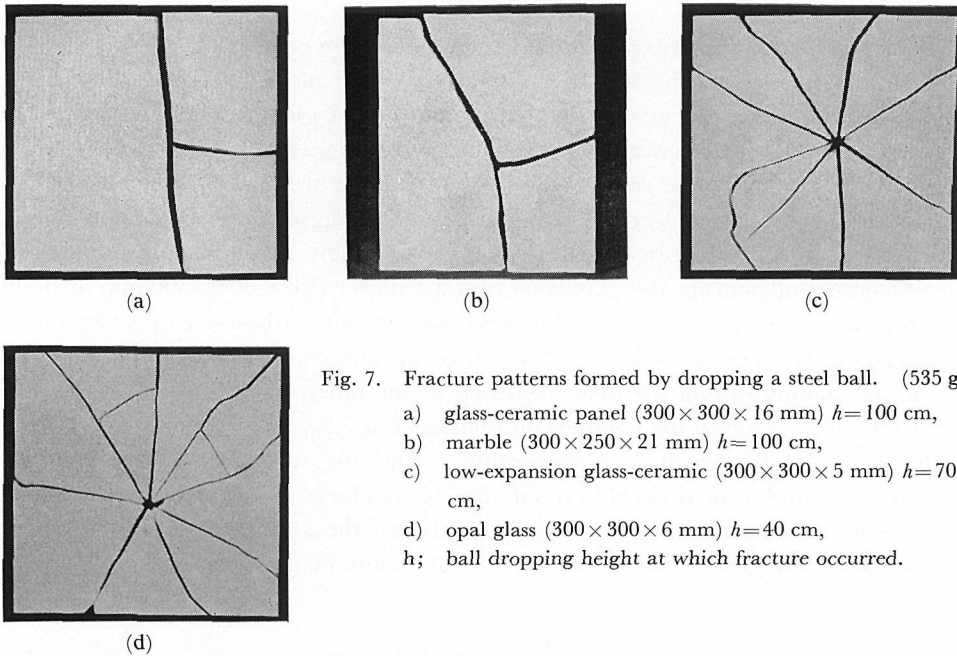


Fig. 7. Fracture patterns formed by dropping a steel ball. (535 g)
 a) glass-ceramic panel ($300 \times 300 \times 16$ mm) $h=100$ cm,
 b) marble ($300 \times 250 \times 21$ mm) $h=100$ cm,
 c) low-expansion glass-ceramic ($300 \times 300 \times 5$ mm) $h=70$ cm,
 d) opal glass ($300 \times 300 \times 6$ mm) $h=40$ cm,
 h; ball dropping height at which fracture occurred.

crystal particles, *ca.* 1 μ in diameter, and therefore, many cracks would easily propagate in the specimens from the origin of the impact.

IV. SOLIDIFICATION OF HIGH LEVEL RADIOACTIVE WASTES BY THE GLASS-CERAMIC PROCESS

The typical oxide composition of the glass batch selected for mixing with high level radioactive waste is given in Table IV. The composition of the waste to be solved with the glass batch mentioned above was assumed to be, for example, Na₂O 33.28, ZrO₂ 9.84, MoO₃ 9.74, Fe₂O₃ 6.50, CS₂O 5.01, BaO 3.30, SrO 2.01, NiO 1.86, MnO₂ 1.41, TeO₂ 1.26, Y₂O₃ 1.22, Rb₂O 0.75, Cr₂O₃ 0.62, CoO 0.57, La₂O₃ 4.26, CeO₂ 5.56, Pr₆O₁₁ 2.51, Nd₂O₃ 9.19, Sm₂O₃ 1.11 by wt %. In the experiment⁸⁾ of the authors' laboratory, the simulated waste was prepared using non-radioactive raw materials.

Table IV. Typical oxide composition of the glass-batch selected for mixing with high level radioactive waste

Composition	(Wt%)
SiO ₂	59.2
Al ₂ O ₃	8.5
CaO	8.5
MgO	8.5
Fe ₂ O ₃	11.9
TiO ₂	3.4

The glass batch was mixed with the simulated waste powders in the weight ratio of 80 to 20 on the oxide basis. The mixture was then melted at 1300°C for 2 h to achieve homogeneity. In general, reheating the mother glass is the standard process for obtaining the glass-ceramics with fine microstructure. The reheating of the radioactive glass under the remote control, however, is technically difficult. Hence the mother glass which can be converted into crystalline aggregate by direct slow cooling from its molten state was used in the present experiment. The cooling process employed consists of pouring the glass melt into a canister (SUS 304), 300 mm in diam. \times 1000 mm in length \times 5 mm in thickness, coated with asbestos cloths, 30 mm in thickness, for its thermal insulation, followed by natural cooling to room temperature. The initial cooling rate of the melt measured at the inner surface of the canister was about 1°C/min. Due to the volume contraction of *ca.* 3%, a few cavities were formed in the center of the resultant glass-ceramic. And the whole glass-ceramic in the canister was found to be divided into only five or six blocks by the formation of cracks. No adhesion was observed at the interface between the glass-ceramic and the inner surface of the canister. The properties of the resultant glass-ceramic are given in Table V.

Glass-Ceramics for Special Applications

Table V. Properties of glass-ceramic obtained in canister by direct slow cooling

Crystal phases	diopside (CaO·MgO·2SiO ₂), Fe ₃ O ₄ , CaTiO ₃ , CaMoO ₄	
Leach resistance*		
Cs ₂ O leached (g/cm ² /day)		5.6 × 10 ⁻⁵
SrO leached (g/cm ² /day)		7.5 × 10 ⁻⁵
Thermal expansion coeff. (30–380°C, × 10 ⁻⁷ /°C)		81.8
Softening temperature (°C)		1,100
Thermal conductivity (at 400°C, Kcal/m. h. °C)		1.66
Density (g/cm ³)		3.01
Thermal stability**	No change after holding at 700°C for 3,000 h	
Young's modulus (at 400°C, Kg/cm ²)		1.02 × 10 ⁶
Bulk modulus (at 400°C, Kg/cm ²)		0.63 × 10 ⁶
Rigidity (at 400°C, Kg/cm ²)		0.41 × 10 ⁶
Poisson's ratio		0.23

* Leach resistance was determined by immersing the specimens in distilled water of 90°C for 24 h.

** Thermal stability of the specimen was determined with the change in the peaks of X-ray diffraction chart of crystal phases or in the leach resistances after heat-treatment.

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