Crystallization of Glass

in the System $PbO-GeO_2-SiO_2$

by

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Contents

Introduction

The success of Stookey [1] in making "Pyroceram " has provoked interest in the development of glass-ceramics with improved thermal, mechanical and electrical properties. Especially, since the discovery of opto-electrical properties of single crystals of $LiNbO_3$, $LiTaO_3$, $BaTiO_3$ and so on, an attempt to fabricate transparent ceramics with ferroelectric properties has been made by means of two different methods. One of them is crystallizing of glass, the glass-ceramic method, and the other is hot-pressing of powder. The glass-ceramic method is very useful for making pore-free densified ceramics with desired shapes. Although some advantages in the glass-ceramic method were found, there are still remained some problems to be solved as mentioned below. First, in general materials with ferroelectric properties are difficult to prepare in the glassy state, so that a sufficient quantity of network-forming oxides such as SiO_2, B_2O_3 etc. has to be added to the above materials in order to obtain a glassy state and to form the glass into a desired shape. However, there is a tendency that an addition of network-forming oxide impairs the characteristics of ferroelectrical materials. Through the process of crystallization of glass, secondly, it often occurs that the primary crystalline phase is not a desired stable phase but a metastable one. Therefore, it is very difficult to determine the optimum composition and crystal-

lizing conditions to prepare the transparent glass-ceramic product in which the major crystalline phase has an ferroelectric property. If opaqueness of the glass-ceramics are caused by intrinsic absorptions of crystals or Rayleigh-scattering at interface between crystalline particles and glass matrix, attainment of transparency needs to take away these phenomena. In transparent glass-ceramics already reported, dissolution of Rayleigh-scattering were generally attained by following methods ; (i) Producing of very small particles whose sizes were less than the wave length of visible light, and (ii) Controlling on differences of refractive indeces at interfaces between the crystalline particles and glass matrix.

From the stand point mentioned above, the fabrication of glass-ceramics of quite new system in which no additional network-forming oxides is required for glass making have been studied.

In the system $PbO-GeO_2$, glass formation is possible over a wide range of lead oxide content and a single crystal of $Pb_5Ge_3O_{11}$ exhibits ferroelectric properties [2, 3]. First, the author attempted to fabricate a transparent glass-ceramic by the crystallization of $Pb_5Ge_3O_{11}$ from lead germanate glasses with the composition near $5PbO \cdot 3GeO_2$. However, phase relations in this system reported by various investigators [4 - 6] were quite confused. Therefore, it is necessary for making glass-ceramics with better quality to examine phase relations in detail. The results of

crystallization of glasses of the system $PbO-GeO_2$ are described, and the phase relations and the crystallization mechanism are discussed in Chapter 2 of this paper.

On the basis of analogy between germanate and silicates, secondly, crystallization of crystalline phase whose structure is similar to that of ferroelectric $Pb_5Ge_3O_{11}$ from lead silicate glasses with the composition near $5PbO \cdot 3SiO_2$ are examined and the detailed results are described in Chapter 3.

The system $PbO-GeO_2$ involves the problem on stability of the base glass during cooling to be solved. It is expected that the addition of SiO_2 enhances the stability of the glass and Ge^{4+} ions are replaced by Si^{4+} ions. So, the present investigation is extended into the $PbO-GeO_2-SiO_2$ system. The phase relations and the crystallization of the glass in the system $PbO-GeO_2-SiO_2$ are discussed in Chapter 4.

In order to enhance the stability of the base glass, several oxides such as SiO_2, Al_2O_3 and so on were added to $5PbO \cdot 3GeO_2$. Effects of added oxides on stability of the base glass and crystallizing phenomena of these glasses are examined in Chapter 5.

Finally, in Chapter 6, properties of glass-ceramics in the systems $PbO-GeO_2$, $PbO-SiO_2$ and $PbO-GeO_2-SiO_2$ are described.

Chapter 1. Experimental procedures

In this chapter, experimental procedures are briefly described.

1-1. Glass preparation

Pure oxide components were used for the preparation of the glasses. They are Nakarai 99.9% lead monoxide, Nakarai 99.999% germanium dioxide, Mallinckrodt silicic acid, Nakarai reagent grade boron trioxide, Yamada 99.9% niobium oxide, Nakarai reagent grade titanium dioxide, Nakarai 99.9% ferric oxide and Nakarai ragent grade zirconium oxide. Stock batches were accurately weighed out in the desired compositions, and carefully mixed in a agate ball mill for 1 day in dry air. About 50 g of the mixed oxides were transferred to a platinum crucible. Melting was carried out using an electric furnace. Batch materials in a platinum crucible was preheated at 550°C for 10 hrs to minimize vaporization of volatile component and then melted at about 800°C for 30 minutes. The melts were readily quenched to an homogeneous glass by dropping the crucible into cold water. The glasses were crushed and remelted again at 800°C for 30 minutes to ensure their

homogeneity. After the melting was completed the melt was poured onto a steel mould and formed into a plate of about 1 mm thickness by pressing.

Microscopic examination of the product indicated that a glass without any bubble and inclusion was formed using the preparation method mentioned above. This preparation technique was employed to produce glass samples for DTA, infrared analysis and X-ray diffraction analysis.

1-2. Differential thermal analysis

Differential thermal analysis (DTA) was used to examine thermal properties of the base glass. The characteristic temperatures such as glass transition temperature, nucleation temperature, crystallization temperature and melting point of the precipitated crystalline phases were determined as the results of the average of three times measurements, and an experimental error for each measurement was at most ± 2°C.

The analysis was made in the temperature range from 20°C to 800°C using RIGAKU thermoflex termal analyser. About 20 mg of the coarse grainded powders of the glass in a platinum cell (5 mmφ x 3 mmH) was heated in air with the heating rate of 10°C/min, and calcined alunima (α-Al_2O_3) was used as an inert reference material. The amplifier sensitivity was set to give a full-scale deflec-

tion of ± 100 μV. Fairly steady base lines were obtained up to 800°C. Since the effects of sample weights and grain sizes on DTA traces were slight, no calibration was made.

1-3. Crystallization

The heat-treatment for crystallization of the glass was conducted using an electric furnace. Bulk sample contained in a platinum basket was placed in the furnace and heated at different constant temperature between 350°C and 700°C for 1 minute to 2 weeks, and then quickly cooled to room temperature. The temperature gradient in the furnace was preexamined and sample was placed in the region where temperature gradient was flat. The temperature controling and monitoring thermocouples were positioned above and below the basket and the temperatures of samples were carefully controlled by the outputfrom these thermocouples. Fluctuation of the temperatures was less than ± 2°C.

1-4. X-ray diffraction analysis

The crystalline products obtained after quenching the specimens from selected temperatures were identified by

means of X-ray diffraction analysis. Each specimen was carefully crushed into fine powder and examined using a RIGAKU automatic recording diffractometer with nickel filtered copper radiation (40 kV, 20 mA). For determination of lattice parameters, an inner standard method was used with 99.999% silicon powder.

1-5. Infrared spectrophotometry

The infrared absorption spectra between 3000 cm^{-1} and 250 cm^{-1} were recorded on a Perkin-Elmer 521 grating IR spectrophotometer or a JASCO IRA-2 spectrophotometer equipped with grating. Each sample was first ground in an agate pestle and mortar. About 1 mg of each powdered sample, -250 mesh, was then mixed with about 200 mg of KBr(Nakarai Chemicals UVS-73 for spectroscopy) and heated for 12 hrs at 80°C in vacuum. The KBr discs were formed by pressing the evacuated mixtures at 10 ton/cm^2 for about 5 min. Scanning speed of every measurements was 500 cm^{-1}/min., but for some detailed measurements in the range from 1200 to 250 cm^{-1}, scanning speed of 10 cm^{-1}/min. was selected.

1-6. Solid state reaction

The chemical compositions of several crystallized phases were determined by usual solid state reaction method. Nakarai 99.9% lead monoxide and Nakarai 99.999% germanium dioxide were accurately weighed out and carefully mixed in an agate ball mill for 1 day in dry air. About 3 g of each mixture was pressed into a disc about 5 mm in diameter and about 3mm thickness. The disc placed in a platinum basket reacted at 450°C to 700°C for 1 week, and then rapidly cooled to room temperature and the phase of product was identified by X-ray diffraction analysis.

1-7. Chemical analysis

Chemical analyses by means of gravimetric methods were performed to examine the difference between crystallized products and initial mixtures of oxides and to determine the chemical composition of the final product. The error was estimated to be less than 0.5% in weight.

1-8. Dielectric measurement.

For dielectric measurement, the glass-ceramic was formed into a paralell plate (10 mm x 10 mm x 2mm). Gold electrode and gard electrode with a gap of 0.5 mm wide were spattered in vacuum, and readwires of copper were fixed to the gold electrode by silver paint. Permittivity of the sample was measured at 1 kHz using a type TR-10 dielectric loss measuring set, Ando Denki Co. , with the comparison of standard sample of $BaTiO_3$.

Chapter 2. System $PbO-GeO_2$

In this chapter, first, the glass formation, some thermal properties and phase relations of products in the chemical composition around $5PbO \cdot 3GeO_2$ in the system $PbO-GeO_2$ are described. Secondary, from the results of infrared absorption measurements, the mechanism of crystallization is examined.

2-1. Glass formation

The chemical compositions of glass specimens used for this study are presented in Table I. In the present experiment, yellowish transparent glasses were easily formed on rapid cooling of the melts. However, in the case of PG-65 glass, a partial devitrification was observed with a rapid cooling.

On microscopic examination of the base glasses, neither bubbles nor inclusions were observed. To confirm homogeneity of the glass, the densities of several parts of the glass block were measured by pycnometric method. No fluctuation in density was observed for the specimens within the limit of error. The results of chemical analysis

Table 1 Chemical compositions of glasses

Sample	mole %		weight %		PbO/GeO_2
	PbO	GeO_2	PbO	GeO_2	
PG-58	58.08	41.92	74.73	25.27	
PG-60	60.00	40.00	76.19	23.81	3/2
PG-61	61.02	38.98	76.96	23.04	
PG-62	61.99	38.01	77.68	22.32	
PG-62.5	62.48	37.52	78.04	21.96	5/3
PG-63	63.17	36.83	78.54	21.46	
PG-65	65.04	34.96	79.88	20.12	13/7

indicated that there is no difference of chemical composition between the glass prepared and the initial mixture of powdered oxides. Therefore, it is said that the glass with homogeneity and desired chemical composition were prepared by the above way.

Although Imaoka [7] reported that the limit of the glass-forming region in the system $PbO-GeO_2$ is 57 mol% PbO, in this study the glass-forming region was extended to the more PbO content of 65 mol%.

The glass transition temperature, density and chemical composition of each glass specimen are tabulated in Table II. As PbO content increased, the glass transition temperature decreased continuously from 337°C for PG-60 glass to 325°C for PG-65 glass. Figure 1 shows the infrared absorption spectra of the glasses tabulated in Table I in the region of 1200-250 cm^{-1}. As shown in this figure, the similar spectra were obtained for all glass specimens with various compositions and characterized by two strong absorption bands around 740 and 380 cm^{-1} and a weak absorption at about 525 cm^{-1}. These results for glass transition temperature and infrared absorption strongly suggest that all the glasses have similar structural unit.

Coordination of Ge^{4+} in germanate glasses has been a serious problem. In Na_2O-GeO_2 system, for instance, Hanada et al. [8] reported that the coordination number of Ge^{4+} ion in the glass changed from 4 to 6 with the increase of alkali contents from the results of fluorescent

Table II. Densities and Tg of glasses in the system $PbO-GeO_2$

Sample	Density	Tg	PbO/GeO_2
PG-58	7.24_8	342°C	58/42
PG-60	7.36_5	337	60/40 (=3/2)
PG-61	7.43_4	336	61/39
PG-62	7.49_4	335	62/38
PG-62.5	7.53_0	334	62.5/37.5 (=5/3)
PG-63	7.55_2	330	63/37
PG-65	7.651	325	65/35

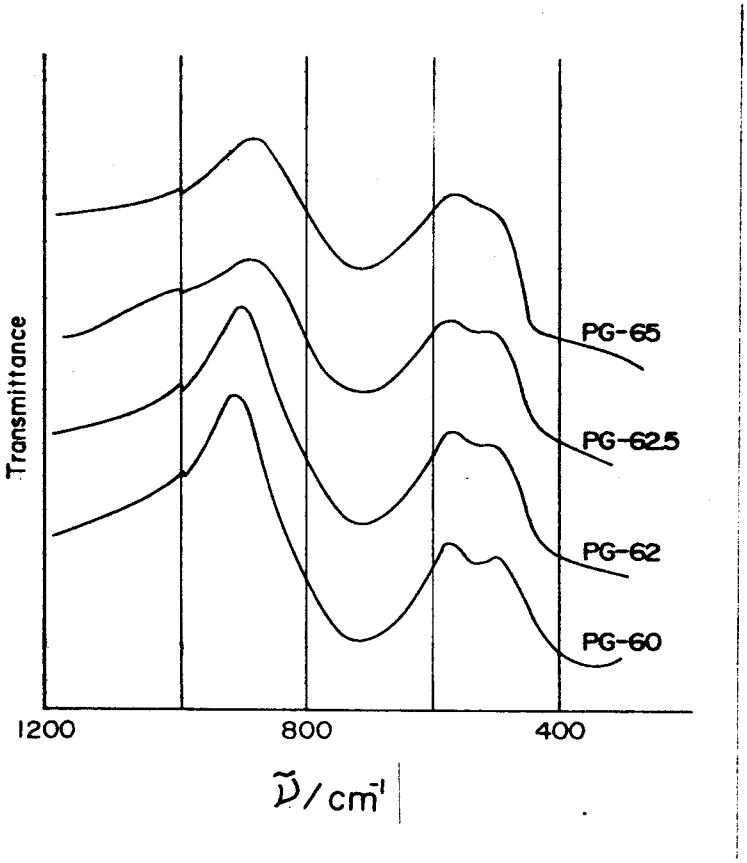


Figure 1. Infrared absorption spectra of glasses in the system $PbO-GeO_2$

X-ray spectrophotometry. Coordination number of Ge^{4+} in GeO_2 glass was determined to be 4 from the result of infrared absorption measurement [9]. In this system, coordination number of Ge^{4+} in the glass was ascertained to be 4 by infrared spectrophotometry. On the other hand, much attention has been focussed on the behavior of Pb ions in the glass. However, in this system, coordinating behavior of lead ions in the glass was obscurely confirmed, but it would be estimated that lead ions contributed to form networks of the glass and linked GeO_4 tetrahedron or Ge_2O_7 groups. The discussions are described in detail in Section 2-3 of this chapter.

2-2. Crystallization during heating

The crystallizing phenomena of glass specimens during heating at a constant rate were examined by DTA. The thermal behaviors of coarse grained samples during heating are illustrated by DTA traces in Figure 2. In the DTA measurements, effects of particle sizes and weights of samples on the shape of the curves were slight. The preliminary tests for the influence of heating rate using the two rates of 5°C/min. and 10°C/min. had indicated that it had a little effect upon the thermal analysis curves. In the present study, sample weights of 20 mg of coarse glass powder and heating rate of 10°C/min. were used, and

the characteristic temperatures were determined as the results of the average of three times measurements at least.

The crystallizations of glass specimen under investigation were classified into the following three groups ;

(1) 58-61 mol% PbO (near $3PbO \cdot 2GeO_2$)

As indicaetd in Figure 2, there were two endotherms and one sharp exotherm. Among them, the first endothermal step at about 340°C corresponded to the glass transition due to the drastic change of specific heat. Sharp exothermal peak at about 390°C was a result of crystallization. From the results of X-ray diffraction analysis, it was concluded that the crystallized phase was a new compound denoted to be "phase A". The X-ray diffraction pattern of phase A belonged to a hexagonal system and lattice parameters were calculated to be a=10.16Å and c=19.37Å. Sharp exothermal peak was observed at 733°C as a result of the melting of this phase.

(2) 62-63 mol% PbO (near $5PbO \cdot 3GeO_2$)

As shown in Figure 2, there were two exotherms and two endotherms in the DTA trace. The first endothermal step at about 335°C was due to the glass transition. Both sharp exothermal peaks at 372-403°C and 482-514°C resulted from crystallizations. X-ray diffraction studies suggested that the crystalline phase appeared at a temperature in the range from 400°C to 480°C was identified to be phase A and the crystallized product obtained above 483°C was identified

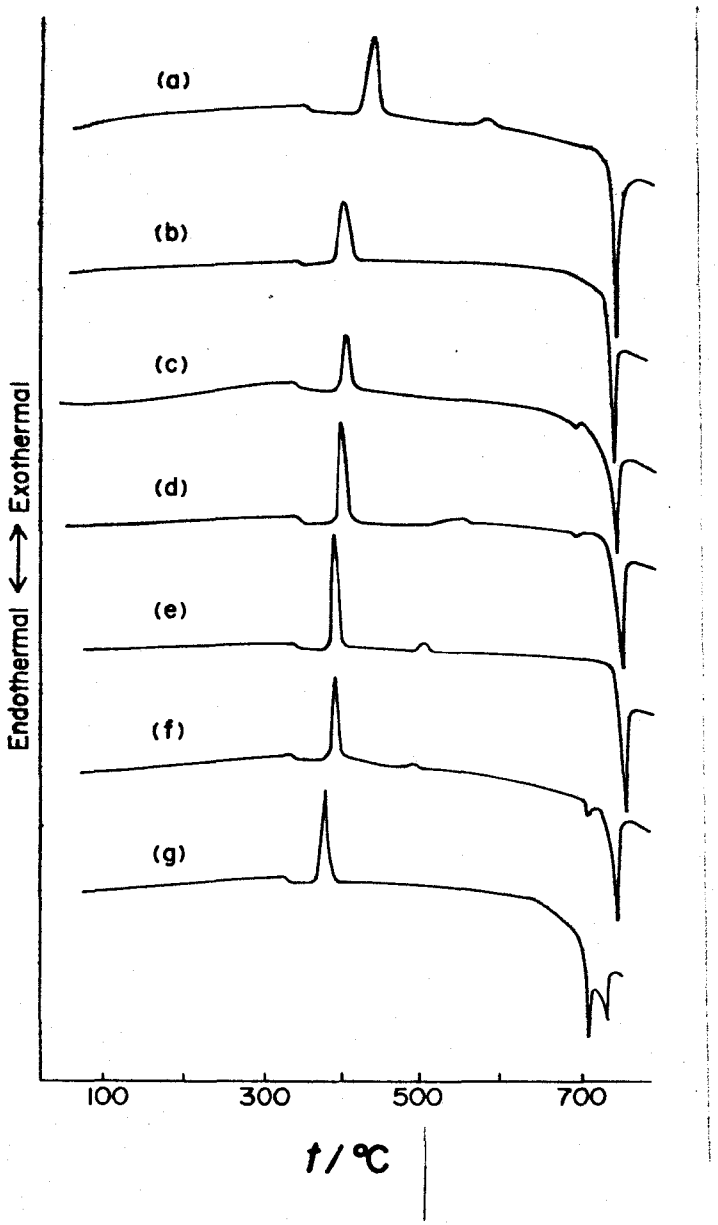


Figure 2. DTA traces of glasses in the system $PbO-GeO_2$

to be $Pb_5Ge_3O_{11}$ already reported by Sugii [2]. Therefore, the second exothermal peak was assigned to the formation of $Pb_5Ge_3O_{11}$ after the reaction between phase A and residual glass matrix. $Pb_5Ge_3O_{11}$ denoted to be "phase B" melted at 737°C congruently.

(3) 65 mol% PbO ($13PbO \cdot 7GeO_2$)

In this case, when the melt with the glass composition was rapidly cooled, a partial devitrification was observed. As seen in DTA trace of Figure 2, the glass transition and crystallization occurred at 325°C and 377°C respectively. The results of X-ray diffraction analysis indicated that after the crystallization process the mixture of phase B and a new crystalline phase denoted to be "phase C" appeared. It was considered that the two endothermal peaks of DTA trace were attributed to the melting of these two crystalline phases.

In this study, three crystalline phases of "phase A", "phase B" and "phase C" were obtained by the crystallization of the glasses. Among them, phase B was identified to be $Pb_5Ge_3O_{11}$. Phase A was determined to be $Pb_3Ge_2O_7$ considering that PG-60 glass ($3PbO \cdot 2GeO_2$ glass) was completely crystallized by the heating and the crystallized phase melted congruently. Moreover, the X-ray diffraction pattern of the product, which was obtained by the slow cooling of the melt with the composition of $3PbO \cdot 2GeO_2$, well agreed with that of phase A. The density of crystalline phase A, which was prepared by a heating of PG-60

glass at 400°C for 110 hrs, was determined to be 7.52_9 g/cm^3 at 30°C by means of pycnometric method. Assuming that the chemical formula of phase A was $Pb_3Ge_2O_7$, the Z number of this phase was calculated to be 26.8_1 by using the observed density of 7.52_9 and the calculated volume of 5195 Å^3. Therefore, it was considered that Z number was equal to be 27. The calculated density was 7.58_2 g/cm^3 with Z=27, in agreement with the observed density of the powdered sample, 7.52_9 g/cm^3. These facts strongly suggested that the chemical composition of phase A was $3PbO \cdot 2GeO_2$. In the present experiments, phase C could not be obtained as a single phase by the crystallization of the glass and it was very difficult to separate crystals from the glass matrix because the crystalline phase consisted of very small particles less than 5000Å. Then an attempt was made to determine the chemical composition and crystal structure of phase C using a solid state reaction process.

After solid state reactions of mixed oxides at 700°C for 24 hrs, the amounts of products were estimated by the measurements of the most intense peaks which corresponded to those of phase B, phase C and yellow PbO in the X-ray diffraction patterns. The amounts of each phases as a function of PbO content are shown in Figure 3. As shown in this figure, in the range where the PbO content is less than 76 mol%, the yield of phase C increases with the increase of PbO content, and in the range where PbO content is more than 76 mol%, the yield is saturated and yellow

PbO appears. The density of the fine powdered sample of phase C, which was prepared by slow cooling of the melt with the composition of $3PbO \cdot GeO_2$, was determined to be 8.61 g/cm^3 at 30°C. Assuming that the chemical formula of phase C was Pb_3GeO_5, the Z number of this phase was calculated to be 5.93_6 by using the observed density 8.61 g/cm^3 and the calculated volume of 886 $Å^3$. Thus, it was considered that Z number was 6. The calculated density was 8.70_3 g/cm^3 with Z=6, in agreement with the observed density of 8.61 g/cm^3. Therefore, the chemical composition and chemical formula of phase C were determined to be $75\%PbO \cdot 25\%GeO_2$ (in mol) and Pb_3GeO_5. The melting point of this phase is 731°C.

As mentioned before, phase relation in the system $PbO-GeO_2$ reported by several investigators [4-6] are quite confused. Phase diagrams of this system reported by previous investigators are given in Figure 4.

Speranskaya [4] studied the phase relations by DTA method as shown in (a) of this figure, and reported the existences of several compounds with different chemical formula such as Pb_6GeO_8, Pb_3GeO_5, $Pb_5Ge_3O_{11}$, $PbGeO_3$ and $PbGe_3O_7$. Using a quenching technique for powdered glass samples belonged to this binary system, Phillips and Scroger [5] obtained five compounds of Pb_4GeO_6, $Pb_3Ge_2O_7$, $PbGeO_3$, $PbGe_2O_5$ and $PbGe_4O_9$ as indicated in (b) of this figure. From the results of solid state reactions between PbO and GeO_2, Gouju et al. [6] suggested that compounds

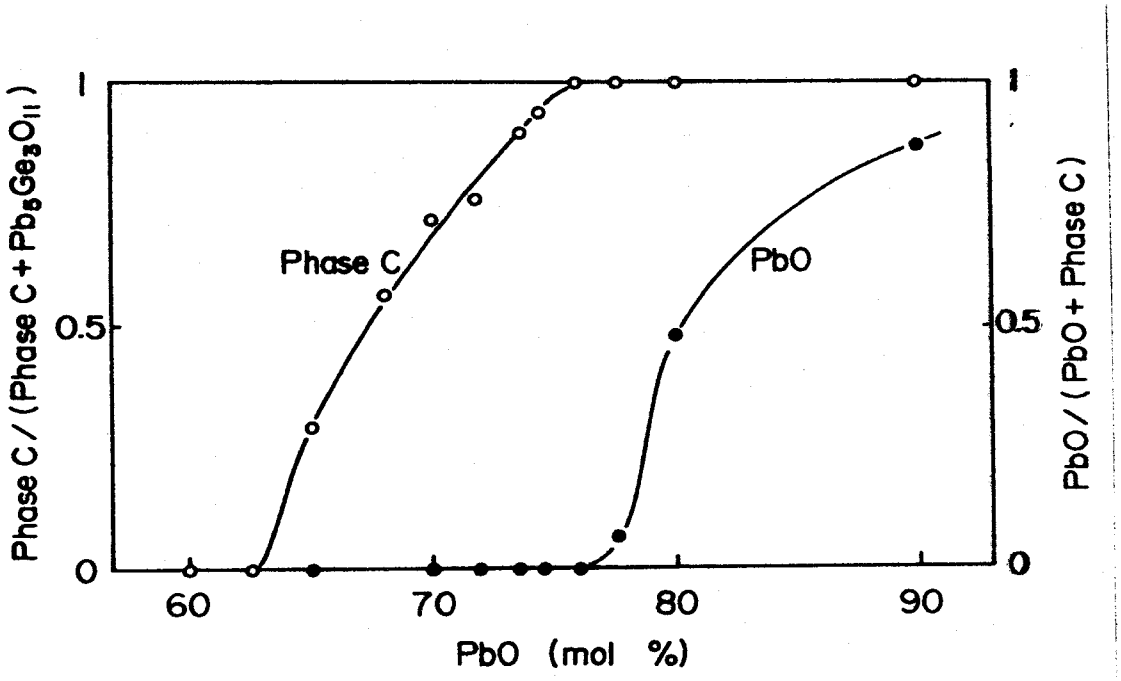


Figure 3. Relative amounts of products after the reaction between PbO and GeO_2 at 700°C for 24 hrs as a function of PbO mol %.

obtained in this system were Pb_3GeO_5, $Pb_3Ge_2O_7$, $PbGeO_3$ and $PbGe_4O_9$. It is obvious from Figure 4 that there are some disagreements between phase relations of these diagrams.

In the present study, three different compounds were obtained by crystallization of glasses and solidification of melts in the region of composition around $5PbO \cdot 3GeO_2$. Chemical formulars of these compounds were given as Pb_3GeO_5, $Pb_5Ge_3O_{11}$ and $Pb_3Ge_2O_7$.

The existence of $Pb_3Ge_2O_7$ was recognized by Phillips and Gouju. From the results of IR measurement on lead germanate glasses, Morozov [10] intimated the presence of $Pb_3Ge_2O_7$, but the crystal data were not given in detail. In the present result, this 3:2 compound denoted to be "phase A" appeared as a stable phase during the crystallization of $3PbO \cdot 2GeO_2$ glass and solidification of the melt with the corresponding composition. From the results of X-ray diffraction analysis, it was considered that the crystal structure of this phase had a hexagonal symmetry with a=10.06Å and c=19.37Å. This X-ray data, however, did not agree with that of $Pb_3Ge_2O_7$ reported by Phillips which was quite similar to that of $Pb_5Ge_3O_{11}$.

$Pb_5Ge_3O_{11}$ crystallized from the PG-62.5 glass ($5PbO \cdot 3GeO_2$ glass) after the heat-treatment at the temperature range from 380°C to 480°C. In the PG-62.5 glass, $Pb_3Ge_2O_7$ precipitated as a metastable phase at lower temperatures, and this phase easily transformed to $Pb_5Ge_3O_{11}$ denoted as "phase B" at 489°C. This X-ray diffraction data

of phase B in this study agreed with that of single crystal of $Pb_5Ge_3O_{11}$ already reported by Sugii [2]. $Pb_5Ge_3O_{11}$ was very stable and no transformation was recognized during the heating up to the melting point.

The 3:1 compound (Pb_3GeO_5) denoted to be "phase C" was formed as a single phase after solidification of melt or solid state reaction between PbO and GeO_2 as shown in Figure 3. Although the existence of Pb_3GeO_5 was suggested by Speranskaya [4], Gouju [6] and Morozov [10], there was no description about X-ray diffraction data. Present data are given in Table III.

As illustrared in Figure 3, thepresence of yellow PbO was recognized in case when the specimen with a high PbO content more than 75 mol% melted and then cooled below a liquidus temperature. Therefore, there was little probability for the existence of the compound with a PbO content higher than that of Pb_3GeO_5 in the system PbO-GeO_2.

A phase of Pb_2GeO_4 reported by Eulenberger et al. [11] could not be detected in the present study. Although the existence of the same phase has already been reported by Merker [12], the X-ray diffraction pattern given by him is completely indexed assuming that the phase was the mixture of $Pb_5Ge_3O_{11}$ and Pb_3GeO_5. If this procedure is reasonable, the presence of Pb_2GeO_4 will be very doubtful.

Crystallization phenomena of the base glasses during isothermal heatings were essentially identical with those observed during the heaing were essentially identical with

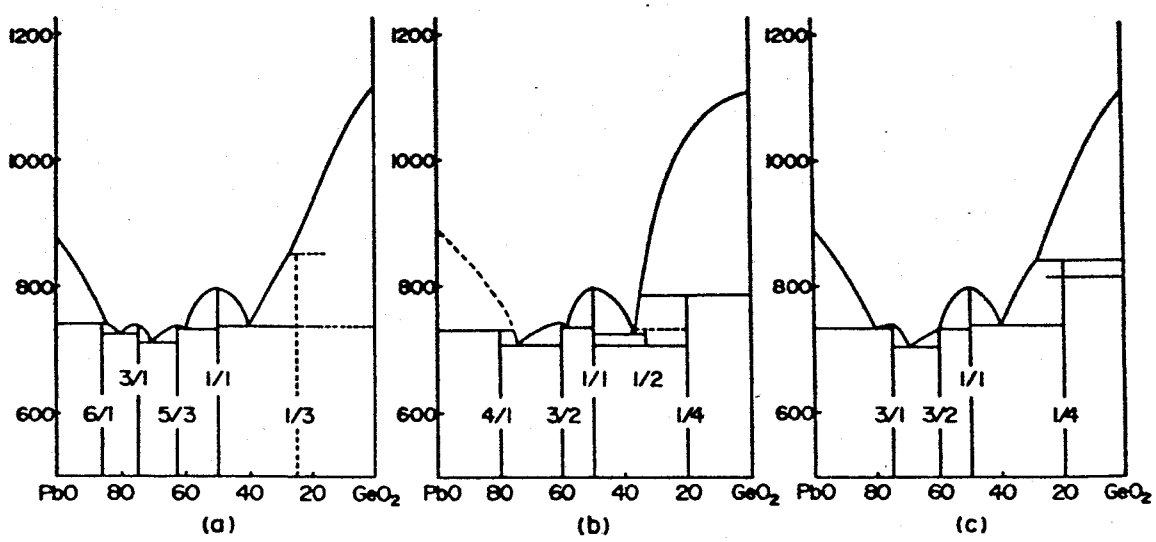


Figure 4. Phase relations in the system $PbO-GeO_2$ proposed by Speranskaya (a), by Phillips (b) and by Gouju (c).

Table III. X-ray diffraction data of phases A, B and C

Phase A; ($Pb_3Ge_2O_7$) hex. a=10.16A c=19.37A			Phase B; ($Pb_5Ge_3O_{11}$) hex. a=10.23A c=10.54A			Phase C; (Pb_3GeO_5) ortho. a= 4.85A b=15.52A c=11.77A		
d	(hkl)	I/I₀	d	(hkl)	I/I₀	d	(hkl)	I/I₀
8.84	(100)	5	8.84	(100)	10	5.50	(012)	5
4.50	(112)	5	5.15	(110)	5	5.27	(030)	10
4.39	(200)	10	4.62	(111)	10	4.87	(100)	5
3.85	(003)	10	4.44	(200)	30	3.78	(013)	5
3.64	(203)	5	4.09	(201)	5	3.72	(102)	10
3.32	(210)	15	3.69	(112)	25	3.65	(112)	5
3.155	(212)	5	3.56	(003)	15	3.35	(122)	5
3.035	(106)	5	3.30	(103)	30	3.206	(043)	10
2.957	(213)	100	3.200	(211)	40	3.118	(050,033)	100
2.947	(300)	70	2.957	(300)	80	3.029	(140)	100
2.887	(205)	5	2.919	(113)	100	2.740	(024)	45
2.720	(116)	5	2.835	(212)	40	2.631	(133)	50
2.194	(400)	5	2.776	(203)	5	2.615	(150)	40
2.083	(403)	25	2.468	(310)	5	2.554	(034)	5
2.019	(320)	5	2.440	(213)	5	2.474	(114)	5
1.924	(410)	5	2.210	(400)	5	2.426	(200)	5
1.816	(406)	5	2.075	(223)	30	2.390	(210,124)	5
1.700	(330)	5	2.030	(320)	10	2.350	(005)	5
1.667	(420)	5	2.021	(313)	15	2.342	(044)	5
1.544	(506)	10	1.996	(105,304)	10	2.191	(230)	5
			1.967	(115)	10	2.170	(063)	5
			1.932	(410)	10	2.135	(035)	5
			1.897	(322)	10	1.940	(080)	10
			1.879	(403)	20	1.890	(172)	15
			1.799	(006)	10	1.854	(214)	30
			1.776	(500)	10	1.799	(180)	5
			1.700	(330)	10	1.724	(090)	5
			1.674	(420)	10	1.659	(056)	15
			1.649	(206,225)	55	1.617	(300)	15
			1.620	(315)	5	1.611	(310)	15
			1.589	(216,503)	10	1.589	(311)	10
			1.572	(414)	5	1.576	(117)	15
			1.536	(306)	5	1.573	(156)	20
			1.523	(512)	15	1.559	(0100)	10
			1.472	(600)	5	1.513	(280)	5

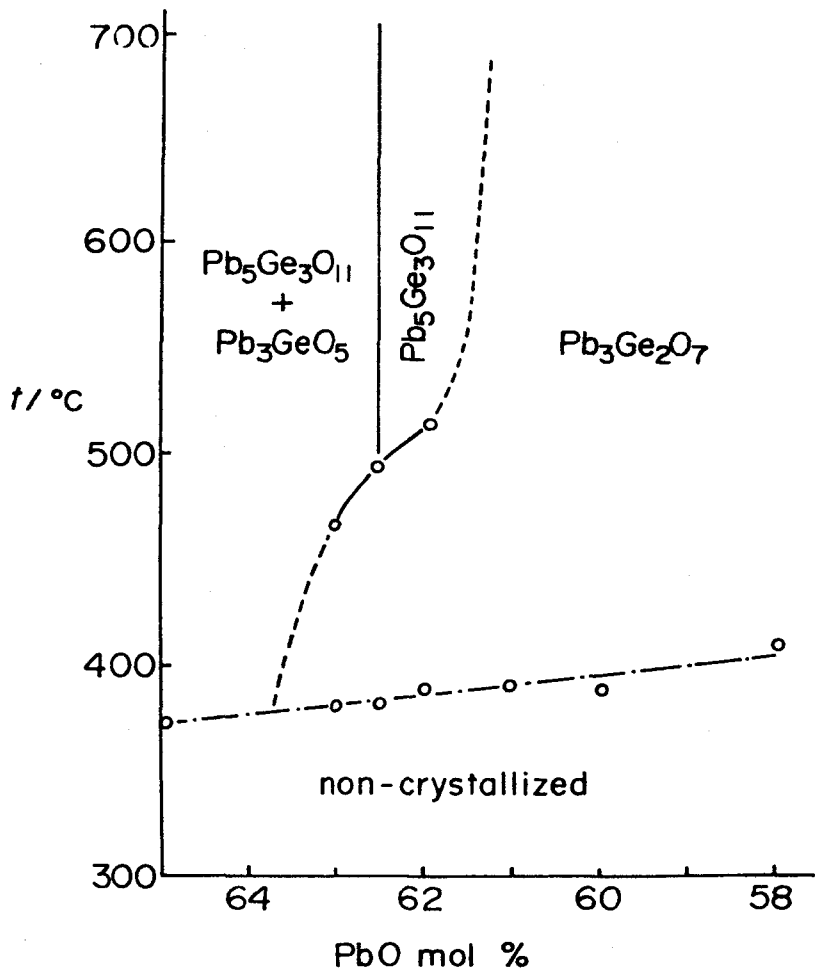


Figure 5. Phase relation of crystallized phases in the system $PbO-GeO_2$.

those observed during the heating at a constant heating rate mentioned before. Below the glass transition temperature, no crystallization was observed. Precipitated phases are quite equal to those obtained by the heating at a constant rate. Phase relations of crystallized phases as a functions of temperature and composition of the base glass are shown in Figure 5.

2-3. Conclusion

The experimental results mentioned before are summarized as follows ;

(1) The yellowish transparent glasses with homogeneity were easily formed by rapid cooling of the melts.

(2) As PbO content increased, the glass transtion temperature decreased continuously from 337°C for PG-60 glass to 325°C for PG-65 glass.

(3) The similar infrared spectra were obtained for all glasses with various compositions.

(4) It is considered that lead ions form networks and linked GeO_4 tetrahedron or Ge_2O_7 groups in all glasses.

(5) A ferroelectric glass-ceramics with high transparency was easily prepared by the crystallization of $Pb_5Ge_3O_{11}$ from $5PbO \cdot 3GeO_2$ glass.

(6) Three different compounds were obtained by crystallization of glass and solidification of melt in the chemical composition around $5PbO \cdot 3GeO_2$.

(7) Two new phases of $Pb_3Ge_2O_7$ and Pb_3GeO_5 were found to exist. The uni cell dimension of $Pb_3Ge_2O_7$ had a hexagonal symmetry with a=10.16Å and c=19.37Å, and Pb_3GeO_5 was classified into orthorhombic system with a=4.85Å, b=15.52Å and c=11.77Å.

Chapter 3. System $PbO-SiO_2$

In Chapter 2, the crystallization of lead germanate glasses were discussed in detail in relation to a fabrication of a new glass-ceramic. On the basis of analogy between silicate and germanate, the crystallization of lead silicate glasses was examined.

In this chapter, the glass formation and some thermal properties of products in the system $PbO-SiO_2$ are described. And from the experimental results of phase relation and of infrared absorption measurements, the existence of new compound $Pb_5Si_3O_{11}$ is discussed.

3-1. Glass formation

The glass compositions used for the present investigation are tabulated in Table IV .

All the glasses were easily formed by rapid cooling of the melts without devitrification. Microscopic examination showed that bubble-free and clarified base glasses were prepared. On quenching, a yellowish glass was formed. Homogeneity of the glass was examined by the measurement of density using a pycnometric method. The change of density did not exceed 0.005 g/cm^3 each other for three

Table IV. Chemical composition of glasses

Sample	wt %		mole %	
	PbO	SiO_2	PbO	SiO_2
PS-50	78.83	21.17	50.06	49.94
PS-53	80.76	19.24	53.03	46.97
PS-57	83.11	16.89	56.96	43.04
PS-60	84.80	15.20	60.01	39.99
PS-61	85.35	14.65	61.04	38.96
PS-62.5	86.09	13.91	62.48	37.52
PS-63.2$_5$	86.50	13.50	63.28	36.72
PS-64	86.86	13.14	64.02	35.98
PS-65	87.35	12.65	65.02	34.98
PS-66.7	88.15	11.85	66.68	33.32
PS-70	89.66	10.34	70.00	30.00

times measurements of the specimens from the different parts of the glass block of same batch. According to the results of chemical analysis for all specimens, it was found that there is no change of chemical composition between the glass and the initial batch powder. Therefore, it is considered that the homogeneous glass with a desired chemical composition was prepared in the present experiment.

The glass transition temperature, density and chemical composition of all glass specimens are listed in Table V. When PbO content increased the glass transition temperature decreased continuously from 414°C to 369 °C.

As for the system $PbO-SiO_2$, many investigators reported that the glass forming region of this system was wide. In the present study, the glass with the composition of 70 mol% PbO was easily obtained and the contribution of lead ion to network forming were confirmed.

Figure 6 shows the infrared absorption spectra of the glass with the chemical composition of $5PbO \cdot 3SiO_2$. As indicated in this figure, the infrared absorption consisted of two strong absorption bands around 850 and 475 cm^{-1} and a weak absorption band at about 665 cm^{-1}. Considering the infrared active frequencies for SiO_4 tetrahedron and Si_2O_7 group, the two strong absorptions around 850 and 475 cm^{-1} were assigned to Si-O stretching vibration ν_3 and bending mode ν_4. And a weak one was due to the ν_1 affected by polarizable lead ion.

Stanworth [13] suggested that the lead ions in lead

Table V Tg and densities of glasses

sample	Tg	density
PS-50	439°C	6.05_4
PS-53	410	6.31_9
PS-57	407	6.62_8
PS-60	394	6.84_2
PS-61	390	6.90_6
PS-62.5	382	6.98_8
PS-63.2_5	380	7.02_9
PS-64	378	7.07_0
PS-65	376	7.12_1
PS-66.7	373	7.19_2
PS-70	369	7.31_9

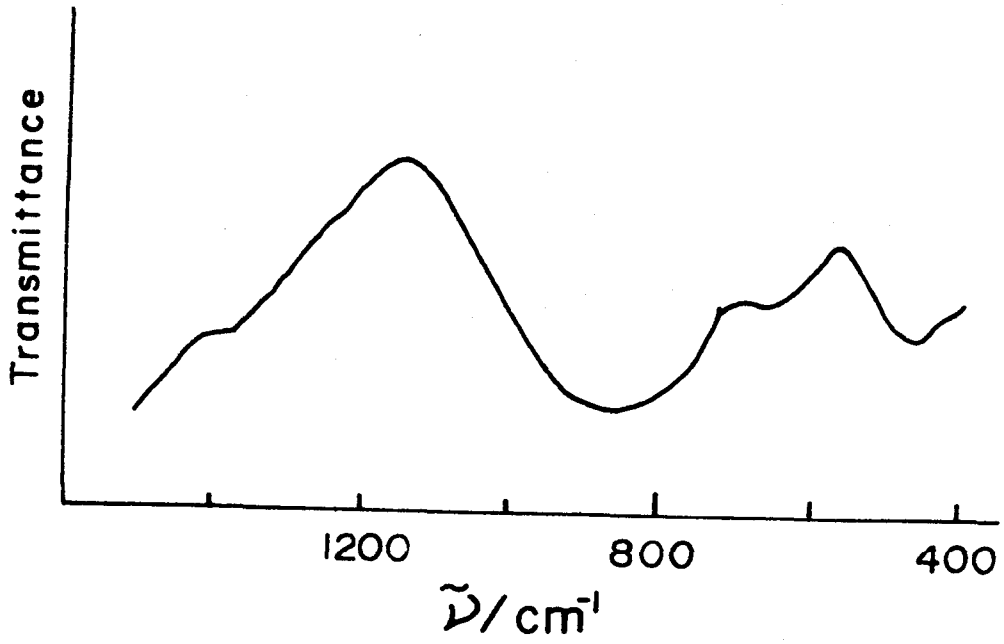


Figure 6 . Infrared spectrum of $5PbO \cdot 3SiO_2$ glass.

silicate glass are bonded to only two oxygens. Fajans and Kleidel [14] advocated that the state of lead ions in glass was similar to that of the tetragonal PbO crystal. In a recent year, Mydlar and Kreidl [15] reported that the lead ion is surrounded by about four oxygens using X-ray diffraction technique. In the present investigation, the coordination of lead ion in the glass was not clear, but it was found that lead ions are symmetrically surrounded by oxygens and coordination number of Si^{4+} is about 4.

3-2. Crystallization during heating

The transformations of the base glass during heating at a constant rate were examined by DTA. The thermal behaviors of coarse grained sample are illustrated by DTA traces in Figure 7 . The effect of particle size of glass powder on the devitrification characteristic was so significant in different from the case of lead germanate glass. Exothermal process with the crystallization of fine powdered sample appeared at a temperature lower than that of coarse grained sample. It was considered that the effect of particle size was due to the contribution of surface energy on crystallizing kinetics. In this investigation, coarse grained sample was adopted and the characteristic temperatures were determined as the results of the average of three times measurements. An experimental error for each measure-

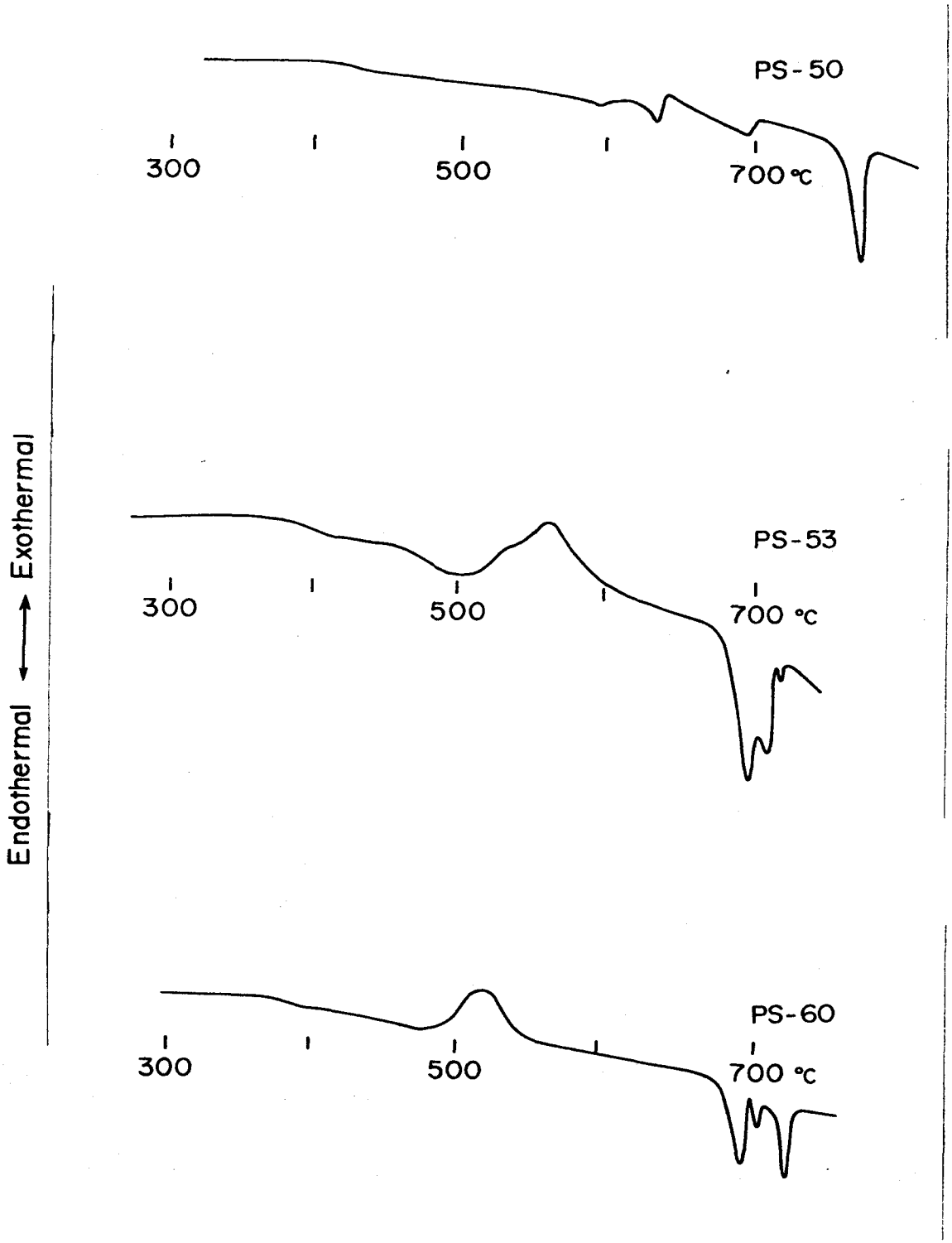


Figure 7 . DTA traces of glasses in the system $PbO-SiO_2$

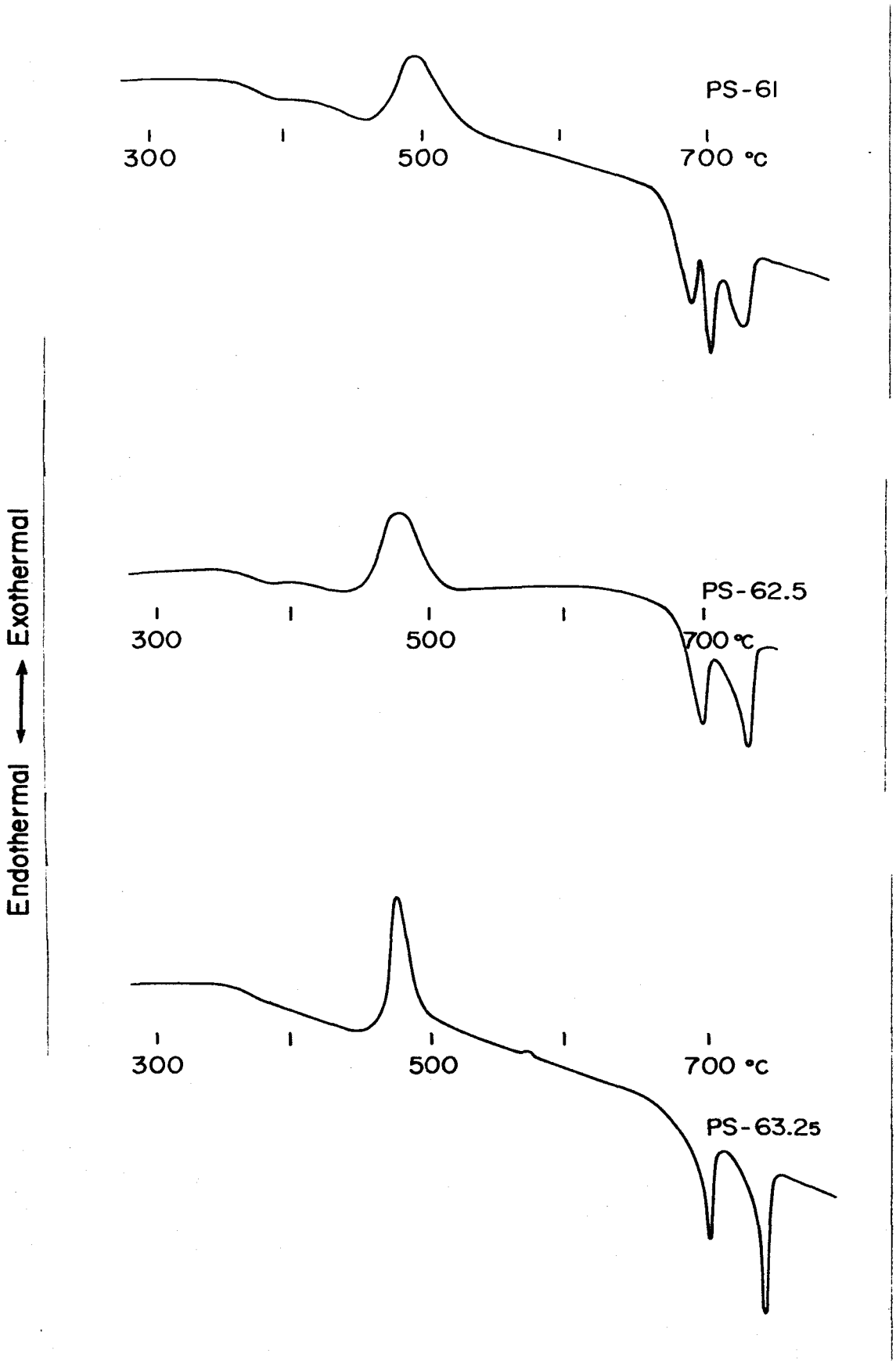


Figure 7. (cont.)

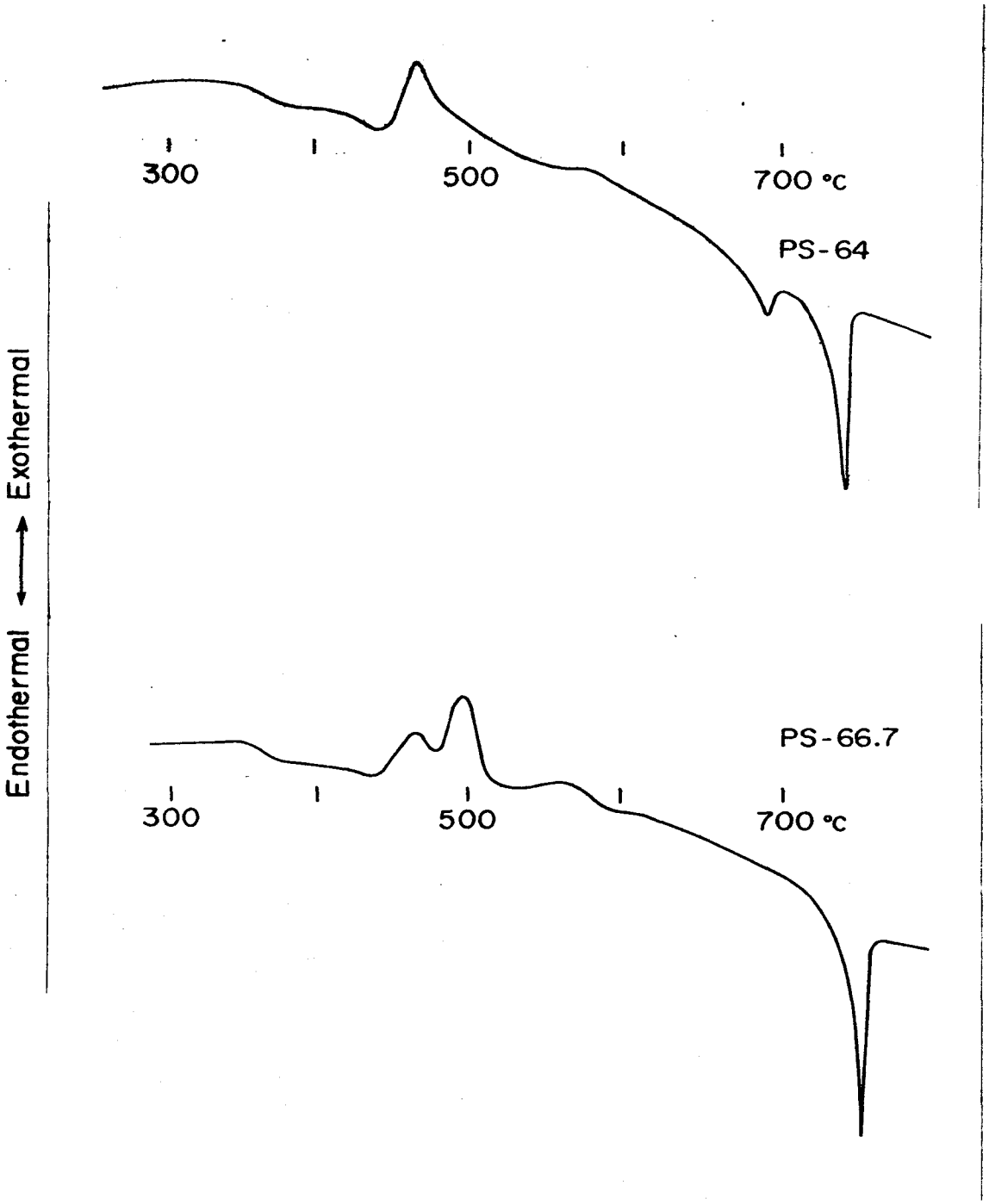


Figure 7. (cont.)

ment was at most ± 2°C.

The crystallizing phenomena of the glass under investigation were classified into the following four groups ;

(1) 63-67 mol% PbO (in the region between $2PbO \cdot SiO_2$ and $5PbO \cdot 3SiO_2$)

As indicated in Figure 7 , three of each exothermic and endothermic processes were observed for the specimens. Among them, the first endothermic step at about 380°C corresponded to the glass transition due to the drastic change of specific heat. Next exotherm was a result of crystallization of the glass. From the results of X-ray diffraction analysis, crystallized phases after this process were a low temperature form of Pb_2SiO_4 (L-Pb_2SiO_4) and a new compound denoted to be "phase X". L-Pb_2SiO_4 changed to a high temperature form (H-Pb_2SiO_4) accompanied with the following exothermic process. This exothermic peak was piled up to the first exotherm in the glass in which PbO content was less than 64 mol%. Small exothermic peak at about 570°C was due to the decomposition of Phase X into H-Pb_2SiO_4 plus $PbSiO_3$. The sharp endotherms caused by a melting process were observed at relatively higher temperatures.

(2) 62.5 mol% PbO ($5PbO \cdot 3SiO_2$)

Glass transition and crystallization took place at 380°C and 480°C respectively. Crystalline material precipitated with an exothermal process was considered to be

phase X. This phase decomposed into H-Pb_2SiO_4 and $PbSiO_3$ at a relatively higher temperature, but an exothermal peak corresponding to this decomposition process was not detected. Two endothermal peaks at 699°C and 730°C were attributed to the melting of these two crystalline phases.

(3) 51-62 mol% PbO (in the region between $5PbO \cdot 3SiO_2$ and $PbO \cdot SiO_2$)

Glass transition occurred at about 400°C. A broadened exothermal peak was observed at 490-560°C assigned to crystallization process. The results of X-ray diffraction analysis indicated that after crystallization there existed the mixture of phase X and $PbSiO_3$. In this system, three or four kinds of endothermal peaks were observed at higher temperatures, some of which were assigned to melting processes.

(4) 50 mol% PbO ($PbO \cdot SiO_2$)

Glass transition, crystallization of $PbSiO_3$ and melting of $PbSiO_3$ were observed at 414°C, 567°C and 753°C respectively.

Crystallization phenomena of the base glasses during the isothermal heating were essentially identical with those observed during the heating at a constant rate.

In order to make the phase relation clear in this system, an attempt was made to determine the chemical composition and crystal structure of new crystalline phase of phase X. The 10 powdered glass samples with different compositions ranging from 50%PbO·50%SiO_2 to 66.7%PbO·

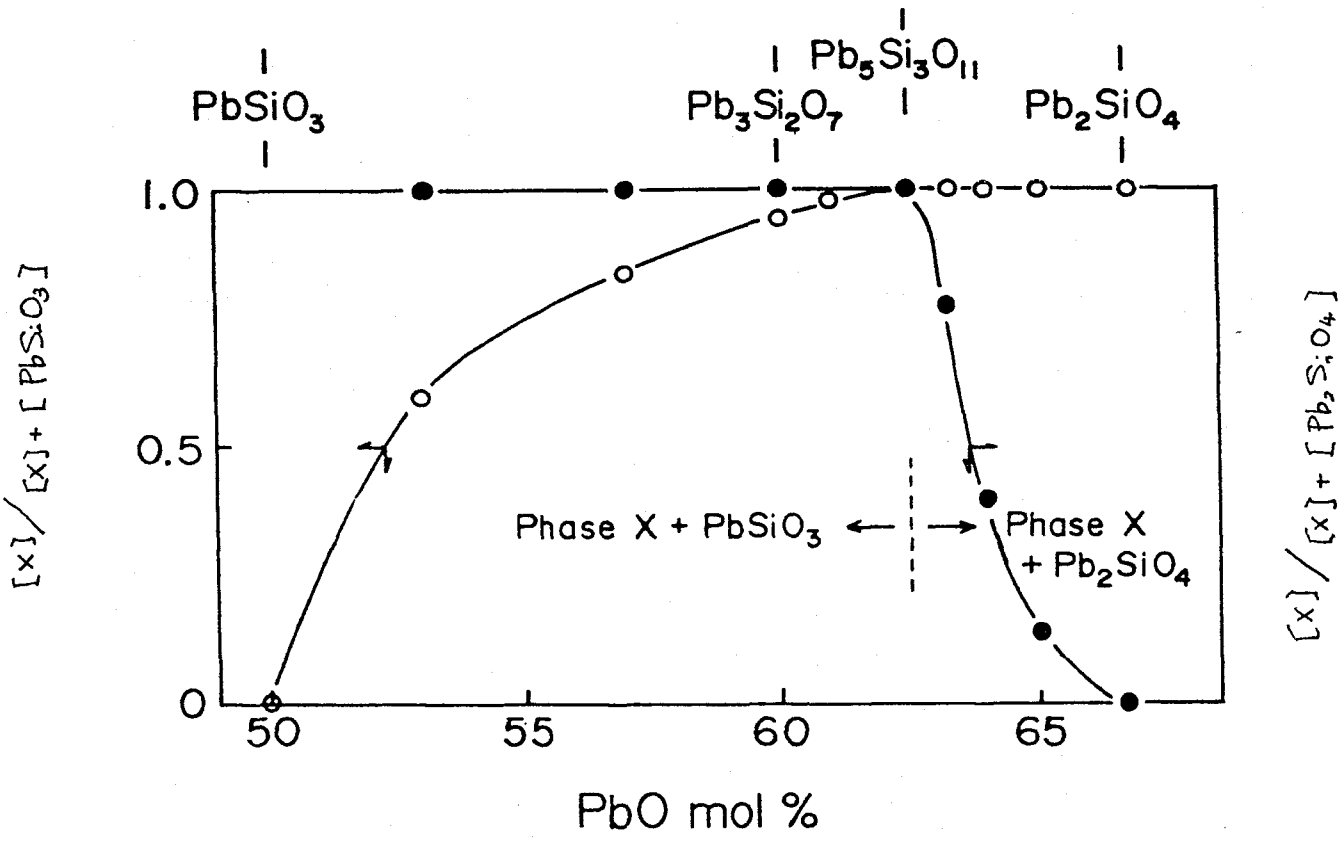


Figure 8. Relative amounts of products after crystallization of lead silicate glasses at 550°C for 116 hrs as a function of PbO mole %.

Table VI. X-ray diffraction data of $Pb_5Si_3O_{11}$

(h k l)	$d_{obs.}$	$d_{cal.}$	I/I_o
1 0 2	8.616	8.600	5
1 0 6	4.962	4.965	10
1 0 7	4.410	4.404	15
2 0 4	4.300	4.300	30
2 1 2	4.111	4.117	5
0 2 4	3.738	3.741	30
1 1 8	3.564	3.564	10
3 0 0	3.294	3.301	30
2 0 8	3.250	3.250	45
1 2 6	3.169	3.168	2
3 0 4	3.076	3.079	40
3 1 4	2.896	2.896	100
3 0 6	2.867	2.867	75
2 0 10	2.821	2.818	45
3 0 7	2.744	2.745	2
0 3 3	2.696	2.693	2
3 2 4	2.480	2.479	2
3 0 10	2.384	2.385	1
1 2 12	2.300	2.296	2
3 0 11	2.274	2.273	2
0 2 13	2.232	2.232	2
4 0 8	2.149	2.150	5
2 1 14	2.125	2.129	1
1 1 16	2.037	2.037	40
5 0 0	1.982	1.986	15
2 0 16	1.976	1.973	10
5 0 4	1.932	1.935	10
5 0 6	1.877	1.877	20
0 1 18	1.864	1.862	15
4 3 2	1.840	1.838	30
2 0 18	1.783	1.784	10
6 0 2	1.646	1.647	2
6 0 4	1.625	1.625	5
6 0 6	1.589	1.590	2
0 0 22	1.562	1.562	5

orthorhombic

a=9.93A

b=8.31A

c=34.4A $(=2\sqrt{3}\cdot a)$

33.3%SiO_2 (in mol) were heated at about 550°C for 340 hrs, and the amounts of products were estimated by the measurement of the intensity of the most intense peaks which corresponded to those of Phase X, Pb_2SiO_4 and $PbSiO_3$. The relation between the amounts of each phases and PbO content was illustrated in Figure 8. As shown in this figure, in the range where the PbO content is less than 62.5%, the yield of phase X increased with increasing of PbO content, and in the range where the PbO content is more than 62.5%, the mixture of phase X and Pb_2SiO_4 were observed. The density of phase X, which was prepared by heating of PS-62.5 glass at 550°C for 340 hrs, was measured to be 6.79_7 g/cm^3 at 30°C. Assuming that the chemical formula of phase X was $Pb_5Si_3O_{11}$, the Z number of this phase was calculated to be 8.96_7 by using the observed density of 6.79_7 g/cm^3 and the calculated volume of 2839Å^3. Therefore, it was considered that Z number was 9. The calculated density was 6.82_2 g/cm$_3$ with Z=9, in agreement with the observed density of 6.79_7 g/cm^3. From these results, the chemical composition and chemical formula of phase X were determined to be 62.5%PbO·37.5%SiO_2 and $Pb_5Si_3O_{11}$. The powder diffraction pattern of phase X synthesized in this way was quite similar to that of crystalline phase obtained from 5PbO·3SiO_2 glass and it was not similar to that of lead barysilite $Pb_3Si_2O_7$ reported by Billhardt [16] but to that of $Pb_5Ge_3O_{11}$ as shown in Figure 9. So, on the basis of the crystal structure of $Pb_5Ge_3O_{11}$, the structure of phase

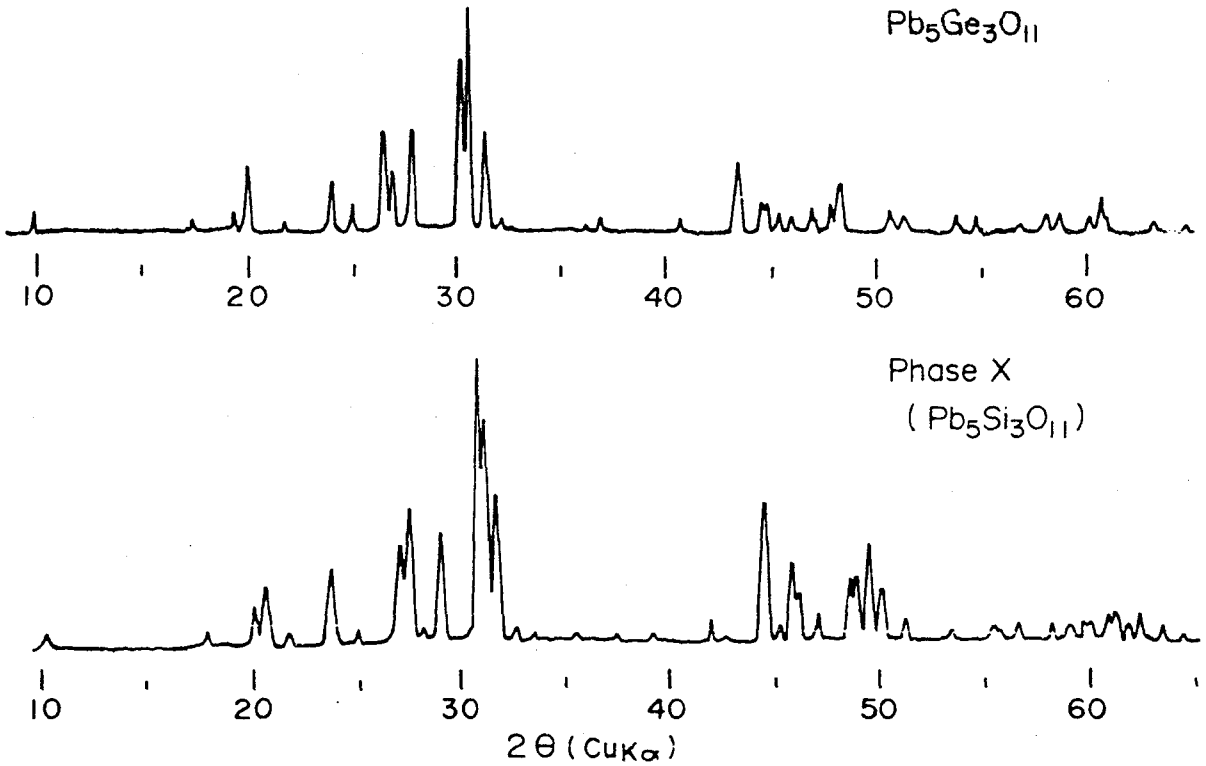


Figure 9. X-ray diffraction patterns of $Pb_5Ge_3O_{11}$ and Phase X.

X was determined to be pseud-hexagonal orthorhombic and lattice parameters were calculated to be a=9.93Å, b=8.31Å and c=34.4Å. X-ray diffraction data of phase X is tabulated in Table VI. Phase X was obtained only through the crystallization of glass, and all the attempts to synthesize phase X failed by the usual solid state reaction method nor by the cooling of the melts.

Phase relations of crystallized phases as a function of temperature and composition of the base glass in this system are shown in Figure 10.

As to the system $PbO-SiO_2$, there are many literatures describing compounds of $PbSiO_3$, Pb_2SiO_4, $Pb_3Si_2O_7$, Pb_3SiO_5 and Pb_4SiO_6.

Ito and Yanagase [17] studied the crystallization of lead silicate glass using DTA method and reported the existence of the compounds of $PbSiO_3$, Pb_2SiO_4, $Pb_3Si_2O_7$ and two unknown phases. Billhardt [18] reported that three crystalline phases such as $Pb_3Si_2O_7$, phase A and phase B were prepared from lead silicate glass. He described that phase A was an unknown phase and phase B was identified to natural barysilite with the idealized chemical formula of $Pb_9Si_6O_{21}$. The existence of $Pb_3Si_2O_7$ and four forms of Pb_2SiO_4 denoted as α, β_1, β_2 and γ were demonstrated by Hermann [19]. Ott and Mclared [20] investigated the phase relations in the system $PbO-SiO_2$ and obtained five compounds of Pb_4SiO_6, Pb_3SiO_5, Pb_2SiO_4, $Pb_3Si_2O_7$ and $PbSiO_3$ after the crystallization of the lead silicate glass with

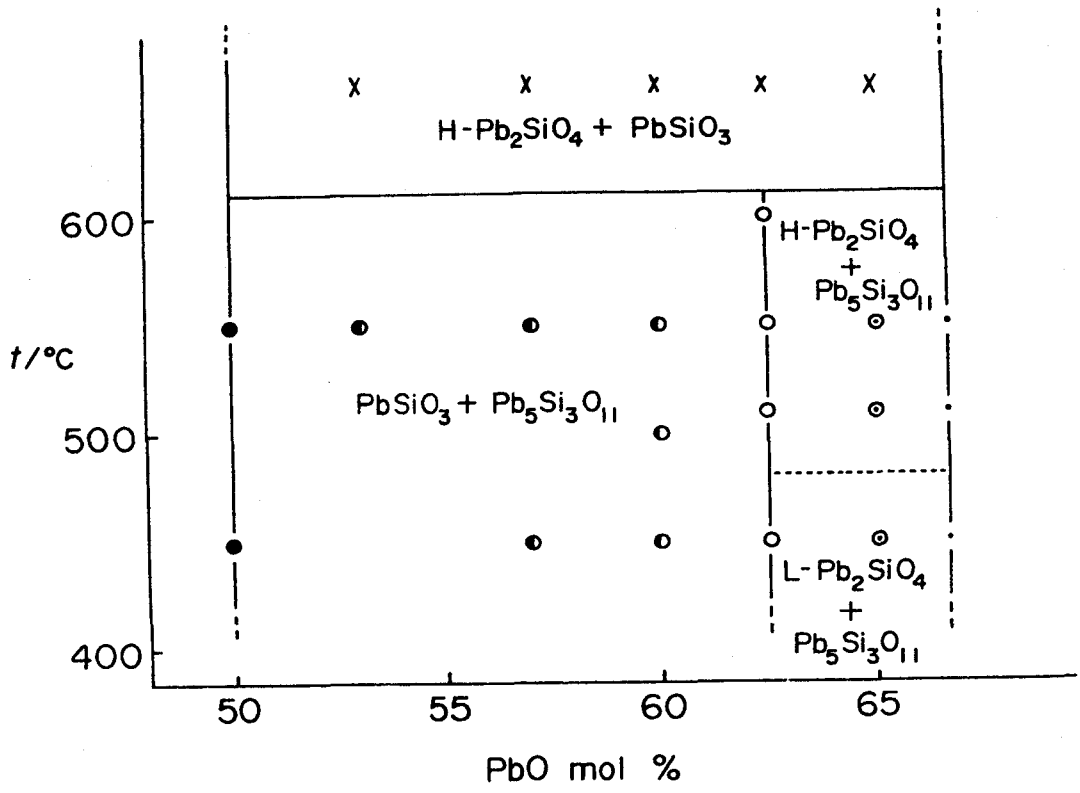


Figure 10. Phase relation of crystallized phases in ths system $PbO-SiO_2$

the composition between $4PbO \cdot SiO_2$ and $PbO \cdot SiO_2$. According to the results reported by Argyle and Hummel [21], the both crystalline phases precipitated from $3PbO \cdot SiO_2$ glass were Pb_4SiO_6 and Pb_2SiO_4, and also a mixture of Pb_2SiO_4 and $PbSiO_3$ was obtained after the crystallization of $3PbO \cdot 2SiO_2$ glass.

In the present work, four phases were synthesized after the crystallization of lead silicate glass. Among them, $Pb_5Si_3O_{11}$ has not yet been reported, however, $Pb_3Si_2O_7$ could not be recognized although its existence was pointed out by some investigators.

The existence of Pb_2SiO_4 was recognized by Hermann [19] and Ott [20]. In the present study, Pb_2SiO_4 was obtained by the crystallization of the glass under investigation. X-ray diffraction pattern of this phase well agreed with that of ASTM card. As shown in Figure 10, in case when PbO content was more than 63 mol%, L-Pb_2SiO_4 precipitated associating with $Pb_5Si_3O_{11}$ at relatively lower temperature, and L-Pb_2SiO_4 changed to a high temperature form at higher temperature. H-Pb_2SiO_4 was stable above 460°C and melted at 746°C congruently.

$Pb_5Si_3O_{11}$ denoted as phase X was prepared as a single phase by the crystallization of $5PbO \cdot 3SiO_2$ glass. Although the existence of $Pb_3Si_2O_7$ was reported by many investigators, the existence of $Pb_5Si_3O_{11}$ has not yet been recognized.

According to the phase diagram of the system $PbO-SiO_2$ reported by Ott and Mclaren [20], the crystalline phases

precipitated by the heat-treatment of the $5PbO \cdot 3SiO_2$ glass were a mixture of $Pb_3Si_2O_7$ and H- or L-Pb_2SiO_4. A $Pb_3Si_2O_7$ was obtained as a single phase by the crystallization of $3PbO \cdot 2SiO_2$ glass.

In this experiment, on the contrary, $Pb_5Si_3O_{11}$ was synthesized as a single phase from $5PbO \cdot 3SiO_2$ glass and a mixture of $Pb_5Si_3O_{11}$ and a small amount of $PbSiO_3$ was produced by the crystallization from $3PbO \cdot 2SiO_2$ glass. A phase of $Pb_3Si_2O_7$ reported by many workers could not be detected in this study. Although the existence of the same phase has been recently reported by Ott, the X-ray diffraction pattern given by them was similar to that of $Pb_5Si_3O_{11}$ mentioned before. Summerizing the present experimental results of DTA, solid state reaction, X-ray diffraction analysis and chemical analysis, the presence of $Pb_3Si_2O_7$ would be very doubtful and the existence of a new compound $Pb_5Si_3O_{11}$ with orthorhombic system was confirmed in this study.

3-3. Conclusion

The experimental results described in this chapter are summarized as follows;

(1) Glasses in the system $PbO-SiO_2$ were easily formed by a rapid cooling of the melts, and they were very homogeneous and yellow in color. On ordinary cooling no devitrification was observed.

(2) The glass transition temperature decreased continuously from 414°C to 369°C with the increase of PbO content.

(3) Four phases could be synthesized by the crystallization of lead silicate glasses. Among them, $Pb_5Si_3O_{11}$ has never been reported so far.

(4) The new compound $Pb_5Si_3O_{11}$ had a pseudo-hexagonal orthorhombic symmetry with a=9.93Å, b=8.31Å and c=34.4Å.

(5) Although the existence of $Pb_3Si_2O_7$ was pointed out by some investigators, $Pb_3Si_2O_7$ could not be prepared in the present study. The presence of $Pb_3Si_2O_7$ already reported would be very doubtful because the X-ray data were very poor and all stronger lines of X-ray diffraction pattern were very resemble to those of the new phase $Pb_5Si_3O_{11}$.

Chapter 4. System $PbO-GeO_2-SiO_2$

The glass-forming tendency of the system $PbO-GeO_2$ is inferior to that of the system $PbO-SiO_2$ as mentioned in Chapters 2 and 3. In the system $PbO-GeO_2$, devitrification were often observed during slow cooling, but there was no problem in the system $PbO-SiO_2$. Because it is expected that the addition of SiO_2 to the lead germanate glass enhances the stability of the base glass and Ge^{4+} are replaced by Si^{4+}, the investigation is extended into the system $PbO-GeO_2-SiO_2$.

Phase relations and crystallizations of glass in the system $PbO-GeO_2-SiO_2$ are investigated by the use of DTA, X-ray diffraction analysis and infrared absorption spectrophotometry, and the results are described in this chapter.

4-1. Glass formation

The glass compositions under the investigation are given in Table VII. The molar ratios of SiO_2/GeO_2 were varied from 0/3 to 3/0, and PbO content was fixed to 62.5 mol% which is equivalent to that of ferroelectric crystal $Pb_5Ge_3O_{11}$.

All the glasses were easily formed from the melts, and

Table VII. Chemical composition of glass

Sample	PbO	GeO_2	SiO_2	SiO_2/GeO_2 #
PGS-0	78.04	21.96	0	0/3
PGS-30	78.78	19.92	1.29	0.3/2.7
PGS-50	79.24	18.56	2.19	0.5/2.5
PGS-75	79.90	16.83	3.27	0.75/2.25
PGS-100	80.60	15.08	4.32	1/2
PGS-125	81.21	13.31	5.49	1.25/1.75
PGS-150	81.86	11.51	6.63	1.5/1.5
PGS-175	82.55	9.67	7.78	1.75/1.25
PGS-200	83.24	7.80	8.96	2/1
PGS-250	84.65	3.97	11.39	2.5/0.5
PGS-300	86.10	0	13.90	3/0

molar ratio

the glass forming tendency increased with increasing of SiO_2 content. The magnitude of supercooling of the melt observed in DTA traces also increased with the substitution of SiO_2 for GeO_2. When the only 1/6 of GeO_2 was replaced by SiO_2 in amount, the base glass was very stabilized. On the other hand, substituting a half amount of SiO_2 for GeO_2 no devitrification was observed during the slow cooling of the melt in a crucible.

In differential thermal analysis, the glass transition and supercooling of the melt were observed for each sample. The results were listed in Table VIII. As SiO_2 content increased, the glass transition temperature increased continuously from 334°C for PGS-0 glass to 380°C for PGS-300 glass. The magnitude of supercooling increased with increasing of SiO_2 content. Therefore, it was considered that the effect of substitution of SiO_2 for GeO_2 in the glass composition may be explained as follows;

(i) The stability of the glass is increased with the reduction of liquidus temperature by making the composition more complex.

(ii) The crystallization is very difficult when the glass composition is more complex.

The similar infrared absorption spectra were obtained for all glasses in this system. Figure 11 shows the characteristic value of absorption bands of the base glass as a function of SiO_2 content. The results for the glass transition temperature and infrared spectra strongly suggest that all the glasses have almost similar structure.

Table VIII. Characteristic temperatures of glass determined by DTA at the heating rate of 10°C/min.

Sample	Tg	Tc	Tt	T_L	T_L'	ΔT_L
PGS-0	334°C	380°C	489°C	737°C	707°C	30°C
PGS-50	350	407	513	735	693	42
PGS-100	355	415	523	724	681	43
PGS-150	358	441	544	714	665	49
PGS-200	369	438	——	695	638	57
PGS-250	375	459	——	710	623	87
PGS-300	380	480	——	730	619	111

Tg; Glass transition temperature

Tc; Crystallizing temperature

Tt; Temperature where the phase change from $Pb_3Ge_{2-y}Si_yO_7$ to $Pb_5Ge_{3-x}Si_xO_{11}$ occurred

T_L; Liquidus temperature observed during heating

T_L'; Liquidus temperature observed during cooling

ΔT_L; Degree of supercooling ($=T_L-T_L'$)

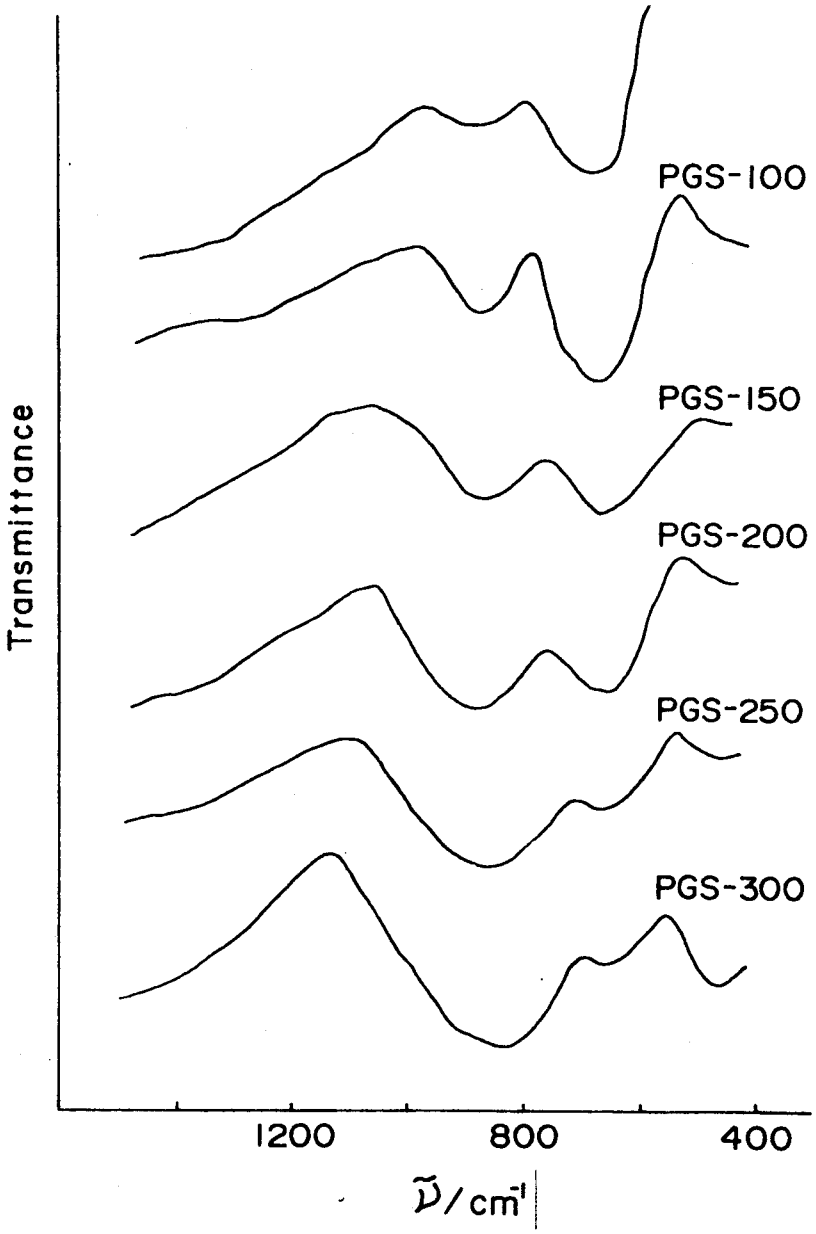


Figure 11 Infrared absorption spectra of glasses in the system $PbO-GeO_2-SiO_2$

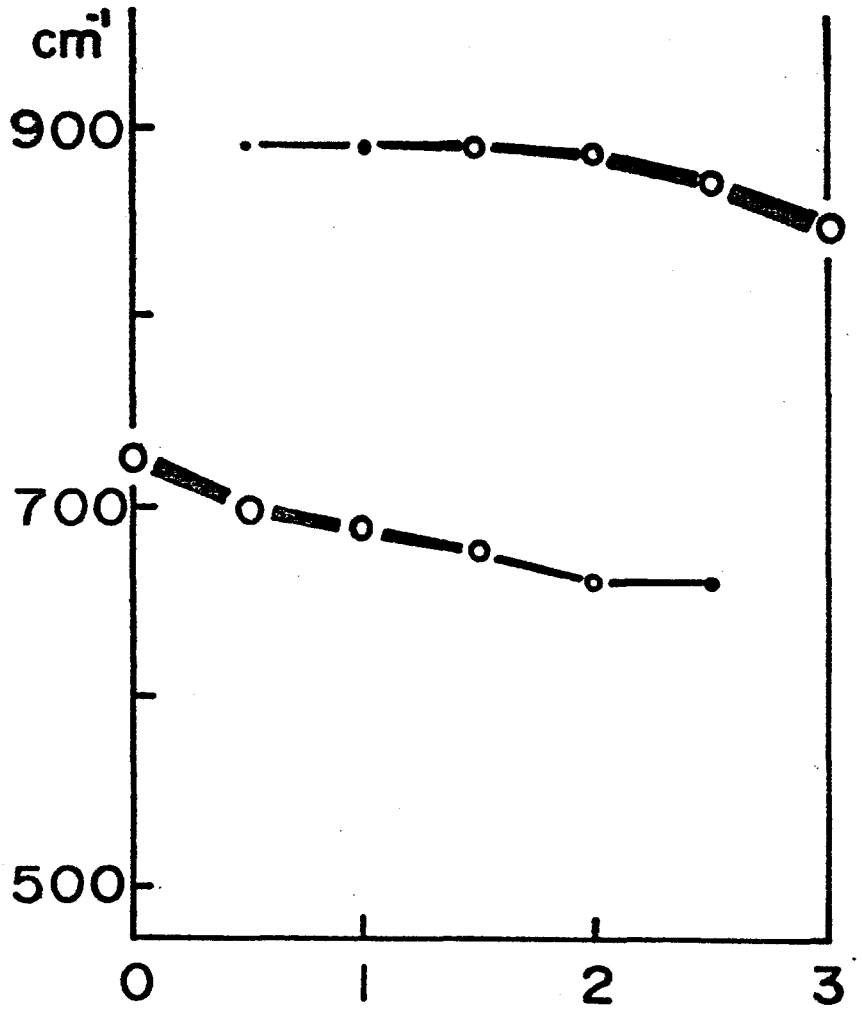


Figure 1[illegible] Characteristic absorptions of glasses as a function of glass composition

4-2. Crystallization during heating

The transformations of glass samples during heating at a heating rate of 10°C/min. are illustrated by DTA traces in Figure 13. All the glasses exhibited an initial endotherm. This first endothermal step corresponded to the glass transition due to an abrupt change in specific heat. A large exotherm was observed at approximately 400 °C. From the results of X-ray diffraction studies, it is supposed that this exotherm was owing to the crystallization. In the composition range where the ratio of SiO_2/GeO_2 was less than 2/1, X-ray diffraction pattern of product after the first exothermic peak was similar to that of $Pb_3Ge_2O_7$ described in Section 2-2 of Chapter 2, and the product was identified to be a solid solution of $Pb_3Ge_{2-y}Si_yO_7$. After the first exothermal peak, there was a smaller exothermal peak at about 500°C, which was essentially identical with the exothermal process observed with lead germanate glass. The X-ray diffraction pattern of crystalline phase after this exothermal process was indexed assuming it has the same structure as $Pb_5Ge_3O_{11}$. Therefore, this exotherm was caused by the recrystallization of $Pb_5Ge_{3-x}Si_xO_{11}$.

In the region where the ratio of SiO_2/GeO_2 is more than 2/1, a broad exotherm and two sharp endotherms are observed in DTA traces. The broad exothermal peak corresponded to the crystallization and the two endothermal ones

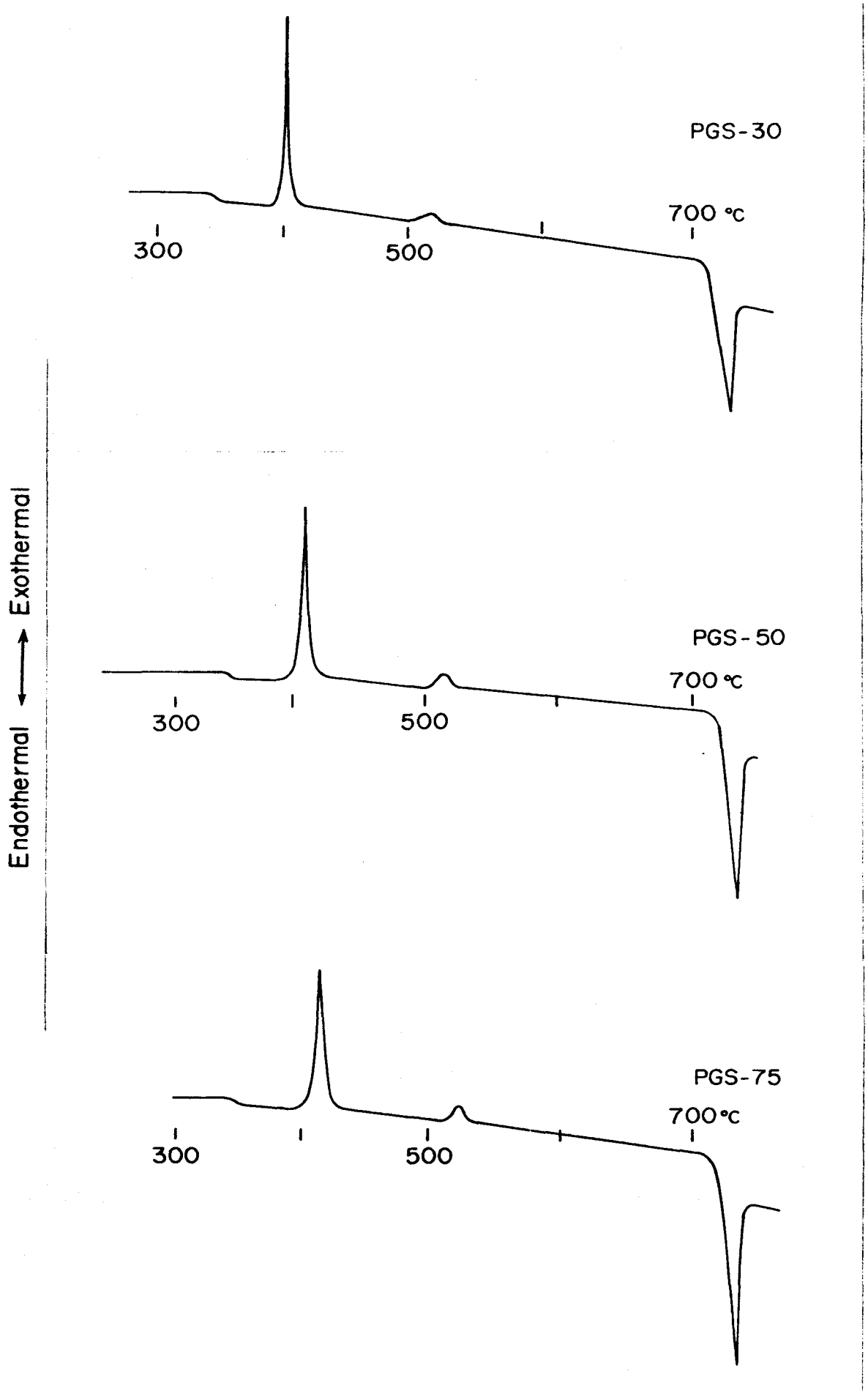


Figure 13. DTA traces of glsses in the system $PbO-GeO_2-SiO_2$

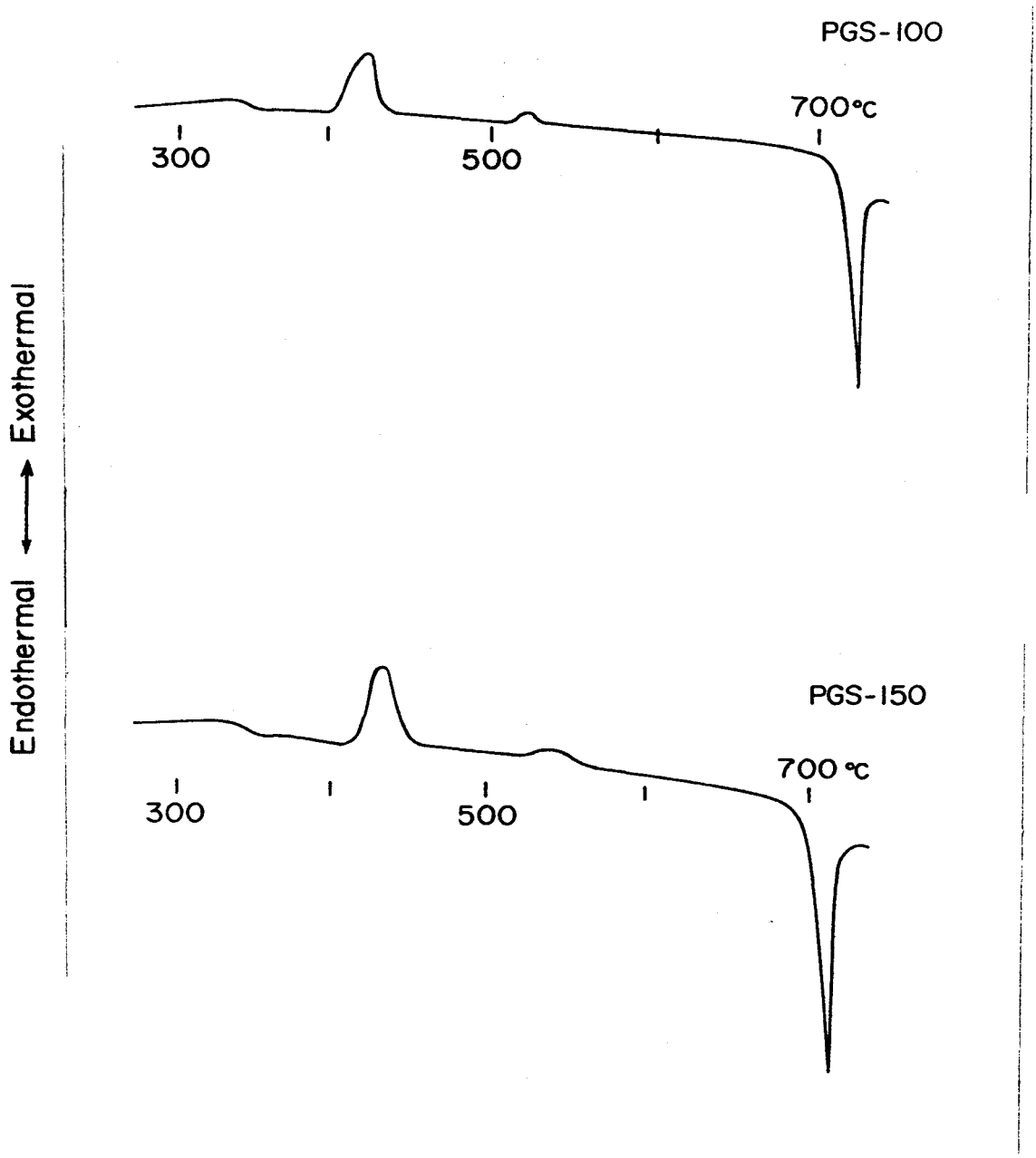


Figure 13. (cont.)

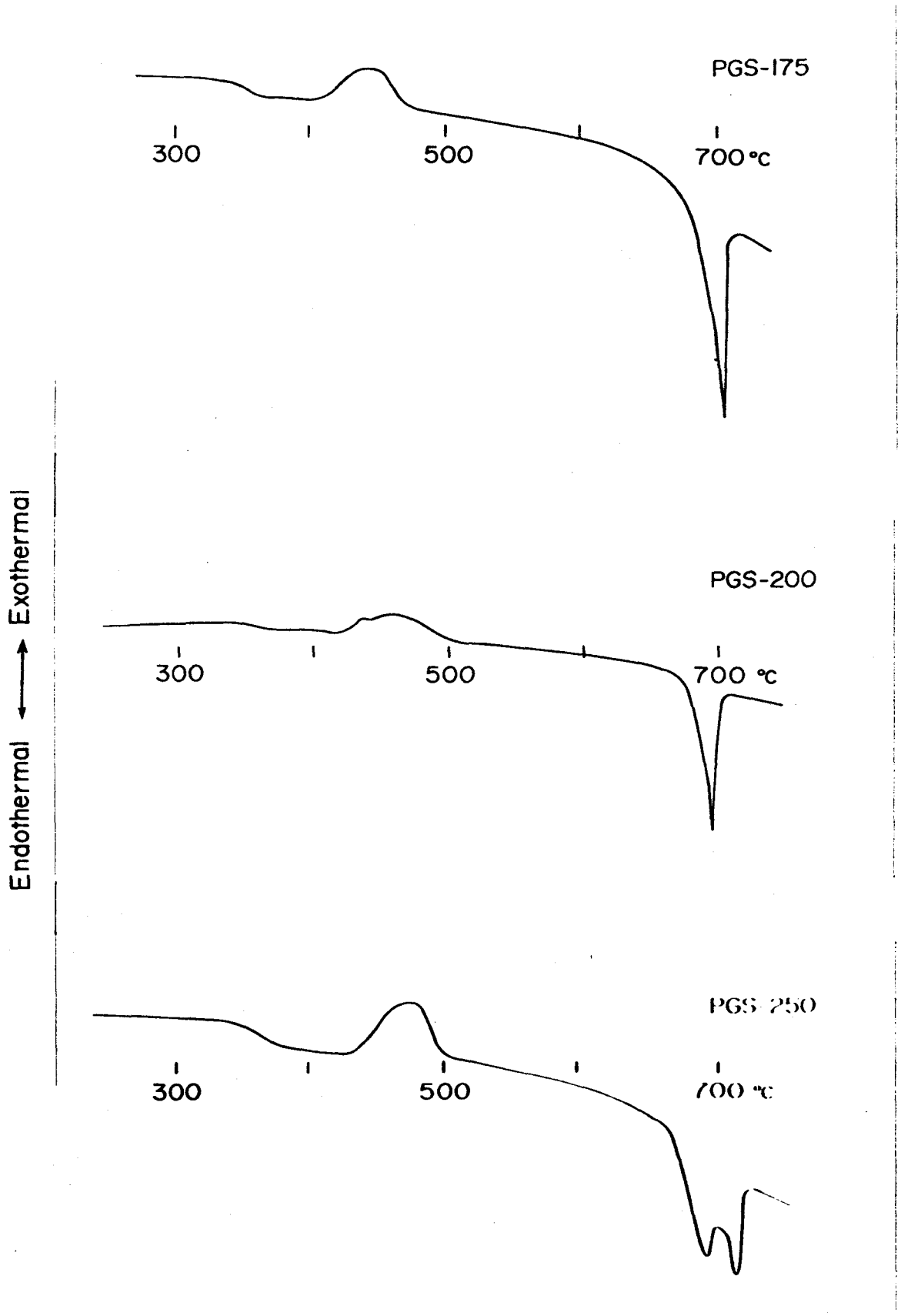


Figure 13. (cont.)

were due to the melt of the different crystalline phases. From the results reported by Ott [20], it was considered that the first and second endothermal peaks were due to the melt of $PbSiO_3$ and Pb_2SiO_4 respectively. From the results of X-ray diffraction analysis, the crystalline phase which appeared at a temperature near 550°C was identified as that having the same structure as $Pb_5Si_3O_{11}$, but around 600°C this phase decomposed into a mixture of Pb_2SiO_4 and $Pb(Si,Ge)O_3$.

Finally, at about 720°C, an endothermic melting process of crystallized phase appeared in all cases. The characteristic temperatures determined by DTA are summarized in Table VIIIfor all specimens.

Figure 18 shows the phase relations of crystalline phases precipitated from the glass during the isothermal heating.

In the system $PbO-GeO_2-SiO_2$, three solid solutions of $Pb_5Ge_{3-x}Si_xO_{11}$, $Pb_3Ge_{2-y}Si_yO_7$ and $Pb_5Si_{3-z}Ge_zO_{11}$ were obtained by the crystallization of the glass. Besides, as shown in Figure 14, a coexistence of two solid solutions of $Pb_5Ge_{3-x}Si_xO_{11}$ and $Pb_3Ge_{2-y}Si_yO_7$ was found.

The crystal structure of product precipitated from GeO_2-rich glasses at relatively higher temperatures was identified to be similar to that of ferroelctric $Pb_5Ge_3O_{11}$. A careful observation on X-ray diffraction pattern showed that diffraction peaks shift to higher angles with the increase of SiO_2 content. This fact strongly suggests

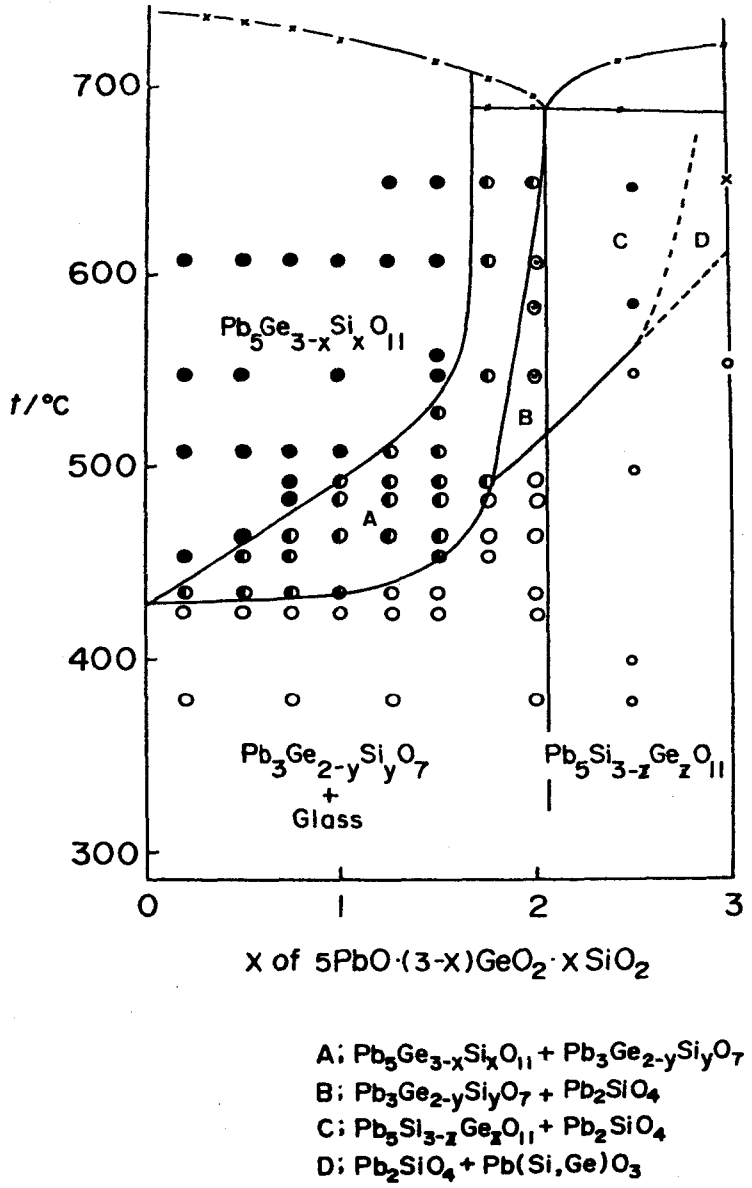


Figure 14 Phase relations of crystallized phases in the system $PbO-GeO_2-SiO_2$

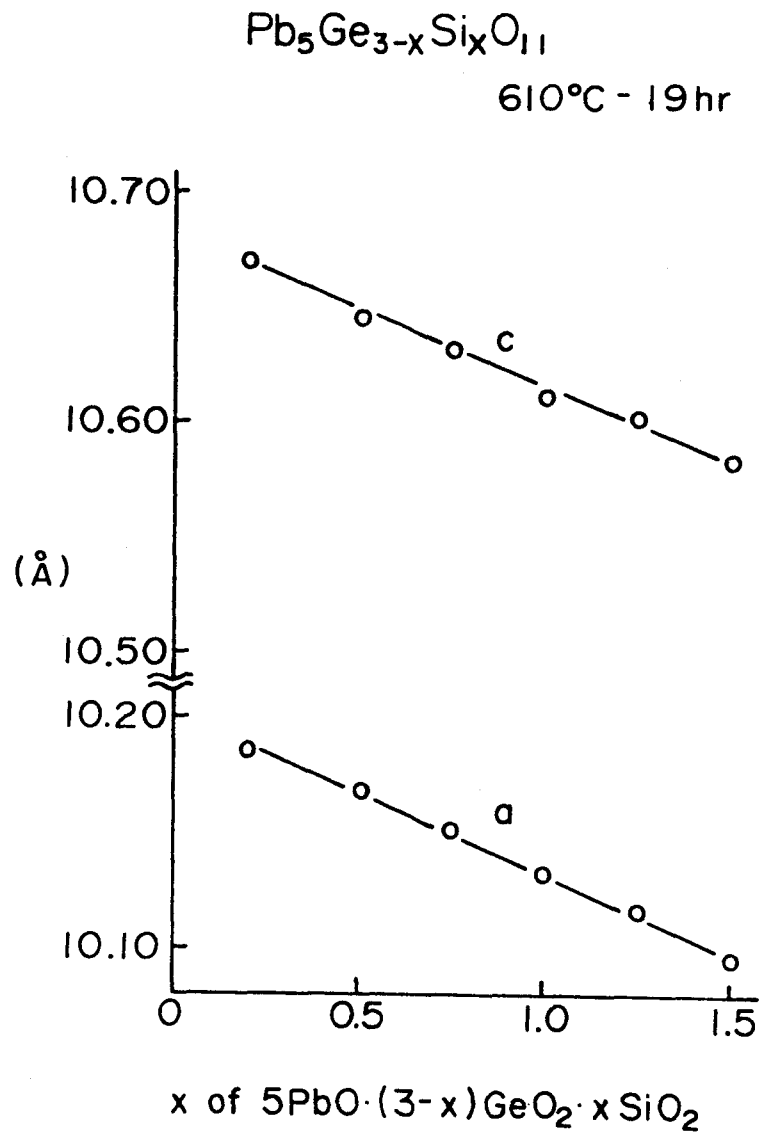


Figure 15 Lattice parameters of $Pb_5Ge_{3-x}Si_xO_{11}$ vs glass composition

that the crystalline phase belongs to a solid solution of $Pb_5Ge_{3-x}Si_xO_{11}$. The X-ray diffraction pattern of this phase was indexed with a hexagonal system, and lattice parameters varied with the SiO_2 content of glass as shown in Figure 15. The calculated lattice parameters a and c were reduced by the replacing of Ge by Si.

Eysel et al. [22] reported that the lattice parameters of $Pb_5(Ge_{1-x}Si_x)_3O_{11}$ ($0 \leq x \leq 0.6$) decreased linearly with Si content and at x=0.6 a and c were determined to be 10.10 and 10.53Å respectively. Therefore, considering the linear variation of lattice parameter a with the substitution of Si for Ge in the present investigation, it seems most reasonable to conclude that the x value of the solid solution of $Pb_5Ge_{3-x}Si_xO_{11}$ was defined by the composition of the base glass.

A solid solution $Pb_3Ge_{2-y}Si_yO_7$ appeared at relatively lower temperature as shown in Figure 14. The X-ray diffraction pattern of the product of this series was similar to that of $Pb_3Ge_2O_7$ in the region where x value of the glass composition is less than 2.0. But at x=2.5, the X-ray diffraction pattern did not resemble to that of $Pb_3Ge_2O_7$ but to that of $Pb_5Si_3O_{11}$. In the hexagonal setting, the relationship between the cell constants of this solid solution series and the composition of the base glass is given in Figure 16. As shown in Figure 14, there was the discontinuous relation-ship in the region at x=2.0.

Mydlar et al. [23] pointed out the existence of the

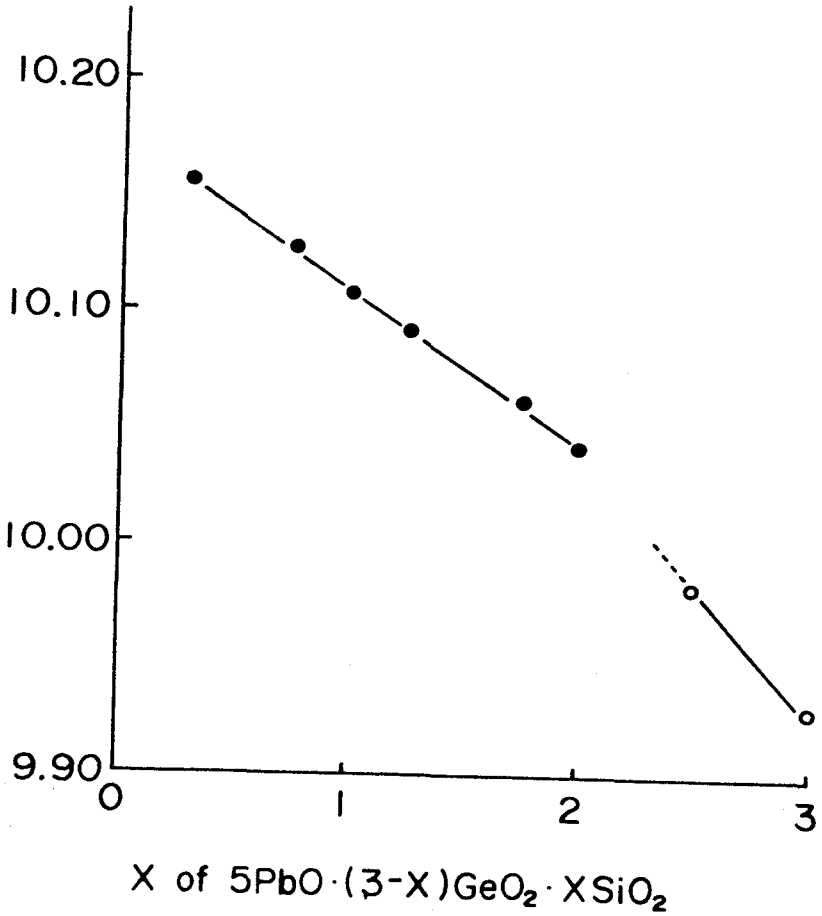


Figure 16 Lattice parameter a of $Pb_3Ge_{2-y}Si_yO_7$ and $Pb_5Si_{3-z}Ge_zO_{11}$

solid solution series $3PbO \cdot 2xGeO_2 \cdot 2(1-x)SiO_2$ (x=0-0.83). Moreover, they estimated that the idealized end-member of the $Pb_3Si_2O_7$ would exist in the temperature region near the melting point. This result was incontradiction to the present experimental results described in Section 3-2 of Chapter 3. It was considered that the present experimental results indicated that the idealized end-member was $Pb_5Si_3O_{11}$ and the solid solution of $Pb_5Si_{3-z}Ge_zO_{11}$ was introduced by the crystallization of the glass with the composition near $5PbO \cdot 3SiO_2$ at relatively lower temperatures. Calculated cell constants increase with the decrease of x-value of the glass composition.

From the results mentioned before, it was found that a complete solid solution between $Pb_5Ge_3O_{11}$ and $Pb_5Si_3O_{11}$ was not observed. As shown in Figure 14, the stable regions of $Pb_5Si_{3-z}Ge_zO_{11}$ and $Pb_3Ge_{2-y}Si_yO_7$ were obviously divided by the straight line. However, each phase of $Pb_3Ge_{2-y}Si_yO_7$ and $Pb_5Si_{3-z}Ge_zO_{11}$ precipiatetd from the glass as a primary crystalline phase at relatively lower temperatures during the heating process.

There have been many studies on the fabrication of glass-ceramics in the system of solid solution. For example, solid solution such as $Na_{1-x}Sr_{x/2}NbO_3$, $Ba_xSr_yPb_zNb_2O_6$, $Na_xK_yLi_zTaO_3$ and so on were obtained by the crystallization of multi-components silicate glasses. However, a control of chemical composition of product was very difficult [24]. In the system $5PbO \cdot (3-x)GeO_2 \cdot xSiO_2$,

contrastively, chemical composition of product was easily controlled by the settlement of the glass composition.

4-3. Conclusion

The above mentioned results are summarized as follows ;

(1) All the glasses were easily formed from the melts and the glass forming tendency increased with increase of SiO_2 content.

(2) The glass transition and supercooling of the melts were observed for each glass. The glass transition temperature increased continuously from 334°C for PGS-0 glass to 380°C for PGS-300 glass. The magnitude of supercooling increased with the increase of SiO_2 content.

(3) The substitution of SiO_2 for GeO_2 enhanced the glass forming tendency and completelt took place in the whole region in this system.

(4) In the system $PbO-GeO_2-SiO_2$, three kinds of solid solution series such as $Pb_5Ge_{3-x}Si_xO_{11}$, $Pb_3Ge_{2-y}Si_yO_7$ and $Pb_5Si_{3-z}Ge_zO_{11}$ were obtained by the crystallization of the glass. A coexistence of two solid solution series of $Pb_5Ge_{3-x}Si_xO_{11}$ and $Pb_3Ge_{2-y}Si_yO_7$ was found.

(5) In the solid solution series of $Pb_5Ge_{3-x}Si_xO_{11}$, the lattice parameters decreased linearly with SiO_2 content. The change of lattice parameters as a function of SiO_2 content in glass-ceramics were well agreement with that of single crystals reported by Eysel. Therefore, the x-value of $Pb_5Ge_{3-x}Si_xO_{11}$ was defined

by the composition of the base glass.

(6) A solid solution series $Pb_3Ge_{2-y}Si_yO_7$ appeared at lower temperatures. In the hexagonal setting, the cell constants as a function of SiO_2 content decreased linearly from x=0 to x=2.0, but there was a discontinuous change at x=2.5.

(7) When the ratio of SiO_2/GeO_2 was above 2.0, a new solid solution series of $Pb_5Si_{3-z}Ge_zO_{11}$ was found.

Chapter 5. Effect of addition of oxide

The fabrication of new glass-ceramic system by the crystallization of lead germanate glass with the composition near $5PbO \cdot 3GeO_2$ involved some problems to be solved. One was an improvement of stability of the base glass during cooling of the melt. Next one was an explanation of the crystallization mechanism as mentioned in Section 2-3 of Chapter 2.

A small amount of third component oxide was added to $5PbO \cdot 3GeO_2$ glass which was suitable for fabrication of transparent ferroelectric glass-ceramics. Effects of added oxides on stability of the base glass and the crystallization of the base glass during heating were examined by DTA and X-ray diffraction analysis, and the results are mentioned in this chapter.

Added oxides are classified into the following three groups ;

(a) SiO_2, B_2O_3 and Al_2O_3 as network-former.

(b) TiO_2 and ZrO_2 as nucleating agent.

(c) Fe_2O_3 and Nb_2O_5 as intermediate.

The compositions of glasses under investigation are listed in Table IX . The crystallization process was examine by DTA. Figure 17 represents the DTA traces of the glasses tabulated in Table IX with a heating rate

Table IX . Chemical compositions of glasses.

Sample	PbO wt%#	GeO_2 wt%#	R_mO_n wt%	$[R_mO_n]$
PGSi-0.5	77.69	22.05	0.44	
PGSi-1	77.24	21.74	1.02	SiO_2
PGSi-2	76.56	21.54	1.90	
PGB-1	77.15	21.71	1.14	
PGB-2	76.49	21.53	1.98	B_2O_3
PGB-3	75.72	21.31	2.97	
PGAl-1	77.22	21.73	1.05	
PGAl-2.5	76.10	21.40	2.50	Al_2O_3
PGAl-5	74.10	20.90	5.00	
PGTi-0.5	77.67	21.86	0.47	
PGTi-1	77.25	21.74	1.01	TiO_2
PGTi-2	76.52	21.53	1.94	
PGZr-0.5	77.65	21.85	0.49	
PGZr-1	77.28	21.74	0.98	ZrO_2
PGZr-2	76.53	21.54	1.93	
PGFe-0.5	77.61	21.84	0.54	
PGFe-1	77.21	21.73	1.06	Fe_2O_3
PGFe-2	76.52	21.53	1.94	
PBNb-0.5	77.68	21.86	0.47	
PGNb-1	77.10	21.70	1.20	Nb_2O_5
PGNb-2	76.47	21.52	2.01	

Molar ratios of PbO/GeO_2 are 5/3 in all samples.

of 10°C/min.

(a-1) B_2O_3

The addition of small amount of B_2O_3 enhanced the glass forming tendency of the melt. On thermal properties of the base glasses, the addition of B_2O_3 led to a reduction of the glass transition temperature. However, when the amount of B_2O_3 was above 2 weight%, the glass transition temperature increased. On the other hand, the temperature of crystallization rapidly increased, but that of phase change from $Pb_3Ge_2O_7$ to $Pb_5Ge_3O_{11}$ slightly changed and above 2 weight% of B_2O_3 exothermal peak due to the phase change disappeared. Moreover, in $5PbO \cdot 3GeO_2 \cdot B_2O_3$ glass, a crystallization did not occurred during the heating up to 700°C.

(a-2) SiO_2 and Al_2O_3

The addition of a small amount of SiO_2 or Al_2O_3 strongly stabilized the base glass. In the $5PbO \cdot 3GeO_2 \cdot SiO_2$ glass, no devtrification was observed during the heating up to 700°C. All characteristic temperatures observed in DTA traces increased with the increase of these oxides content. Moreover, the exothermal peak caused by the crystallization of the base glass were broadened by the addition of these oxides.

In the case of SiO_2, the X-ray diffraction patterns of precipitated phases are almost similar to those of $Pb_3Ge_2O_7$ and $Pb_5Ge_3O_{11}$, but small shifts of peaks were observed. Therefore, the crystalline phases were identified to be $Pb_3Ge_{2-y}Si_yO_7$ and $Pb_5Ge_{3-x}Si_xO_{11}$ already discussed in Section 4-2 of Chapter 4.

(b) TiO_2 and ZrO_2

The addition of less than 2 weight% of TiO_2 or ZrO_2 to the base glass was well effective for a advancement of stabilization of the glass. By the addition of above 2 weight% of these oxides, liquidus temperature was rapidly raised up above 1000°C and glass formation became very difficult. Above 1000°C volatilization of PbO and GeO_2 took place.

Effective action as a nucleating agent was not observed with the addition of these oxides.

(c) Fe_2O_3 and Nb_2O_5

The base glass was colored to brown by an addition of Fe_2O_3. The effect of addition was similar to that of TiO_2. In this system, when these oxides were added by above 2.5 weight%, quenched glasses always involved undissolved inclusions. The inclusions may be those added oxides.

The results mentioned above were shown in Figure 18. As shown in this figure, although the added oxides played a role either as a nucleating agent or as a glass-stabilizer, effects on the crystallization of the base glass were quite similar. This fact suggested that homogeneous nucleation process took place spontaneously and rapidly in $5PbO \cdot 3GeO_2$ glass.

An attempt to determine the growth rate did not succeed because the growth rate was so large and subsequently particle size of crystals was too small to be detected under a microscope.

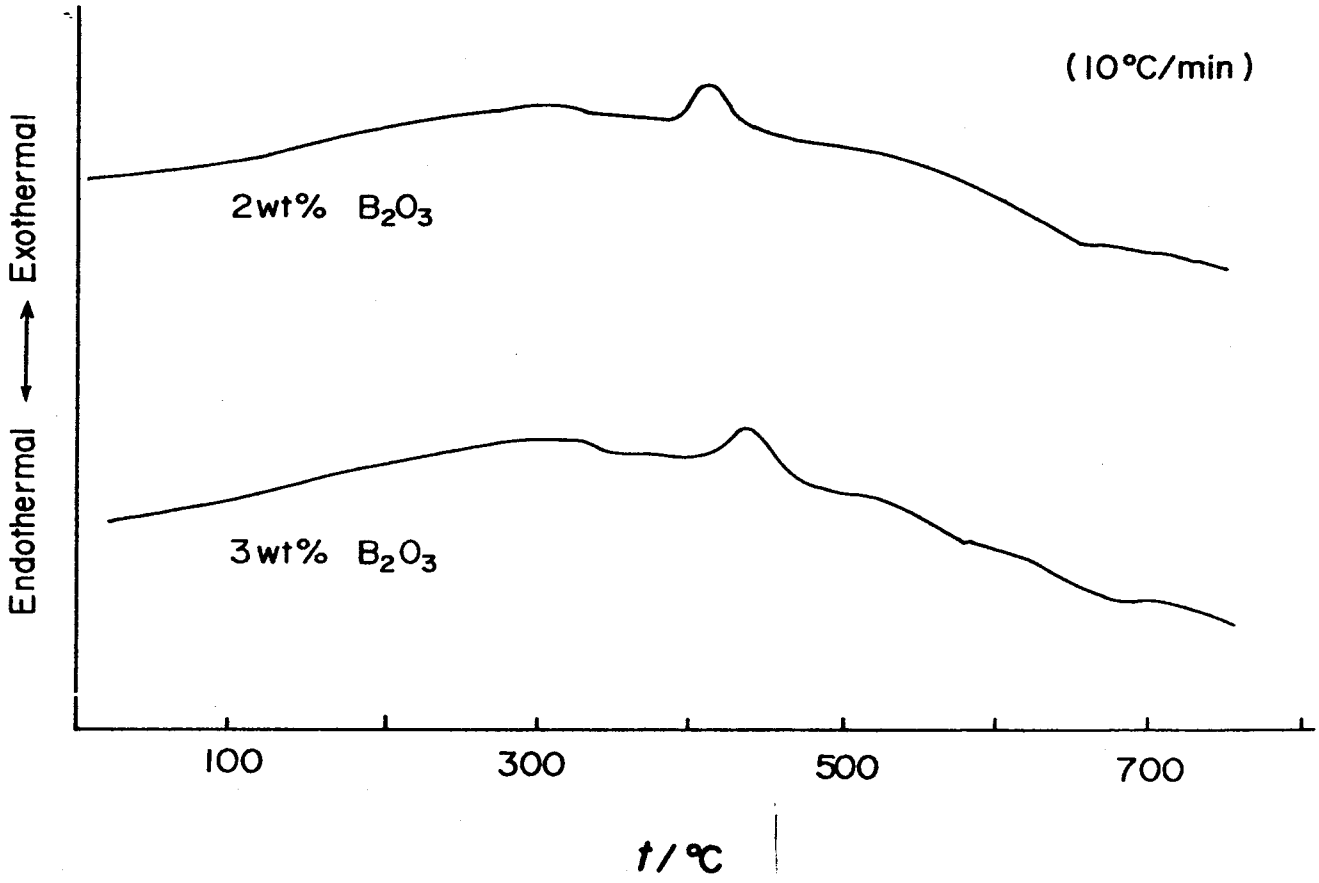


Figure 17 DTA traces of glasses in the system $PbO-GeO_2-R_mO_n$

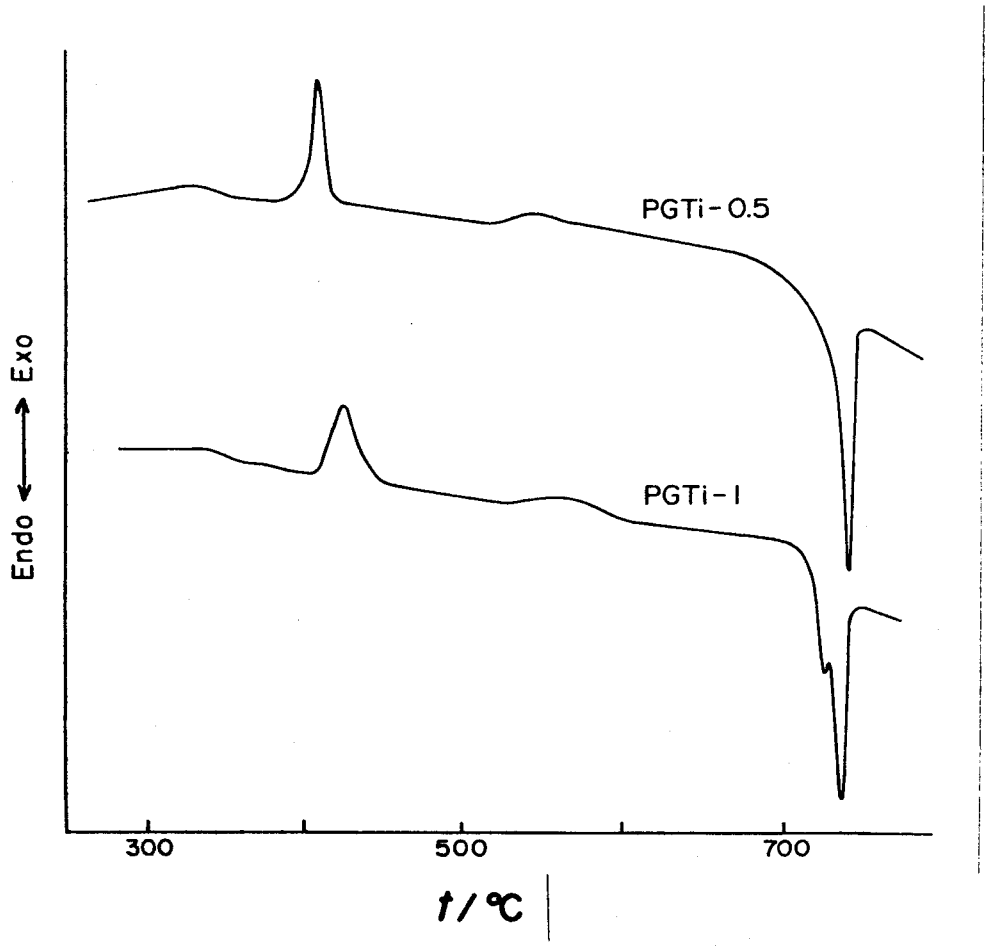


Figure 17. (cont.)

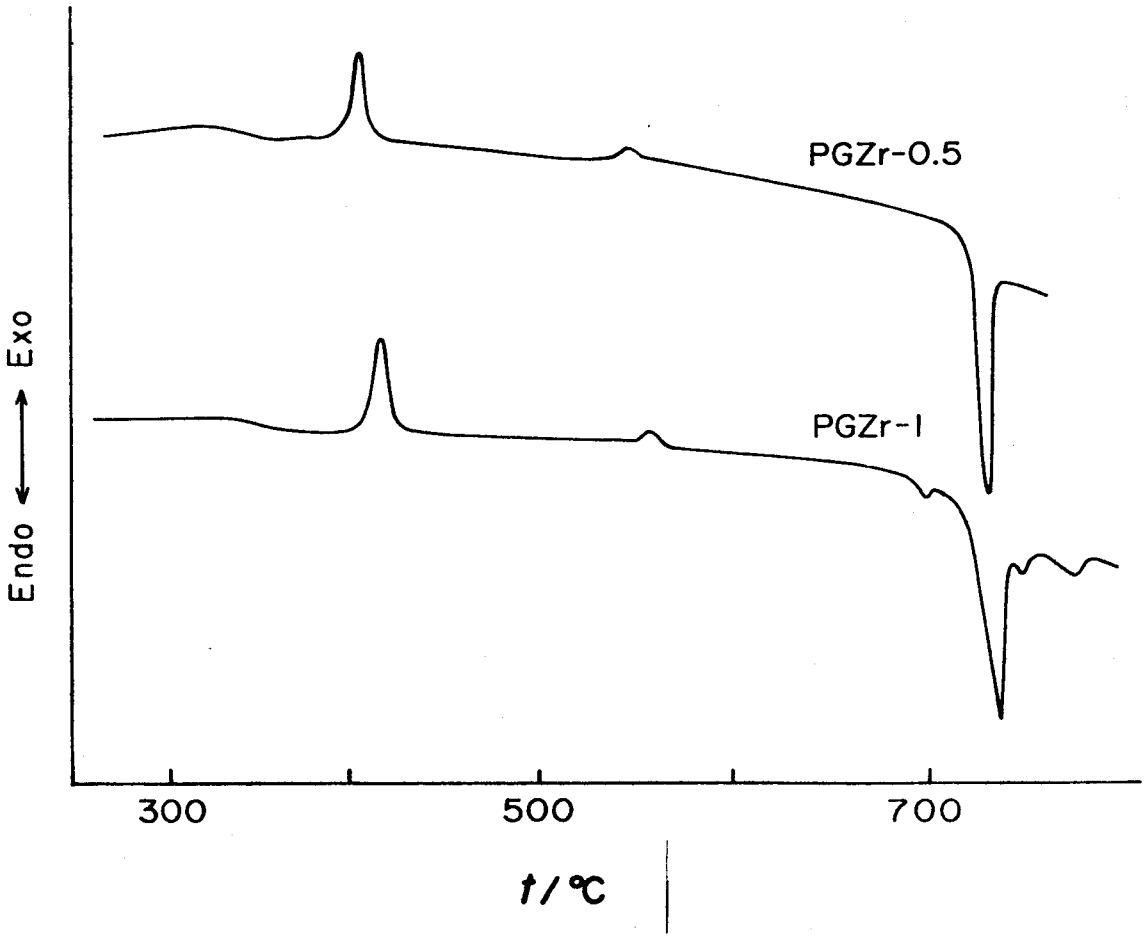


Figure 17. (cont.)

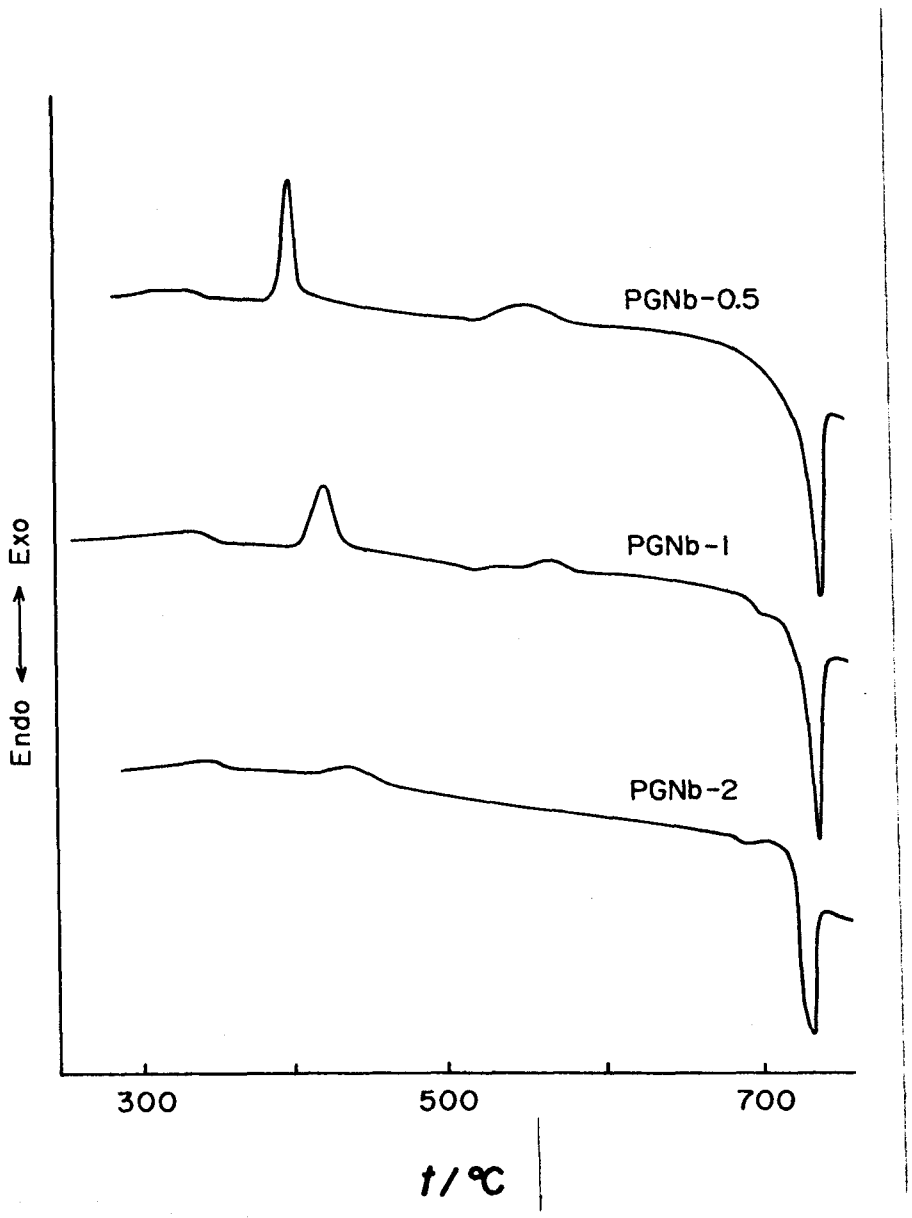
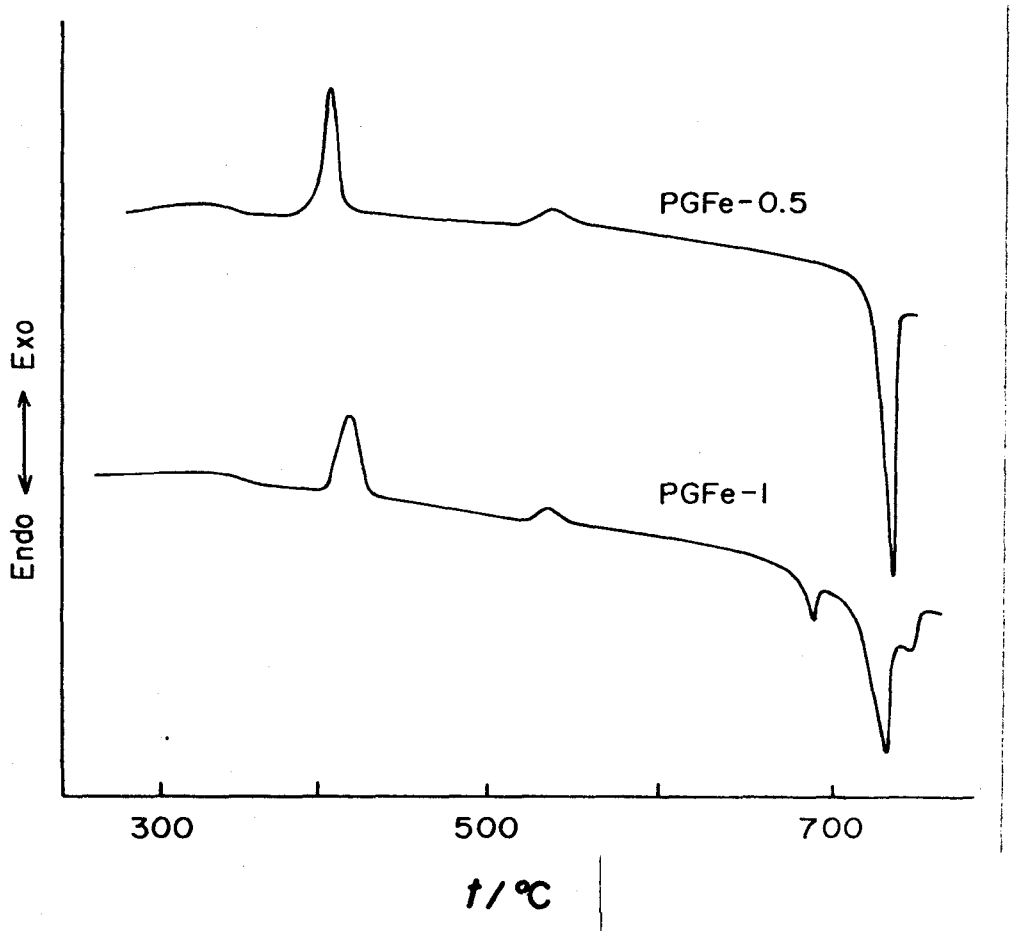


Figure 17. (cont.)



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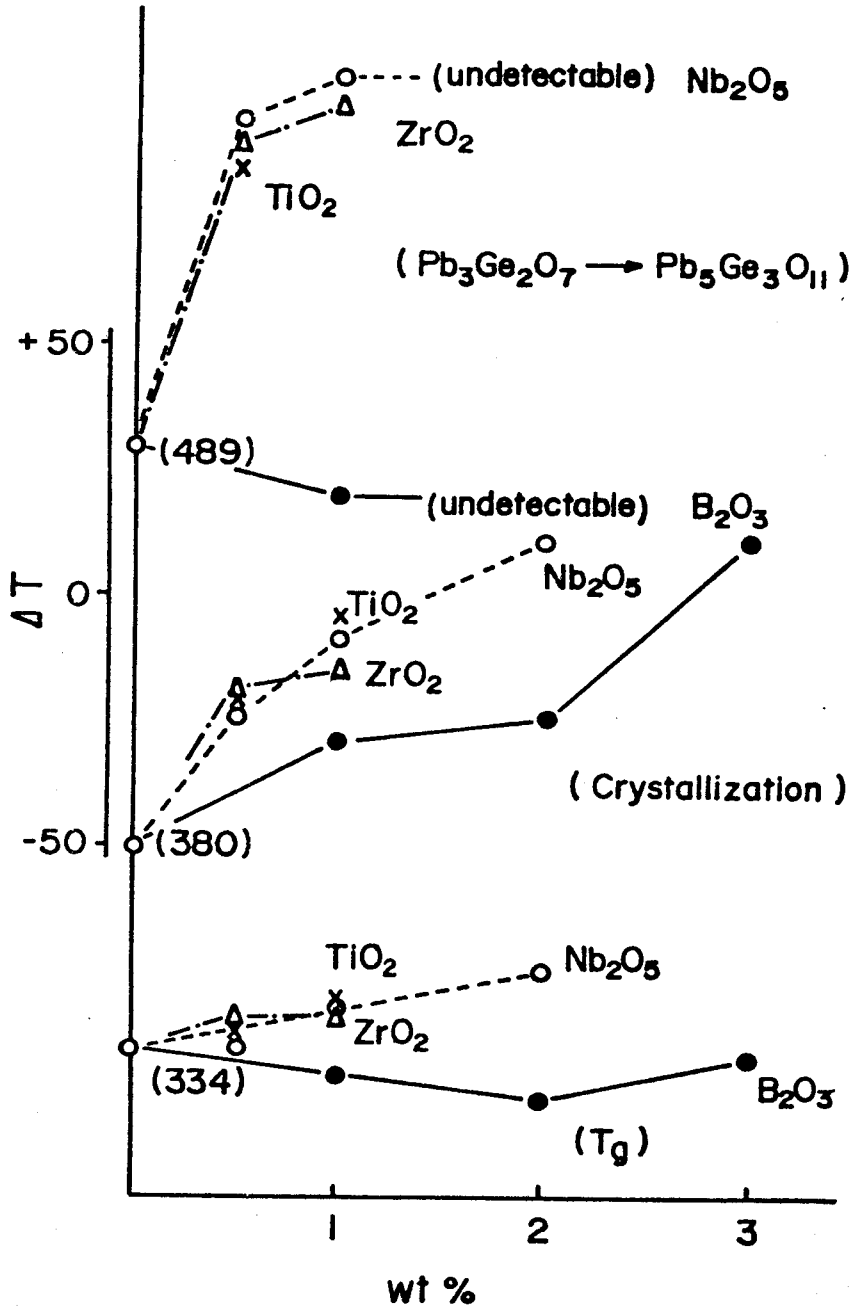


Figure 18. Effects of additions of oxides on characteristic temperatures

Chapter 6. Properties of glass-ceramics

As mentioned in Sections 2-2, 3-2 and 4-2, glass-ceramics were formed by the crystallizations of lead silicate glass, lead germanate glass and lead germanosilicate glass. In this chapter, the properties of these glass-ceramics are described.

6-1. Transparency

In every systems under investigation, the base glass was transparent and yellowish in color. After the crystallization, glass-ceramics were easily formed. Some of them were transparent or transluscent, and the others were opaque in compliance with heating conditions and glass compositions. Transparent glass-ceramics were obtained only in case when the crystalline phase precipitated as a sigle phase from the base glass.

For instance, a ferroelectric glass-ceramics with high transparency was prepared by the crystallization of ferroelectric $Pb_5Ge_3O_{11}$ from $5PbO \cdot 3GeO_2$ glass. Figure 19 shows the PG-62.5 glass ($5PbO \cdot 3GeO_2$ glass) and a transparent crystallized body produced by the crystallization at 530 °C for 1 hr. From the result of observation on transparent body as shown in the figure, particle sizes of

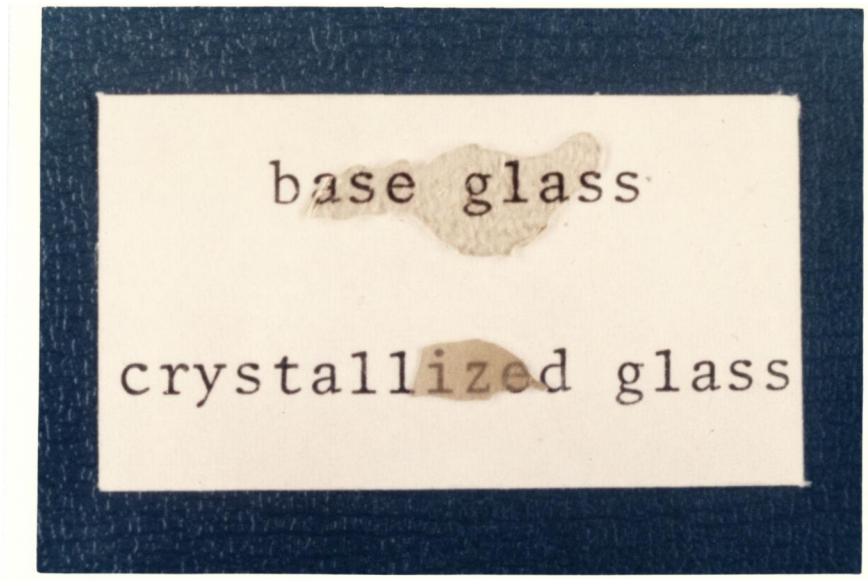


Figure 19. PG-62.5 glass and transparent glass-ceramic prepared by the crystallization of PG-62.5 glass at 530°C for 1 hr.

precipitated crystal $Pb_5Ge_3O_{11}$ were determined to be about 3000Å using the electron microscope. Therefore, the transparency observed in this system would be attained by the spread of small particles whose sizes were less than the wave length of visible light.

6-2. Dielectric property

In the present investigation, two ferroelectric crystalline phases were obtained. One was $Pb_5Ge_3O_{11}$ and the other was a solid solution series $Pb_5Ge_{3-x}Si_xO_{11}$ ($0 \leq x \leq 1.75$). Dielectric properties of glass-ceramics were measured with the frequency of 10^3 Hz. The temperature dependency of permittivity of glass-ceramics of $Pb_5Ge_{3-x}Si_xO_{11}$ (x=0, 0.5 and 1.0) was measured in the temperature region from 200°C to room temperature. The results are shown in Figure 20 . As shown in this figure, maximum peak in permittivity was found at about 175°C for glass-ceramic of $5PbO \cdot 3GeO_2$, 115°C for $5PbO \cdot 2.5GeO_2 \cdot 0.5SiO_2$ and 65°C for $5PbO \cdot 2GeO_2 \cdot SiO_2$ respectively. These values were in good agreement with those of single crystals reported by Eysel et al. [22]. When the SiO_2 content increased, Curie temperature and peak permittivity decreased.

On the other hand, it was expected that new compound $Pb_5Si_3O_{11}$ obtained in the present study exhibited a ferroelectric property because of a structural similarity with

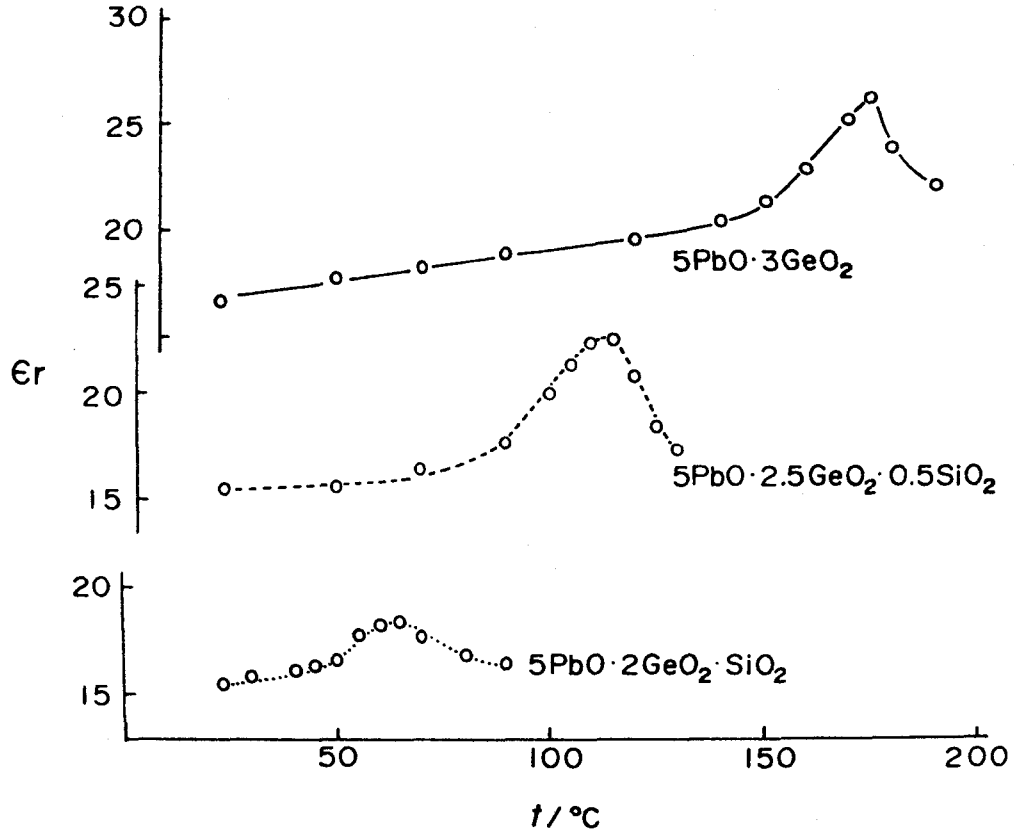


Figure 20. Permittivity of glass-ceramics as a function of temperature.

ferroelectric $Pb_5Ge_3O_{11}$. However, the glass-ceramic specimen including $Pb_5Si_3O_{11}$, which was prepared by the crystallization of $5PbO \cdot 3SiO_2$ glass at 550°C for 333 hrs, had a constant permittivity of 17 in the temperature region from 7 K to room temperature.

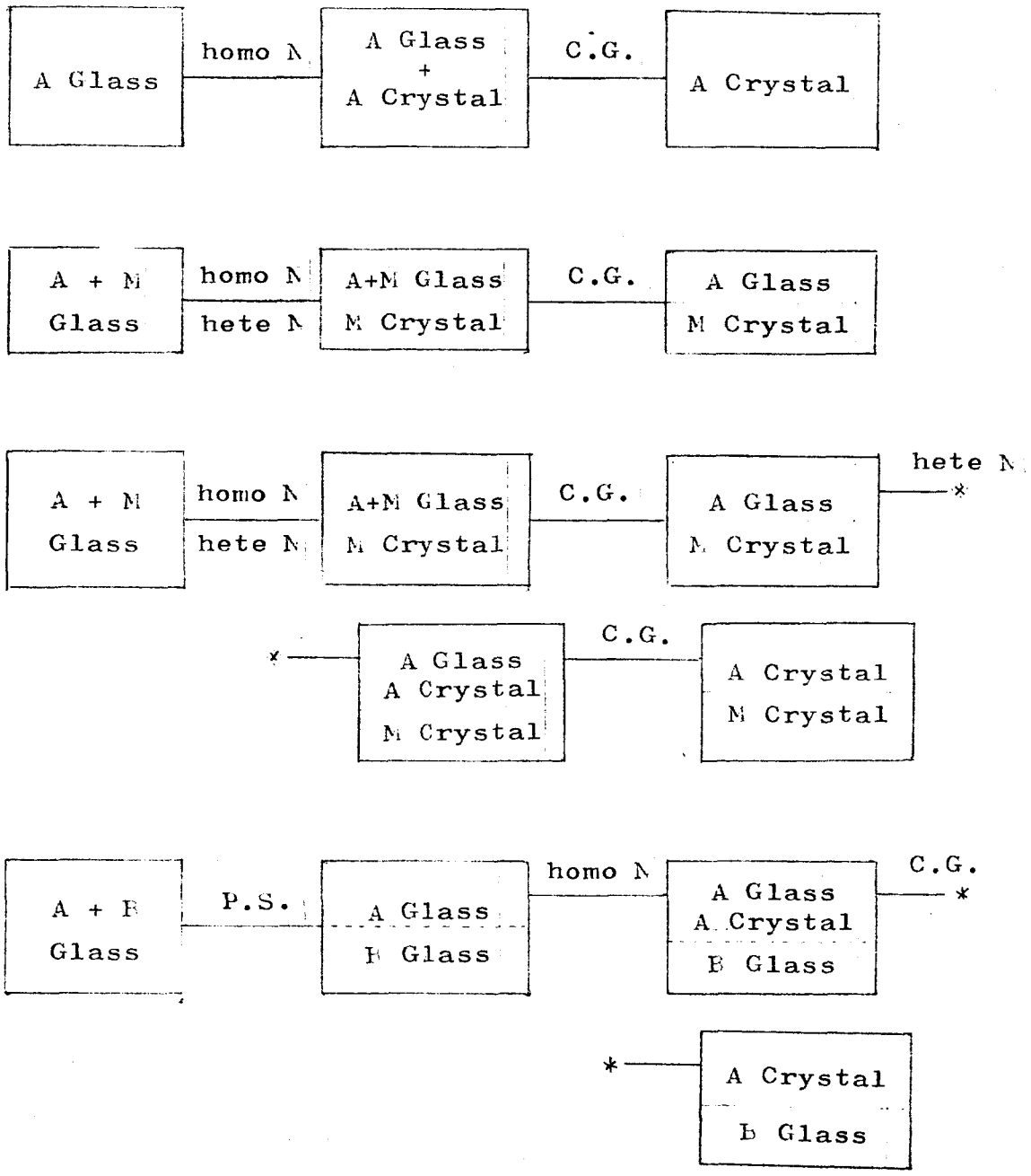
Chapter 7. General consideration

On the basis of the present experimental results, the process and distinctive features of crystallization of glass to yield a metastable phase are discussed in this chapter.

The crystallization of glass is generally viewed as a two-step process. The first step involves the foramation of a stable nucleus and the second one does the growth of the nucleus to form a crystal.

Nucleation is very important even in case when a crystalline phase precipitates from the glass with the same composition. Nucleation is classified into either homogeneous or heterogeneous. When nucleation occurs within a pure phase with no interface, the process is defined as homogeneous. Heterogeneous nucleation involves the formation of a nucleus at an interface such as container walls, bubble surface, or particle surface of a second phase which serve to catalyze the reaction. The classification of nucleation processes are schematically shown in Figure 21.

We consider the formation of a spherical particle



homo N ; homogeneous nucleation
hete N ; heterogeneous nucleation
C.G. ; crystal growth
P.S. ; phase separation

Figure 21. Schematic representation of the classification of crystallization processes.

from a homogeneous supercooled liquid at a constant temperature-pressure through a homogeneous nucleation process. The free energy change which occurs in the process to form the praticle can be expressed as follows;

$$\Delta Gr = 4\pi r^2 \gamma_{LS} + \frac{4}{3}\pi r^3 \Delta Gv \qquad \cdots (1)$$

where r is the radius of particle, γ_{LS} is the liquid-solid interfacial energy and ΔGv is the free energy change per unit volume accompanying the liquid-solid phase transformation. Gr can posses the maximum value ΔGr^* ($= 16\pi\gamma_{LS}^3/3\Delta Gv^2$) at $r=r^*$ ($= 2\gamma_{LS}/\Delta Gv$). Particles with a radius greater than r^* are called "nuclei" and are stable since growth is accompanied by a decrease in free energy. From Boltzmann's law, the number of nuclei with a given size r^* at a temperature T is given by

$$Nr^* = K \exp(-\Delta Gr^*/kT) \qquad \cdots (2)$$

where K is a constant and k is the Boltzmann's constant.

On the other hand, the formation of a stable nucleus needs a diffusion of atoms from a liquid to a nucleus through the liquid-solid interface. Thus, the rate of nucleation is given by

$$I = K' \exp[-(Gr^* + Q)/kT] \qquad \cdots (3)$$

where Q is the activation energy of diffusion process at the liquid-solid interface.

ΔGv , at a temperature near the liquidus temperature

T_L, is approximately given by

$$\Delta Gv = \lambda (T_L - T)/T_L \qquad \cdots (4)$$

where λ is the heat of fusion. By using equation (4), equation (3) can be written finally as follows;

$$I = K'' \exp\left[- \frac{1}{kT} \left\{ \frac{16\pi \gamma_{LS}^3}{3} \cdot \frac{T_L^2}{\lambda^2 (T_L - T)^2} + Q \right\} \right] \qquad \cdots (5)$$

Therefore, the rate of nucleation is defined by the degree of undercooling $(T_L - T)$ and Q related with the diffusion process.

The rate of nucleation with a heterogeneous process is given by

$$I' = K''' \exp[-(\Delta Gr^* \cdot f(\theta) + Q)/kT] \qquad \cdots (6)$$

where $f(\theta)$ is a function of the contact angle θ.

On the other hand, the growth rate of nuleus is given by the followinf formula,

$$u = K'''' \exp(-Q'/kT) \left\{ 1 - \exp(\Delta Gv/RT) \right\} \qquad \cdots (7)$$

where Q' is the activation energy of diffusion process at the liquid-crystal interface and ΔGv is the free energy change per unitvolume. This equation indicates that the rate of crystal growth depends on both values of thermodynamic and kinetic barriers.

(i) System $PbO-GeO_2$

As mentioned in section 2-2, in this system, $Pb_3Ge_2O_7$ precipitated as a metastable phase at a relatively lower temperature and transformed to $Pb_5Ge_3O_{11}$ at 489°C during the heating of $5PbO \cdot 3GeO_2$ glass.

Crystallization of metastable phase has been observed in many glass systems. For example in the system with one component oxide glass, it is well known that cristobalite is formed after the devitrification of fused silica above 1000°C in spite of the fact that cristobalite is not stable below 1470°C. This phenomenon was explained by the assumption that the structure of fused silica is "cristobalite-like", so that the formation of cristobalite nuclei requires the least drastic rearrangement of the structure [25]. For multi-components system, the same phenomenon could be found in case of wollastonite ($CaO \cdot SiO_2$) with two modifications (the α-hexagonal form is stable from 1150°C to the melting point and the β-orthorhombic form is stable below 1150°C). Morey [26] suggested that α-$CaO \cdot SiO_2$ could be obtained from the glass even below 1150°C. In other systems, crystallization of metastable phase from the glass was often observed and the structure of the glass was identified to that of the metastable crystalline phase which is usual a high temperature modification. On the other hand, in the multi-component systems such as Li_2O-SiO_2, the crystallization of metastable phase was enhanced by the phase separation [27]. Therefore, it is sufficient to understand that

crystallization of a metastable phase is induced by the structural similarity between the glass and the high temperature modification or by the phase separation as kinetic treatment. In $5PbO \cdot 3GeO_2$ glass, however, $Pb_3Ge_2O_7$ was not only stable at relatively higher temperature but also phase separation was recognized. A new mechanism should be proposed for the crystallization of $Pb_3Ge_2O_7$ from $5PbO \cdot 3GeO_2$ glass.

The crystallization mechanism has been investigated by various methods including X-ray diffraction technique, electron microscopy, small angle X-ray scattering, light scattering, differential thermal analysis and infrared absorption spectrophotometry. Recently, Gregory and Verssey [28] reported that infrared absorption spectoro-photometry is useful for the examination of crystallization processes. In this study, crystallization process of the glass is investigated by infrared absorption analysis.

In Figure 22, the spectra of PG-62.5 glass ($5PbO \cdot 3GeO_2$) and its crystallized products are shown. According to the results of phase relation described in section 2-2 of Chapter 2, the PG-62.5 glass crystallized at 387°C and phase change of the crystallized phase took place at 489°C. In the PG-62.5 glass, the existence of crystalline phase of $Pb_3Ge_2O_7$ was observed after the heating at 375°C for 50 hrs, and the crystallized product exhibited sharp absorption peaks in the infrared spectrum at 720, 520, 413, 383 and 345 cm^{-1} (Figure 22). The crystallized glass containing a crystalline phase of $Pb_5Ge_3O_{11}$, which

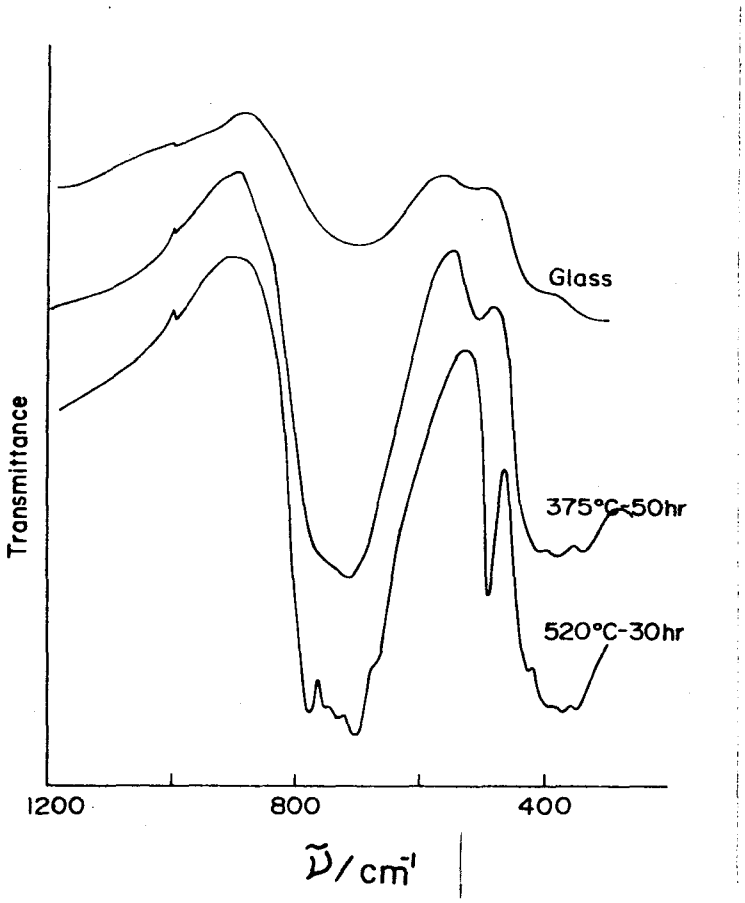


Figure 22. Infrared absorption spectra of PG-62.5 glass and crystallized products

was heat-treated at 520°C for 30 hrs, displayed sharp absorption peaks at 799, 755, 734, 708, 673, 493, 429, 413, 397, 352 and 327 cm^{-1} (Figure 22).

The infrared absorption spectra for crystals of $Pb_3Ge_2O_7$, $Pb_5Ge_3O_{11}$ and Pb_3GeO_5 obtained by slow cooling of the melts are shown in Figure 23. As shown in this figure, they are composed of two absorption bands around 730 and 380 cm^{-1} and one characteristic absorption at about 500 cm^{-1}. Characteristic absorptions of the glass, crystallized products and crystals are listed in Table X.

To assign absorptions of each spectrum in detail, the contribution of GeO_4 tetrahedron to infrared absorptions was examined in comparison with the results of SiO_4 tetrahedron. Infrared spectra of silicate minerals have been studied by many investigators and infrared active frequencies were calculated for several structures as listed in Table XI.

The crystal structures of $Pb_3Ge_2O_7$ and Pb_3GeO_5 are not still determined, but that of $Pb_5Ge_3O_{11}$ was determined by Newnham et al. [29], which consists of an isolated GeO_4 tetrahedron and Ge_2O_7 unit as illustrated in Figure 24.

For Ge_2O_7 group in minerals, calculated infrared active frequencies of 764, 741, 701, 686, 395, 352 and 325 cm^{-1} were reported with the assuming that Ge_2O_7 had C_{2v}(Ge-O-Ge=140°) symmetry.[30]. Absorptions at 755, 734, 708, 673, 397,352 and 327 cm^{-1} of $Pb_5Ge_3O_{11}$ observed in the present experiment agree with the caluculated values. Assignments of absorptions are tabulated in

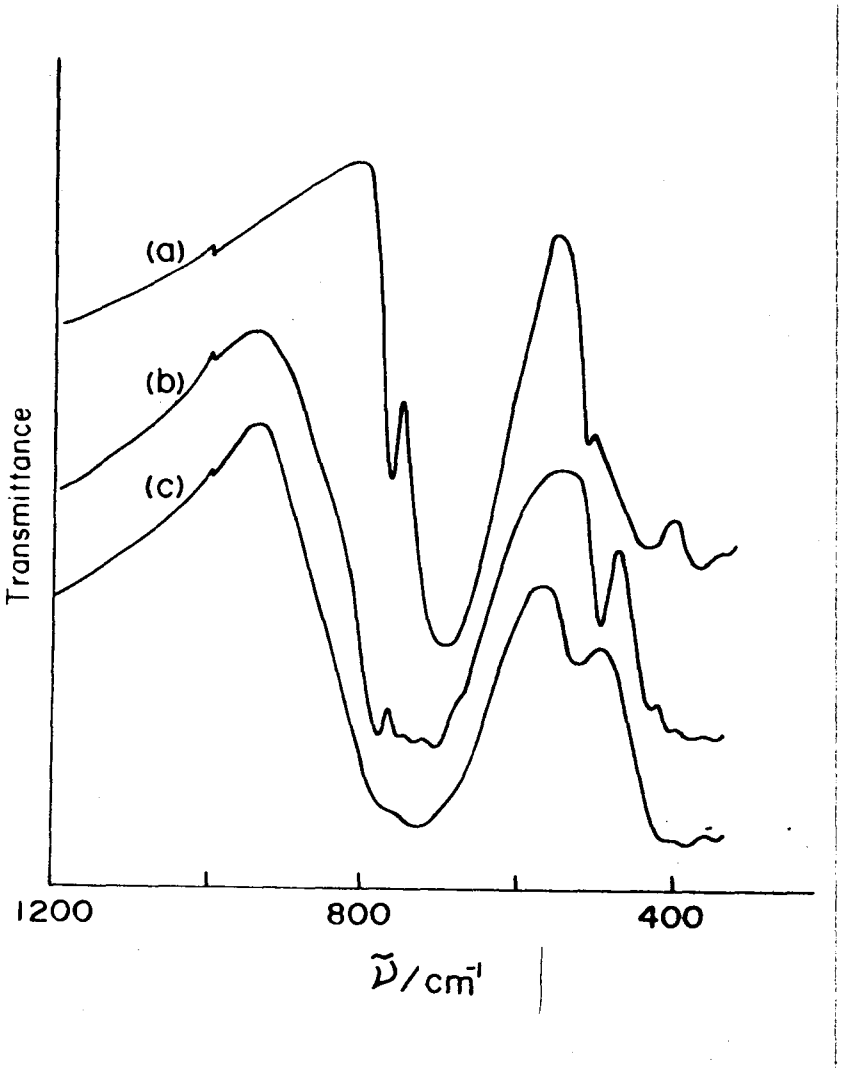


Figure 23 Infrared absorption spectra of Pb_3GeO_5 (a), $Pb_5Ge_3O_{11}$ (b) and $Pb_3Ge_2O_7$ (c)

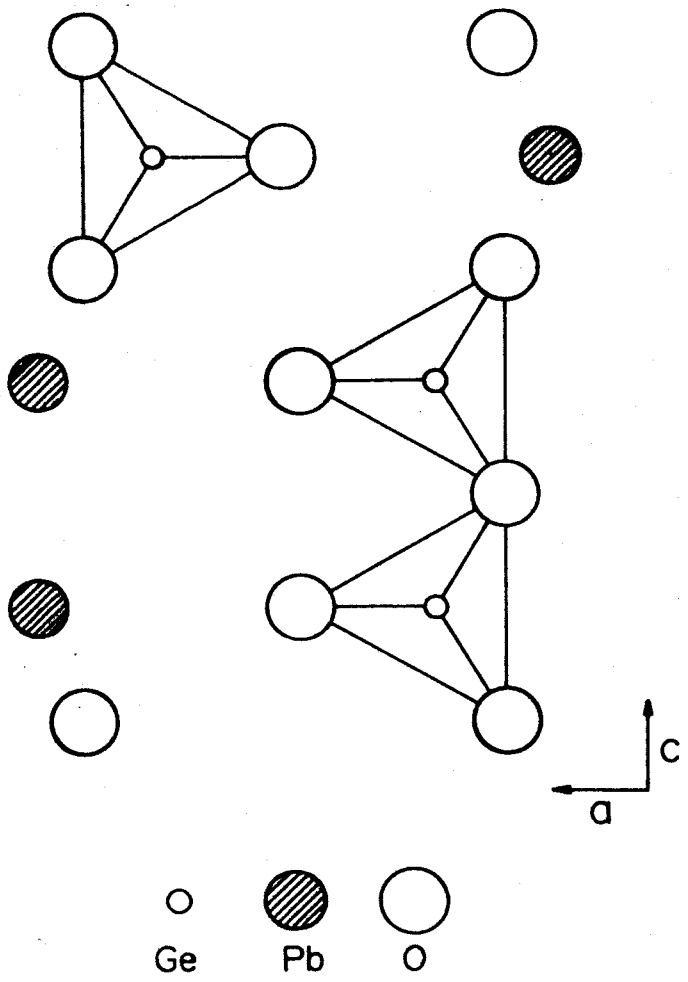


Figure 24. Prototype structure of ferroelectric $Pb_5Ge_3O_{11}$
(after Newnham)

Table X. Characteristic absorption at about 500 cm^{-1}

Sample	peak position (cm^{-1})
PG-62.5 glass	525
PG-62.5 glass containing $Pb_3Ge_2O_7$	520
PG-62.5 glass containing $Pb_5Ge_3O_{11}$	493
$Pb_3Ge_2O_7$ crystal	524
$Pb_5Ge_3O_{11}$ crystal	493

Table XI. Calculated infrared active frequencies for various silicates.

	D_{3h}	1082	1043	904	766	567	470	404	203
Cyclosilicates	D_{4h}	1106	1043	910	684	566	564	412	245
	D_{6h}	1114	1043	949	602	567	589	484	182
Sheet structures		1128	1007		650			344	
Chain structures		1149	1037		800	620	529	439	
Si_2O_7 structures		1107	1030		774	580	523	479	
Isolated SiO_4 structures			1031		770		493	473	

Table XII. Assignments of infrared absorptions of $Pb_5Ge_3O_{11}$.

$\tilde{\nu}_{observed}$	assignment	
799	ν_3 GeO_4,	
755	ν_3 GeO_4,	A_1 Ge_2O_7
734	ν_3 GeO_4,	B_2 Ge_2O_7
708	ν_3 GeO_4,	A_1 Ge_2O_7
673		B_1 Ge_2O_7
493	ν_1 GeO_4	
429	ν_4 GeO_4	
413	ν_4 GeO_4	
397		A_2 Ge_2O_7
352		B_2 Ge_2O_7
327		A_1 Ge_2O_7

Table XII.

In the cases of $Pb_3Ge_2O_7$ and Pb_3GeO_5, since the structures of these phases are not still determined, an attempt to assign infrared absorptions.

The spectra of all the glasses are quite similar in shape. As shown in Figure 22, the spectrum of PG-62.5 glass ($5PbO \cdot 3GeO_2$) is essentially identical with that of $Pb_3Ge_2O_7$ crystal. Especially the broad band of the glass at about 525 cm^{-1} is rquivalent to the weak peak of $Pb_3Ge_2O_7$ crystal at 524 cm^{-1}. The broadening of the absorptions of glass is due to the variety of Ge-O bonds in the glass. Therefore, it is considered that the glass has a structural unit similar to that of $Pb_3Ge_2O_7$ crystal.

To obtain the information on the nucleation and crystal growth, microscopic observation was carried out for many specimens. On microscopic examination of the base glass under the investigation, neither bubbles nor undissolved refractory inclusions were observed. The base glass did not involve an additional nucleating agent. Moreover, it was found that the crystallization occured uniformly on the whole body in every specimens. These results suggest that the nucleation proceeds with a homogeneous process and a large number of nulei are spreaded throughout the body.

It is expected that nucleation takes place when the melt with the composition of $5PbO \cdot 3GeO_2$ is cooled from the liquidus temperature to room temperature. At a temperature near the liquidus temperature T_L, first, nucleation of a crystalline phase is very difficult due to the small nucleation rate I caused by the small degree of undercooling (T_L-T) and the fast cooling rate. Secondarily at temperature near the glass-transition temperature and/or at lower temperature, Q of equation (5) possesses a very large value and the nucleation rate falles down remarkably. Therefore nucleation does not occur. On the other hand, since the (T_L-T) is relatively large and Q is adequately small at a temperature suitable for nucleation, the nucleation rate is determined by the interfacial energy γ_{LS}. In this case, γ_{LS} is affected by the difference of composition between nucleus and liquid matrix and

by incoherency of atoms at the interfaces.

Consequently, for the discussion of metastable crystallization of $Pb_3Ge_2O_7$ in prior to the crystallization of $Pb_5Ge_3O_{11}$ in the present investigation, it is sufficient to consider the interfacial enegy between the matrix and each crystal.

As mentioned above, it is expected from the results of infrared absorption measurements that the structure of glass is similar to that of $Pb_3Ge_2O_7$ crystal. This structural similarity induces the smaller interfacial energy between the nucleus of $Pb_3Ge_2O_7$ and the base glass. Therefore, when the melt was quenched from the liquidus temperature to the room temperature, the formation of numerous nuclei of $Pb_3Ge_2O_7$ occurs easily and rapidly through a homogeneous nucleation process.

Crystallization process during the heating of the base glass including the numerous nuclei of $Pb_3Ge_2O_7$ crystal is considered as follows.

As shown in Figure 2, the exothermal process caused by the crystallization gave rise to a sharp peaks in DTA trace and completed in a narrow temperature region. And crystal particles precipitated from the glass are too small to determine the shape and particle size by a optical microscope. These results suggest that the crystallization process completely finishes in a short time. The fact that the crystallization of $Pb_3Ge_2O_7$ occurs quickly at a temperature higher than the glass

transition temperature by about 50°C suggests that this crystallization does not proceed by the rearrangements of structural units such as GeO_4 tetrahedra, Ge_2O_7 and PbO_4 groups, but by the migrations of lead ions as network modifier.

However, the phase transformation from $Pb_3Ge_2O_7$ to $Pb_5Ge_3O_{11}$ gave raise to a broade exothermal peak in a DTA trace. At the temperature where this broad exothermal process was observed, the migrations of network-forming atoms such as Ge^{4+} ion and Pb^{2+} ion must be possible. Thus, it seems that this process is also attended with the migrations of Ge^{4+} and Pb^{2+} ions as network-formers. The rate of this process involving the rearrangements of network depends on the viscocity of residual glass matrix, and the boundary between the stable region of $Pb_3Ge_2O_7$ and that of $Pb_5Ge_3O_{11}$ (or $+Pb_3GeO_5$) is set up as a function of temperature and glass composition.

In the PG-62.5 glass, both phases of $Pb_5Ge_3O_{11}$ and Pb_3GeO_5 were precipitated as primary crystalline phase simultaneously. Since, in the composition of this glass, it is considered that the tempearture region where the assemblage of $Pb_3Ge_2O_7$ and glassy phase existe as meta-stable will be lower than the glass transition temperature, $Pb_3Ge_2O_7$ can not crystallize. If $Pb_5Ge_3O_{11}$ appears as a primary crystalline phase, the residual glassy phase becomes richer in PbO content and consequently glassy phase can not exist as a stable phase, but crystallization of Pb_3GeO_5 would occur at once.

(ii) System $PbO-SiO_2$

As discussed in section 2-2 of chapter 2, during the heating of $5PbO \cdot 3GeO_2$ glass the crystallization process took place as follows;

$$\text{Glass} \longrightarrow \text{Glass} + Pb_3Ge_2O_7 \longrightarrow Pb_5Ge_3O_{11}$$

In case of $5PbO \cdot 3SiO_2$ glass, however, the following reaction process was observed;

$$\text{Glass} \longrightarrow Pb_5Si_3O_{11} \longrightarrow Pb_2SiO_4 + PbSiO_3$$

Therefore it is considered that in the glass of $5PbO \cdot 3SiO_2$ and $5PbO \cdot 3GeO_2$ analogous crystallization processes do not take place. And each crystalline phase precipitated from the glass are in equilibrium states.

In lead silicate system, the structural similarity between the glass and each crystal was also examined by means of infrared absorption spectorophotometry. Infrared spectra of the glass and the crystallized products containing $Pb_5Si_3O_{11}$ are illustrared in Figure 25 by KBr method.

In the $5PbO \cdot 3SiO_2$ glass heated at 550°C for 333 hrs, the existence of crystalline phase of $Pb_5Si_3O_{11}$ was recognized and crystallized product exhibited sharp absorption peaks in the infrared spectrum at 1055, 990, 935, 880, 845, 820, 790, 660, 600, 510, 465 and 425 cm^{-1}. On the other hand, after the heat-treatment of $5PbO \cdot 3SiO_2$ glass at 458°C for 45 hrs, absorptions were observed at 930, 875, 845, 660, 605, 510, 465 and 425 cm^{-1} in the infrared spectrum of the crystallized product. Sample obtained by slow cooling of the melt with the composition of $5PbO \cdot 3SiO_2$

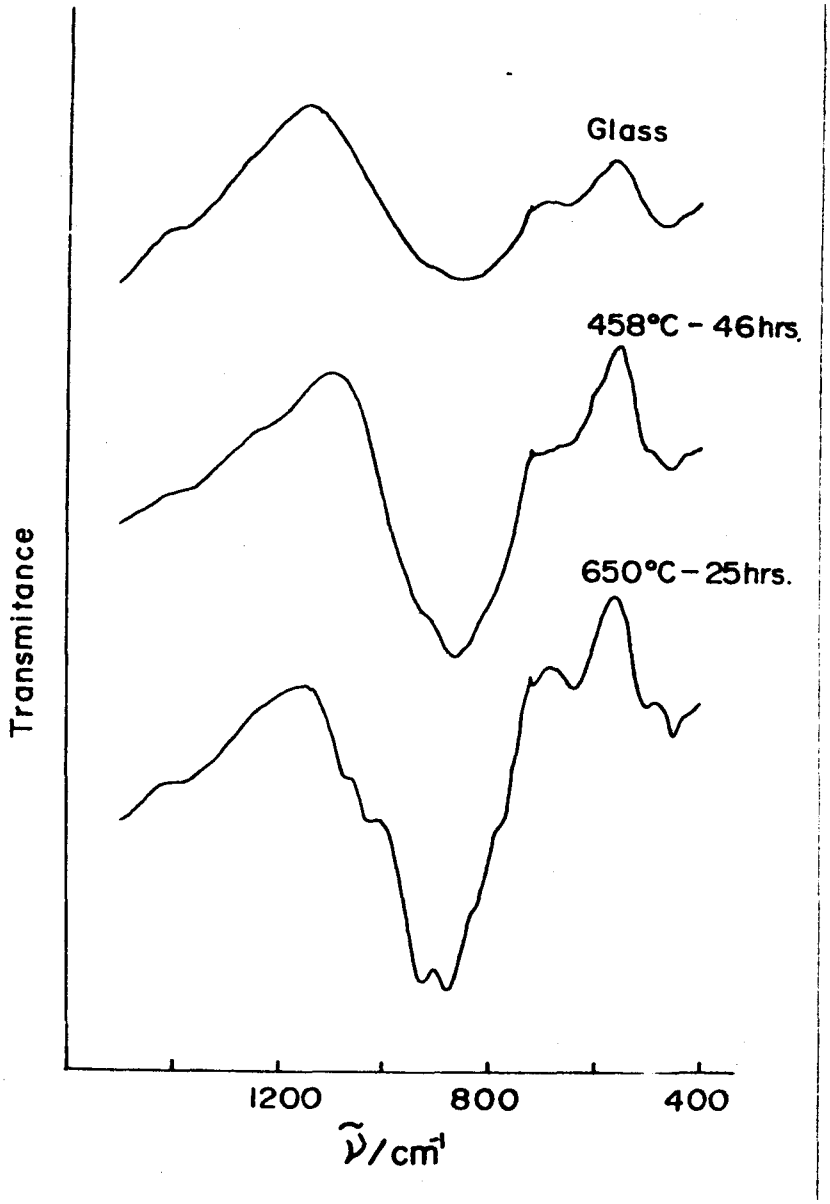


Figure 25. Infrared absorption spectra of products crystallized from PS-62.5 glass

exhibited strong absorptions at 1115, 1075, 1030, 930, 880, 855, 835, 680, 645,620, 610, 585, 520, 510 and 460 cm^{-1} as shown in Figure 25. From the X-ray diffraction analysis, the existences of H-Pb_2SiO_4 and $PbSiO_3$ recognized in this sample. The infrared spectrum of this sample suggests that there are many kinds of chemical bonds between lead, silicon and oxygen atoms. Especially the existences of several kinds of environments for lead ions are surmised by the characteristic aborptions at about 600-700 cm^{-1}.

The infrared absorption spectra of the $5PbO \cdot 3SiO_2$ glass and of $Pb_5Si_3O_{11}$ crystal are almost similar in shape and the characteristic absorptions of both the glass and crystal appeared at same wave number within an experimental error. Therefore, the structure of the glass is idealized to that of $Pb_5Si_3O_{11}$ crystal.

As discussed above, the structural similarity between the glass and $Pb_5Si_3O_{11}$ crystal induces a lower interfacial energy γ_{LS} for the interface between the glass matrix and nucleus of $Pb_5Si_3O_{11}$, and caused the crystallization of $Pb_5Si_3O_{11}$ from the $5PbO \cdot 3SiO_2$ glass to be easy.

In this system, as compared with the case of the system $PbO-GeO_2$, a broad exothermal process caused by a crystallization of $Pb_5Si_3O_{11}$ is observed at a relatively lower temperature in DTA traces. Therefore, it is concluded that this exothermal process involves the nucleation process. During the melt is cooled to room temperature, namely, nucleation merely occurs.

(iii) System $PbO-GeO_2-SiO_2$

In this system, the crystallization process is explained with a combination of those of systems $PbO-GeO_2$ and $PbO-SiO_2$. As shown in Figure 14, the stable region of $Pb_5Si_{3-z}Ge_zO_{11}$ was in contact with the stable region of $Pb_3Ge_{2-y}Si_yO_7$. Moreover, $Pb_3Ge_{2-y}Si_yO_7$ or $Pb_5Si_{3-z}Ge_zO_{11}$ precipitated from the glass as a primary crystalline phase at relatively lower temperature during the heating process.

To elucidate the crystallization process in this system and the phase relation between $Pb_3Ge_{2-y}Si_yO_7$ and $Pb_5Si_{3-z}Ge_zO_{11}$, infrared absorption spectra of crystallized products were measured. The absorption bands as a function of SiO_2 content in the composition of base glasses are shown in Figure 12. As shown in this figure, two characteristic features for infrared absorptions were observed in this system. First was that there is a sharp discontinuity at X=2.0 on the ν_3 vibrations of Si-O bond. In the solid solution series $Pb_5Si_{3-z}Ge_zO_{11}$ (z=0.5 and 0), ν_3 Si-O splits into five lines observed at the region of 820-990 cm^{-1}. But in the region below X=2.0 (X-value shows the glass composition) where the solid solution series $Pb_3Ge_{2-y}Si_yO_7$ appeared, there are three lines of ν_3 Si-O at 830-930 cm^{-1}. This phenomenon would be explained by the different tetrahedral environments due to the structural symmetries of $Pb_5Si_{3-z}Ge_zO_{11}$ and $Pb_3Ge_{2-y}Si_yO_7$. Therefore, this result well agrees with that of X-ray diffraction

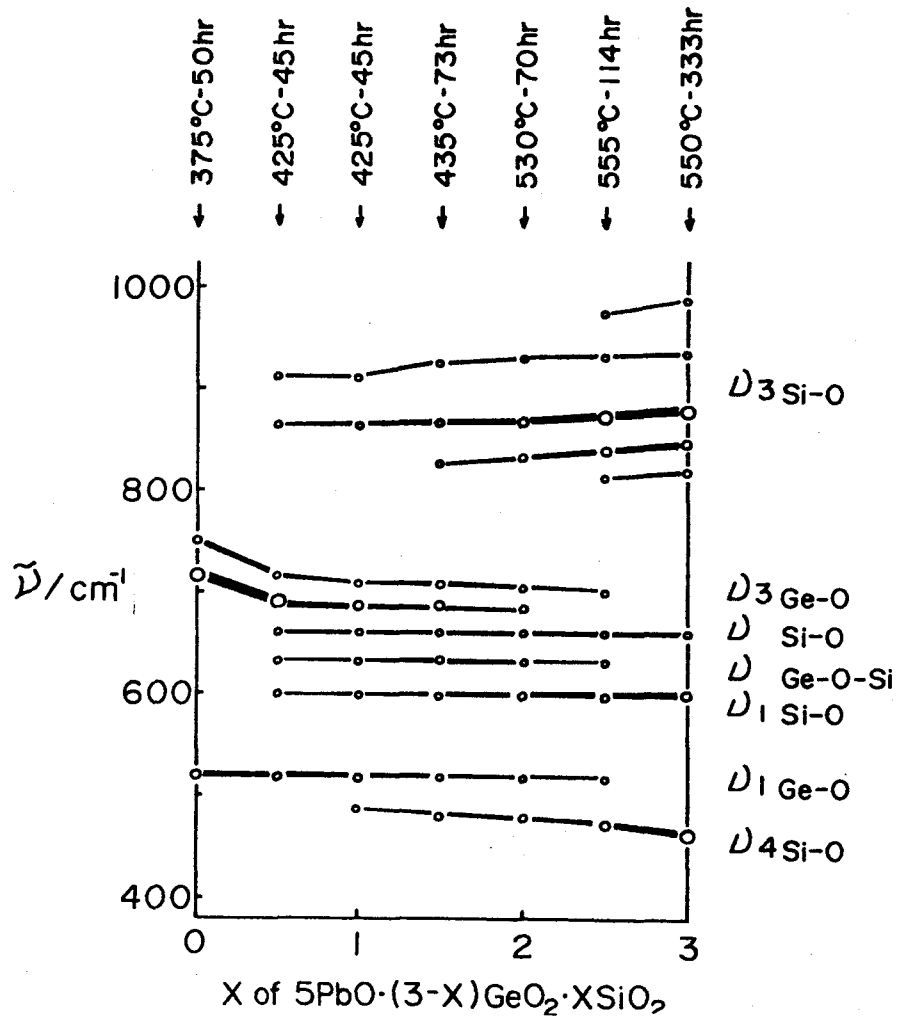


Figure 26. Characteristic absorptions of $Pb_3Ge_{2-y}Si_yO_7$ and $Pb_5Si_{3-z}Ge_zO_{11}$

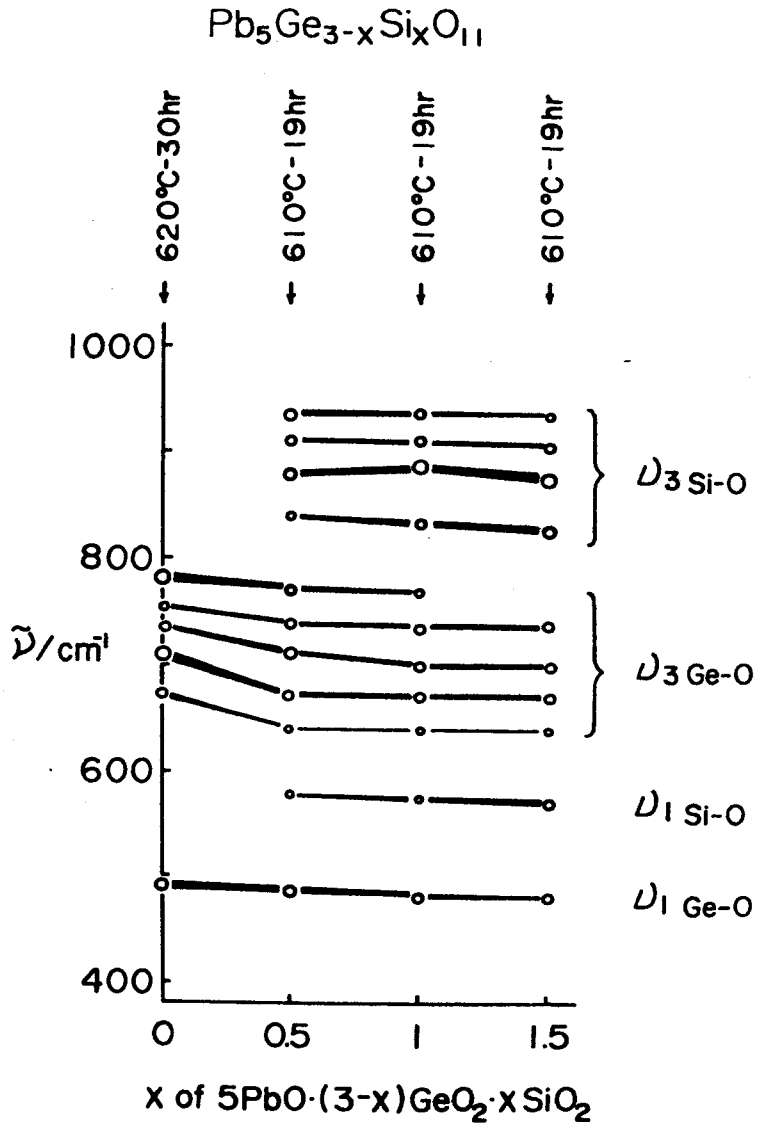


Figure 27. Characteristic absorptions of $Pb_5Ge_{3-x}Si_xO_{11}$ as a function of glass composition.

analysis. In X-ray diffraction analysis, when ratio of SiO_2/GeO_2 was less than 2.0, the product belonged to hexagonal symmetry and when the ratio was more than 2.5, the product belonged to orthorhombic symmetry.

On the other hand, second one is that ν_1 vibrations caused by Si-O and Ge-O bonds are independent of the chemical composition of the base glass. As mentioned above, ν_1 vibration is very sensitive for the environment of lead ion, and no change of ν_1 vibrations of two solid solution series strongly suggests that the environment of lead ions in $Pb_5Si_{3-z}Ge_zO_{11}$ was similar to that in $Pb_3Ge_{2-y}Si_yO_7$. Moreover the wave number of ν_1 vibration observed on solid solution series are quite equal to that observed on the base glass.

However, infrared absorption spectra of $Pb_5Ge_{3-x}Si_xO_{11}$ are different from those of another two kinds of solid solution series.

Consequently, it is concluded that there exist the structural similarities between the base glass and both phases of $Pb_3Ge_{2-y}Si_yO_7$ and $Pb_5Si_{3-z}Ge_zO_{11}$. On the basis of the experimental results such as DTA and infrared absorption measurements, in the region where the ratio of SiO_2/GeO_2 is less than 2.0, it is concluded that the crystallization proceeds as same manner as in the case of the system $PbO-GeO_2$ and same process with the case of the system $PbO-SiO_2$ occurs in the region where the SiO_2/GeO_2 ratio is more than 2.0.

Of course, in this system, lower interfacial enegy between the glass and these crystal is induced by the structural similarity between the glass and these crystals.

Summary

Results and considerations in this paper are summarized as follows ;

(1) The yellowish transparent glass with homogeneity was easily formed in the present experiment. The substitution of SiO_2 for GeO_2 enhanced the glass forming tendency.

(2) The glass transition temperature decreased continuously with the increase of PbO content in the $PbO-GeO_2$ and $PbO-SiO_2$ systems. However, the glass transition temperature increased when Ge^{4+} were replaced by Si^{4+} in the system $PbO-GeO_2-SiO_2$.

(3) A ferroelectric glass-ceramic with high transparency was easily prepared by the crystallization of $Pb_5Ge_3O_{11}$ from $5PbO \cdot 3GeO_2$ glass. The Curie temperature Tc of glass-ceramics of $Pb_5Ge_3O_{11}$ was determined to be 175 °C. Increasing the Si content lowered the melting point and Curie temperature. The value of Tc were determined to be 115°C and 65°C for the glass-ceramics of $Pb_5Ge_{2.5}Si_{0.5}O_{11}$ and of $Pb_5Ge_2SiO_{11}$. From the results of change of Tc and lattice parameters of $Pb_5Ge_{3-x}Si_xO_{11}$ as a function of Si content, it is indicated that the composition of the glass defines the x-value in this solid solution system.

(4) Effects of added oxides on the crystallization of the $5PbO \cdot 3GeO_2$ were quite similar whether they behaved as a nucleating agent or as a glass stabilizer. This fact suggested that homogeneous nucleation took place sponteneously and rapidly.

(5) A new phase of $Pb_3Ge_2O_7$ was synthesized. The crystal structure had a hexagonal symmetry with a=10.16Å and c=19.37Å. This phase was paraelectric.

(6) A new phase of Pb_3GeO_5 with orthorhombic system was prepared and its lattice parameters were determined to be a=4.85Å, b=15.52Å and c=11.77Å.

(7) A new phase of $Pb_5Si_3O_{11}$ had a orthorhombic system with a=9.93Å, b=8.31Å and c=34.4Å. This material was paraelectric down to 7 K and its value of permittivity was 17.

(8) Considering infrared absorption spectra of glasses and their crystallized products, it is confirmed that structural similarities exist between the glass and metastable crystalline phases.

(9) The preferential crystallization under present investigation was due to the easy rearrangement of structure produced by the structual similarity between the glass and crystals.

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References

[1] S.D.Stookey,
Corning Research, 178 (1961)

[2] K.Sugii, H.Iwasaki and S.Miyazawa,
Mater. Res. Bull., 6 503 (1971)

[3] H.Iwasaki,
Appl. Phys. Japan, 41 415 (1972)

[4] E.I.Speranskaya,
Izv. Akad. Nauk SSSR, Otdel. Khim. Nauk 162 (1959)

[5] B.Phillips and M.G.Scoroger,
J. Am. Ceram. Soc., 48 398 (1965)

[6] D.Gouju, J.Fournier and R.Kohlmuller,
C. R. Acad. Sc. Paris, Ser C 266 1063 (1968)

[7] M.Imaoka,
"Advances in Glass Technology Part I",p149,
Plenum Press, New York, 1962

[8] S.Hanada, N.Soga and M.Kunugi,
Proc. XII-th Confer. Basic. Sci. Ceram. Kyoto,
p95. (1974)

[9] N.F.Borrelli,
Phys. Chem. Glasses, 10 431 (1969)

[10] V.N.Morozov,
Zh. Prikl. Spektrosk., 8 830 (1968)

[11] G.Eulenberger, A.Wittmann and H.Nowotny,
Monatsh. Chem., 93 1046 (1962)

[12] L.Merker and H.Wondratscek,
Glastech. Ber., 30 471 (1957)

[13] J.E.Stanworth,
J. Soc. Glass Technol., 32 154 (1948)

[14] K.Fajans and N.J.Kleidel,
J. Am. Ceram. Soc., 31 105 (1948)

[15] M.F.Mydlar, N.J.Kreidl and G.T.Clayton,
Phys. Chem. Glasses, 11 196 (1970)

[16] H.W.Billhardt,
Am. Mineral., 54 510 (1960)

[17] H.Ito and T.Yanagase,
Tran. Japan Inst. Metal., 1 115 (1960)

[18] P.J.Bray and M.Leventhal,
Phys. Chem. Glasses, 4 47 (1963)

[19] W.Hermann,
Glastech. Ber., 42 498 (1969)

[20] W.R.Ott and M.G.Mclaren,
J. Am. Ceram. Soc., 53 374 (1970)

[21] J.F.Argyle and F.A.Hummel,
J. Am. Ceram. Soc., 43 452 (1960)

[22] W.Eysel, R.W.Wolfe and R.E.Newnham,
ibid, 56 185 (1973)

[23] M.Mydlar, H.Nowotny and K.J.Seifert,
Monatsh. Chem., 100 191 (1969)

[24] N.F.Borrelli and M.M.Layton,
J. Non-cryst. Solid, 6 197 (1971)

[25] J.M.Stevels,
J. Soc. Glass Technol., 35 284 (1951)

[26] G.W.Morey,
"Properties of Glass" p50, Renhold, 1954

[27] K.Nagaoka and M.Hara,
Bull. Gov. Indust. Res. Inst. Osaka, 11 115 (1960)

[28] A.G.Gregory and T.J.Versey,
J. Mater. Sci., 7 1327 (1972)

[29] R.E.Newnham, R.E.Wolfe and C.N.W.Darligton,
J. Solid State Chem., 6 378 (1973)

[30] A.N.Lazarev,
Dokl. Akad. Nauk SSSR, 183 325 (1968)