

**SOLIDIFICATION OF HLLW
BY
GLASS-CERAMIC PROCESS**

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**動力炉・核燃料開発事業団
東海事業所**

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SOLIDIFICATION OF HLLW BY GLASS-CERAMIC PROCESS

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ABSTRACT

The compositions of glass-ceramics for the solidification of HLLW were studied and the glass-ceramics in the diopside system was concluded to be the most suitable. Compared with the properties of HLW borosilicate glasses, those of diopside glass-ceramic were thought to be almost equal in leach rate and superior in thermal stability and mechanical strength. It was also found out that the glass in this system can be also crystallized simply by pouring it into a thermally insulated canister and then allowing it to cool to room temperature.

1. INTRODUCTION

For the solidification of HLLW the glass process has been extensively studied. It is pointed out, however, that glass is apt to phase-separate or devitrify due to the decay heat of the fission products in the glass and result in deterioration of leach resistance. Glass-ceramics are obtained by heat-treatment of glass, converting it into a thermodynamically more stable state. It can be expected, therefore, that the above-mentioned weakpoints of HLW glass are removed in an HLW product made by the glass-ceramic process.

The one object of this study is to determine the most suitable glass-ceramic composition for the solidification of HLLW. The glass-ceramic systems studied were similar to those which were described as the candidates of HLW glass-ceramics [1]. Simulated oxides of HLLW from the reprocessing plant of PNC Japan were incorporated into the base glasses in the amount of 20 - 30 wt.%. The maximum melting temperature of the glasses was limited to 1300°C.

The other object of this study is to simplify a process for the crystallization of glass. To crystallize a glass, it is necessary to heat treat it. Especially in the case of hot cell operation, this process must be as simple as possible. Studies were carried out to crystallize the glass in a canister during the course of cooling it without another independent heating process.

2. COMPOSITIONS

The chief crystal phase compositions surveyed in this study were 1) CaO-MgO-Al₂O₃-SiO₂ (D system), 2) BaO-Al₂O₃-SiO₂ (C system), 3) CaO-TiO₂-Al₂O₃-SiO₂ (P system) and 4) Li₂O-Al₂O₃-SiO₂ (E system). Simulated oxides of HLLW of PNC Japan comprised 20-30 wt.% in the base glasses of these systems. The composition of simulated HLW oxides are: 30.6 Na₂O, 9.05 ZrO₂, 8.96 MoO₃, 5.97 Fe₂O₃, 4.61 Cs₂O, 3.03 BaO, 1.85 SrO, 1.71 NiO, 1.30 MnO₂, 1.16 TeO₂, 1.12 Y₂O₃, 0.69 Rb₂O, 0.57 Cr₂O₃, 0.52 CoO, 3.92 La₂O₃, 5.11 CeO₂, 2.31 Pr₆O₁₁, 8.45 Nd₂O₃, 1.02 Sm₂O₃ by wt.%. Glasses were melted at 1300°C for 2 hrs, then cast into a mould and annealed. The homogeneous glasses obtained were crystallized by heating at a rate of 300°C/hr from room temperature to 500°C then heating at a rate of 33°C/hr from 500°C to the maximum (crystallization) temperatures and finally holding for 1-3 hrs at these temperatures.

For the fine grained glass-ceramic obtained in each system, characteristics such as crystal phases, leach rate, thermal conductivity, thermal stability, etc. were evaluated. Crystal phases were identified by X-ray diffraction XRD. In the measurement of leach rate, samples of 25×25×5 mm were immersed in 500 ml of distilled water at 90°C for 24 hrs, and weight loss and the amounts of Cs₂O and SrO dissolved into the water were measured. To evaluate thermal stability, specimens were kept at 700°C for 1000 ~ 3000 hrs and the change in crystal phases and leach rate were examined.

1) Glass-ceramics containing 20% HLW

In the D system, the compositions in the series 67.8(CaO+MgO+Al₂O₃+SiO₂)·9.5 Fe₂O₃·2.7 TiO₂·20HLW (wt.%), the CaO/MgO ratio being 3/1 ~ 1/1, were

studied. In the C system, the compositions in the series $70(\text{BaO}+\text{CaO}+\text{ZnO}+\text{Al}_2\text{O}_3+\text{SiO}_2)\cdot 5\text{TiO}_2\cdot 5\text{B}_2\text{O}_3\cdot 20\text{HLW}$ (wt.%), the ratio BaO:CaO:ZnO being 10:3:2, were studied. In the P system, the compositions in the series $65(\text{CaO}+\text{Al}_2\text{O}_3+\text{SiO}_2)\cdot 10\text{TiO}_2\cdot 5\text{B}_2\text{O}_3\cdot 20\text{HLW}$ (wt.%) were studied. In the E system, the compositions in the series $70(\text{Li}_2\text{O}+\text{Al}_2\text{O}_3+\text{SiO}_2)\cdot 6\text{TiO}_2\cdot 4\text{ZnO}\cdot 20\text{HLW}$ (wt.%) were studied. The glass-ceramics of the following compositions, D-62 (D system), C-27 (C system), P-50 (P system) and E-63 (E system) were excellent from the view point of texture, deformation during heat-treatment and physical and chemical properties. Compositions, crystal phases, leach rate and thermal stability are shown in Table 1, 2 and 3, respectively. Thermal conductivity is shown in Fig. 1, and bending strength, thermal expansion coefficient and thermal shock resistance are given in Table 4.

2) Glass-ceramics containing 30% HLW

In the D system, the compositions in the series $54.7(\text{CaO}+\text{MgO}+\text{Al}_2\text{O}_3+\text{SiO}_2)\cdot 8.7\text{Fe}_2\text{O}_3\cdot 3.2\text{TiO}_2\cdot 3.5\text{B}_2\text{O}_3\cdot 30\text{HLW}$, the ratio CaO/MgO being 3/1 were studied. Without B_2O_3 addition it was difficult to obtain homogeneous glass because of marked phase separation (formation of a Mo-phase). Addition of B_2O_3 more than 5% reduced the crystallization tendency and increased the deformation during heat-treatment. Therefore, the addition of B_2O_3 should be limited to less than 5%. The glass-ceramic of D-210 composition was the most successful. Compositions and crystal phases are shown in Table 1, and other properties are shown in Table 2, 3 and 4.

In the P system, the compositions in the series $56.5(\text{CaO}+\text{Al}_2\text{O}_3+\text{SiO}_2)\cdot 10\text{TiO}_2\cdot 3.5\text{B}_2\text{O}_3\cdot 30\text{HLW}$ (wt.%) were studied and it is concluded that the P-71 glass-ceramic was the most suitable. Chemical composition and crystal phases

are shown in Table 1 and other properties are shown in Table 2, 3 and 4. In the C and the E systems, homogeneous glass was not obtained because of marked phase separation.

The results of the evaluation for glass-ceramics containing 20 ~ 30% HLW are summarized as follows: a) The leach rate of D62 was the lowest (Table 2), with a total weight loss of 3.6×10^{-5} g/cm²·day, a Cs₂O leach rate of 5.3×10^{-5} and a SrO leach rate of 7.0×10^{-5} . The deposition of a CaMoO₄ phase was not harmful to the leach resistance. b) Thermal stabilities (Table 3) of D-62, C-27, D-210 and P-71 were good and almost no changes in crystal phases and leach rates were observed. In the P-50, precipitation of NaAlSi₃O₈ (nepheline) and growth of sphenes were observed, and the leach rate increased by a factor of 3. In E-63 growth of Li₂SiO₃ was observed and the leach rate increased by a factor of 3. c) In thermal conductivity, D-62 was the highest over the entire temperature range (Fig. 1), which is most advantageous for the diffusion of decay heat. d) D-62 was the highest in bending strength (1320 kg/cm²) and the lowest in thermal expansion coefficient. (Table 4). D-62 also had a high value in T_g and T_f and good thermal shock resistance. e) An SEM photograph (Fig. 2) shows that the D-62 glass-ceramic consists of fine grained crystals 0.2 to 1.5 micron in size.

As the conclusion of these evaluations, the D-62 glass-ceramic was considered to be the most suitable for the solidification of HLLW.

3. PROCESS FOR CRYSTALLIZATION

In the experiment described above, the glasses were crystallized by reheating from room temperature to crystallization temperatures as in the case of the production of commercial glass-ceramics. However, it will be complicated to apply such a reheat treatment process to the crystallization of glass already cast into a canister because of the very large volume of glass. It is more desirable to crystallize the glass by slowly cooling after casting it into a canister. It is a well known fact that a crystalline body is obtained when a melt is cooled slowly. It has been proposed to make HLW product using this fact [2]. In general, however, it is difficult to obtain a fine grained crystalline body having good mechanical strength as the solid formed by this method tends to be coarse grained. On the other hand, a melt of basalt can be converted into a fine grained crystalline body during the course of cooling [3]. As the D system mentioned above is close to basalt in its composition, a fine grained crystalline body can be expected to be obtained during the cooling process.

The following is a description of experiments carried out for the D-62 glass (Table 1). The DTA of the cooling process of D-62 glass melt showed the exothermic peaks corresponding to the precipitation of diopside crystal at $900 \sim 1000^{\circ}\text{C}$, when the cooling rate was slower than $10^{\circ}\text{C}/\text{min}$.

The cooling condition necessary to obtain a fine grained crystalline body was studied. D-62 glasses were melted at 1300°C for 1 hr in alumina crucibles, then placed in temperatures of $750 \sim 1050^{\circ}\text{C}$ for 2 hrs and finally allowed to cool to room temperature. Thin section microphotographs are shown in Fig. 3 and crystal phases and leach rate are shown in Table 5.

It can be seen from Fig. 3, that a fine grained texture was obtained at 800 ~ 850°C. The leach resistances in Table 3 are similar to those obtained by the reheat-treatment (Table 2) and there was little change when the maintained temperature was varied.

Since the optimum temperature to obtain a fine grained body was relatively low, it was thought that a fine grained glass-ceramics might be obtained by cooling the glass in a canister which is sufficient by thermally insulated so that it would be difficult for the heat of the glass melt to escape.

An experiment was carried out using a cylinder made of stainless steel SUS304 which was 300mm in diameter, 350mm high, 5mm thick and the wall of which was insulated with asbestos clothes of total thickness 30 mm. 65 kg of D-62 glass was melted at 1250°C, poured into the cylinder (Fig. 4(a)), and allowed to cool to room temperature after putting on a lid insulated similarly. Cooling curves measured by the thermocouples inserted in the center and near the inside wall of the cylinder are shown in Fig. 5. The whole glass was converted into glass-ceramic (Fig. 4(b)) and the properties are given in Table 6. Although the texture became somewhat more coarse than desired because of the slower cooling rate, glass-ceramic had good properties. In the inside of the glass-ceramic a number of small cavity appeared. This may be attributed to the volume contraction (c.a. 2%) during crystallization of the inner glass which crystallized later after the hard shell had been formed by the crystallization of the glass in the circumference. No adhesion at the interface between the glass-ceramic and stainless steel was found, so defects caused by stress development (cracking, etc.) was not observed.

4. SUMMARY

The glass-ceramic in the Diopside system (D-62) was found to be suitable for the solidification of HLLW. This glass-ceramic was produced by slow cooling of the glass melt cast into a thermally insulated canister. By the process developed in this study a stable HLW glass-ceramic can be produced by almost the same method as the HLW glass process.

REFERENCES

1. A. K. Dé, et al., Development of Glass ceramics for the Incorporation of Fission Products, Bull. Am. Ceram. Soc. 55, 500-503 (1975).
2. A. E. Ringwood, Safe Disposal of High Level Nuclear Reactor Waste: A New Strategy, Australian National University Press, Canberra, Australia, 1978.
3. For example, Ten Voldán, The Melting and Crystallization of Basic Eruptive Rocks, Advances in Glass Technology, p.382-396, VI ICG in Washington, U.S.A., July 8-14, 1962, Plenum Press, New York, 1962.

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A and B represents measured position.

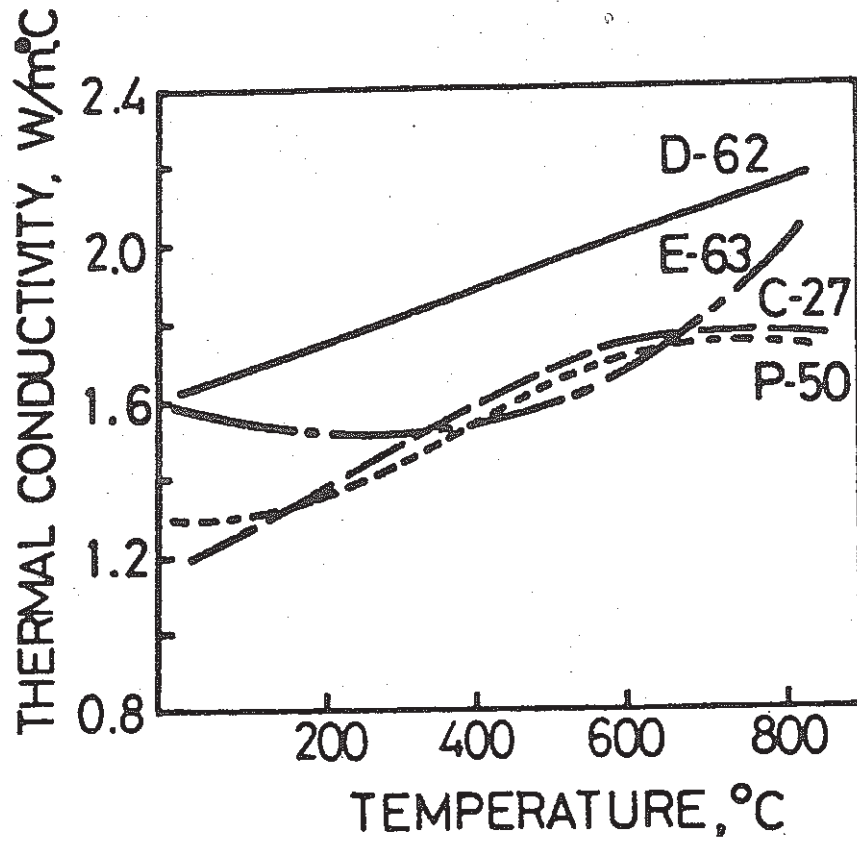
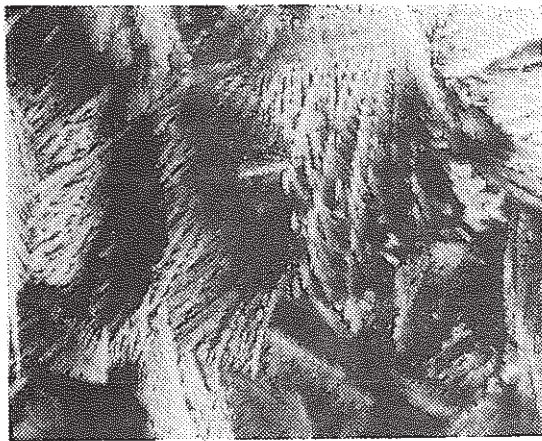


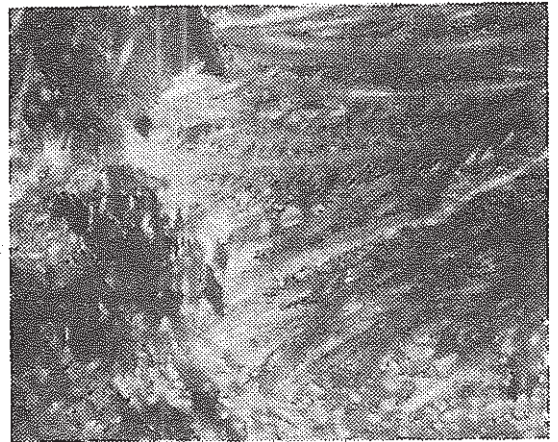
Fig. 1 Thermal conductivity of obtained glass-ceramics.



Fig. 2 Secondary electron image of diopside-system(D-62)



a) 1050°C



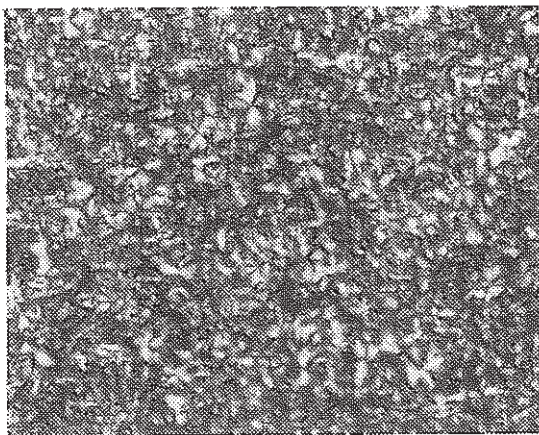
b) 1000°C



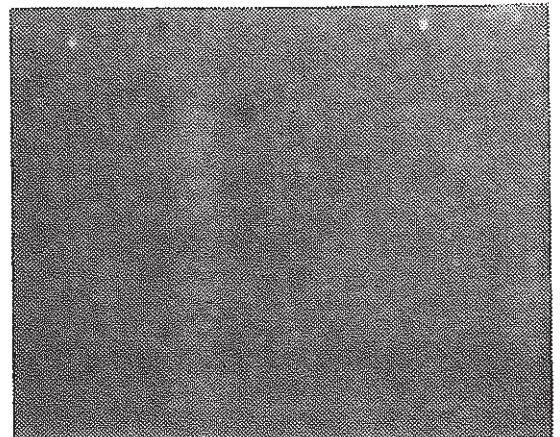
c) 950°C



d) 900°C



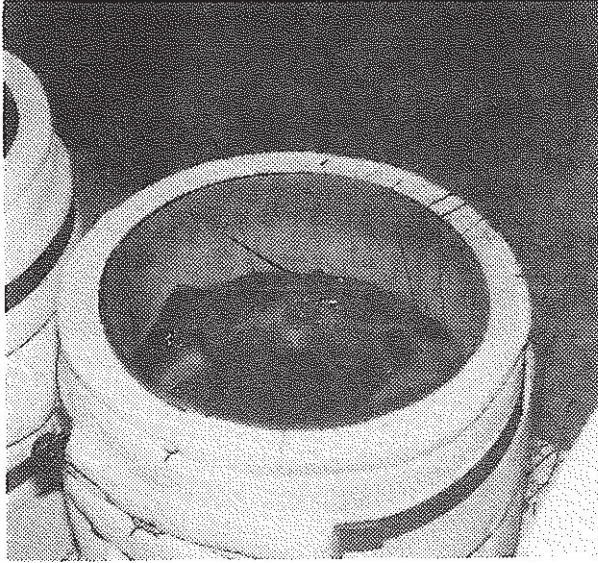
e) 850°C



f) 800°C

0.1 mm

Fig. 3 Keep temperature and microstructure (thin section microphotograph)



a)



b)

Fig. 4 a) Canister of $300\phi \times 350h \times 5t$ in size.

b) D-62 glass-ceramic crystallized in the canister.

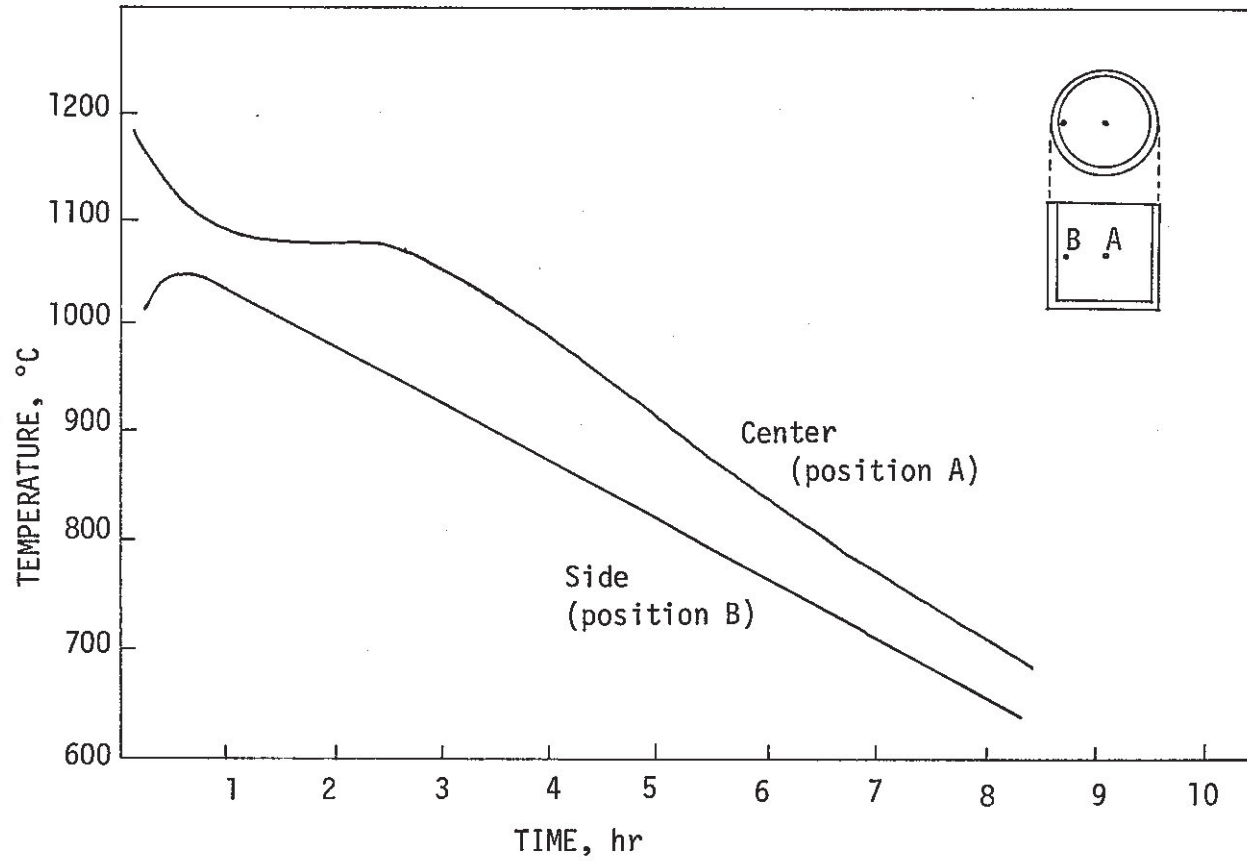


Fig. 5 N. OGUINO

TABLE 1
Compositions and Crystal Phases of Glass-Ceramic

Sample No.	D-62	C-27	P-50	E-63	D-210	P-71
SiO ₂ (wt%)	47.5	35.0	30.0	50.0	41.02	40.0
Al ₂ O ₃	6.8	15.0	10.0	12.5	8.20	6.5
B ₂ O ₃		5.0	5.0		3.50	3.5
Fe ₂ O ₃	9.5				8.70	
TiO ₂	2.7	5.0	10.0	6.0	3.20	10.0
CaO	6.8	4.0	25.0		4.10	10.0
MgO	6.8				1.37	
BaO		13.3				
ZnO		2.7		4.0		
Li ₂ O				7.5		
HLW	20.0	20.0	20.0	20.0	30.0	30.0
Total	100.0	100.0	100.0	100.0	100.0	100.0
Crystal Phases	Diop.* Fe ₂ O ₄ CaMoO ₄ CaTiO ₃	h-Cel.** CaMoO ₄ CaTiO ₃	Pero.*** CaSiO ₃ CaMoO ₄ Sphene	β-Sp.# Li ₂ SiO ₃	Diop. CaMoO ₄ Fe ₃ O ₄ CaTiO ₃	Sphene## CaMoO ₄
Heat treatment	1100°C 1hr	850°C 1hr	900°C 3hr	800°C 2hr	900°C 1hr	900°C 1hr

*) Diopside(CaO·MgO·2SiO₂) **) hexa-Celsian(BaO·Al₂O₃·2SiO₂)

***) Perovskite(CaTiO₃) #) β-Spodumene(Li₂O·Al₂O₃·4SiO₂)

##) CaO·TiO₂·SiO₂

TABLE 2

Leach Rate of Glass-Ceramics

Sample No.	Leach Rate (g/cm ² ·day)		
	Weight loss	Cs ₂ O	SrO
D-62	3.6 x 10 ⁻⁵	5.3 x 10 ⁻⁵	7.0 x 10 ⁻⁵
C-27	1.8 x 10 ⁻⁴	1.1 x 10 ⁻⁴	2.9 x 10 ⁻⁴
P-50	5.6 x 10 ⁻⁴	3.3 x 10 ⁻⁴	9.0 x 10 ⁻⁴
E-63	2.1 x 10 ⁻⁴	1.9 x 10 ⁻⁴	1.1 x 10 ⁻⁴
D-210	6.5 x 10 ⁻⁵	5.9 x 10 ⁻⁵	7.4 x 10 ⁻⁵
P-71	1.2 x 10 ⁻⁴	-	-

Leach rate after immersion at 90°C for 24 hrs in distilled water.

Surface of 25 x 25 x 5 mm sample was polished by 1,000 mesh abrasive powder.

TABLE 3

Changes of Crystal Phases and Leach Rate of Glass-Ceramics,
After Heating at 700°C for 1,000 ~ 3,000 hrs

Sample No.	Description of X-ray trace	Leach Rate (Weight loss, g/cm ² day)		
		0 hr	1,000 hrs	3,000 hrs
D-62	No change	3.6×10^{-5}	3.6×10^{-5}	3.6×10^{-5}
C-27	No change	1.8×10^{-4}	1.9×10^{-4}	-
P-50	Precipitate of NaAlSiO ₄ Appearance of Sphene (111) peak	5.6×10^{-4}	8.5×10^{-4}	1.6×10^{-3}
E-63	Increase of intensity in Li ₂ SiO ₃ (110) peak)	2.1×10^{-4}	5.6×10^{-4}	-
D-210	No change	6.5×10^{-4}	6.5×10^{-5}	6.6×10^{-5}
P-71	No change	1.2×10^{-4}	9.3×10^{-5}	-

TABLE 4

Bending Strength, Thermal Expansion and Thermal Shock
Resistance of Glass-Ceramics

Sample No.	Bending Strength	Thermal Expansion	Transf. Pt.	Deform. Pt.	Thermal Shock Resistance
	(kg/cm ²)	$\alpha \times 10^7$ (1/°C) (30 ~ 380°C)	Tg* (°C)	Tf** (°C)	Temp. difference, ΔT (°C)
D-62	1320	79	794	>1000	150
C-27	760	91	545	838	120
P-50	870	81	582	>734	120
E-63	1270	78	502	734	150
D-210	1050	85	555	696	120
P-71	980	89	557	684	120

* Tg Dilatometric transformation point

** Tf Dilatometric deformation point

TABLE 5

Keep Temperatures vs. Crystal Phases and Leach Rate

Temperature	Crystal phases and XRD peak-height (arbitrary unit, in parentheses)	Leach rate 10^{-5} g/cm ² ·day		
		Wt. loss	Cs ₂ O	Sr ₂ O
1050°C	Diopside, Fe ₃ O ₄ , CaTiO ₃ , CaMoO ₄ (88) (8) (14)	5.65		
1000°C	Diopside, Fe ₃ O ₄ , CaTiO ₃ , CaMoO ₄ (118) (8) (12)	4.50	5.85	12.1
950°C	Diopside, Fe ₃ O ₄ , CaTiO ₃ (160) (8)			
900°C	Diopside, Fe ₃ O ₄ , CaTiO ₃ (164) (12)	3.90	5.62	7.52
850°C	Diopside, Fe ₃ O ₄ , CaTiO ₃ (154) (10)	4.20		
800°C	Diopside, Fe ₃ O ₄ , CaTiO ₃ (128) (10) ³	4.32	6.82	9.05
750°C	Amorphous (glass)			
Quench	Quenched glass body (Annealed)	~ 20		

TABLE 6

Properties of D-62 Glass-Ceramic Crystallized in Canister
During Cooling

Crystal phases	Diopside, Fe_3O_4 , CaTiO_3 , CaMoO_4
Leach rate wt.loss	4.3×10^{-5} g/cm ² ·day
Cs_2O	5.6×10^{-5} g/cm ² ·day
SiO_2	7.5×10^{-5} g/cm ² ·day
Bending strength	1100 kg/cm ²
Thermal expansion coeff.	$81.8 \times 10^{-7}/^\circ\text{C}$ (30 ~ 380°C)
Softening temp.	>1100°C
Thermal conductivity	1.93 w/m·°C
Density	3.00 g/cm ³
Thermal stability	No change after heating at 700°C for 3,000 hrs.