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Phase relations and crystallization of glass in the system PbO-GeO_2

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Thermal properties and chemical compositions of glasses suitable for crystallization of ferro-electric $Pb_5Ge_3O_{11}$ are described. The crystallization of lead germanate glass was investigated by DTA and X-ray diffraction. In the range from 62 to 62.5 of PbO in mole per cent, $Pb_5Ge_3O_{11}$ was obtained as a single phase after a heat treatment. In the chemical composition around $5PbO{\cdot}3GeO_2$ in the binary system of PbO-GeO_2, $Pb_5Ge_3O_{11}$ and two new phases of $Pb_3Ge_2O_7$ and Pb_3GeO_5 were found to exist. The crystal structure of $Pb_3Ge_2O_7$ had a hexagonal symmetry with $a = 10.16$ Å and $c = 19.37$ Å, and Pb_3GeO_5 was classified into orthorhombic system with $a = 4.85$ Å, $b = 15.52$ Å and $c = 11.77$ Å.

1. 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. Since the discovery of opto-electrical properties of single crystals of $LiNbO_3$, $LiTaO_3$, $BaTiO_3$ etc, an attempt to fabricate transparent ceramics with ferro-electrical properties has been made by means of two different methods. One of these is by crystallization of glass, the glass-ceramic method, and the other is by the 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 still remain some problems to be solved as mentioned below. First, in general, materials with ferro-electrical properties are difficult to prepare in the glassy state, so that a sufficient quantity of network-forming oxides 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 for the addition of network-forming oxide to impair the characteristics of ferro-electrical materials. Secondly, through the process of crystallization of glass, the primary crystalline phase is very often not the desired stable phase but a metastable one. Therefore, it is very difficult to determine the optimum composition and crystallizing conditions to prepare the transparent glass-ceramic product in which the major crystalline phase has a ferro-electrical property.

From the stand-point mentioned above, we have studied the opto-electrical properties of crystallized glasses of a quite new system in which no additional network-forming oxide is required for glass making.

In the system of PbO-GeO_2, glass-formation is possible over a wide range of lead oxide content and a single crystal of $5PbO{\cdot}3GeO_2$ shows opto-electrical effects [2, 3]. This crystal is optically uniaxial and ferro-electric below 177°C.

The synthesis and investigation of physical properties of products in this system have been carried out by many investigators [2, 4-9]. However, phase relations in this system reported by various workers [5-7] were quite confused. During the study on crystallization of glasses and opto-electrical properties of glass-ceramic products in the system of PbO-GeO_2, the phase relations were examined in detail by the authors.

The present paper deals with the phase relations in the chemical composition around $5PbO{\cdot}3GeO_2$ of the system of PbO-GeO_2 and some thermal properties of lead germanate glasses.

2. Experiments

2.1. Glass preparation

In the preparation of starting materials having the molar composition ranging from $58PbO{\cdot}42GeO_2$ to $65PbO{\cdot}35GeO_2$ in the system of

PbO-GeO_2, the required amounts of lead oxide (99.99% PbO) and germanium dioxide (99.999% GeO_2) were carefully mixed. About 50 g of batch material was pre-heated at 550°C for 10 h and melted in a platinum crucible at 1000°C in an electric furnace. After melting was completed, the melt was poured onto a steel mould and formed into a plate of about 1 mm thickness.

2.2. Crystallization

The heat-treatment for crystallization was conducted using an electric furnace. The specimen contained in a platinum basket or a fused-quartz basket was placed in the furnace and kept at 350 to 700°C for 1 min to 3 days, and then quickly cooled to room temperature. Crystallized phases were identified by X-ray diffraction.

2.3. Differential thermal analysis

Differential thermal analysis (DTA) was used to examine thermal properties of the mother glass. About 20 mg of the coarse grained powders of glass sample contained in a platinum cell (5 mm in diameter and 3 mm height) was heated in air up to 800°C with the heating rate of 10°C min^{-1} by an electric furnace. The reference material was calcined alumina (α-Al_2O_3).

2.4. Solid reaction

The chemical composition of the crystallized phase was determined by solid reaction. A mixture of lead oxide (99.99% PbO) and germanium dioxide (99.999% GeO_2) was pressed into a disc of about 5 mm in diameter and about 3 mm thickness. The specimens placed in a platinum basket reacted at 450 to 700°C for 1 to 3 days, and then rapidly cooled to room temperature and the product was identified by X-ray diffraction.

3. Results

The glass compositions used in this study are presented in Table I.

The transformations of these glasses during heating at the constant rate of 10°C min^{-1} are illustrated by the DTA traces in Fig. 1, and the characteristic temperatures are summarized in Table II.

The crystallizing phenomena of glass specimens under investigation were classified into the following three groups, (i) PG-58, PG-60 and PG-61, (ii) PG-62, PG-62.5 and PG-63, and (iii) PG-65. Each group was exemplified by PG-60, PG-62.5 and PG-65 as mentioned below.

TABLE I Chemical compositions of glasses

Sample	(mol %) PbO	(mol %) GeO_2	(wt %) PbO	(wt %) 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

TABLE II Characteristic temperatures of glasses determined by DTA at the heating rate of 10°C min^{-1}

Sample	T_g (°C)	T_c (°C)	T_t (°C)	T_L (°C)
PG-58	342	408	—	730
PG-60	337	387	—	733
PG-61	336	387	—	734
PG-62	335	387	510	735
PG-62.5	334	380	489	737
PG-63	330	380	466	735
PG-65	325	373	—	729

T_g, glass transition temperature; T_c, crystallizing temperature; T_t, temperature where the phase change from $Pb_3Ge_2O_7$ to $Pb_5Ge_3O_{11}$ occurs; T_L, liquidus temperature.

3.1. PG-60 glass

The batch material with PG-60 glass composition easily melted above 730°C in air. On quenching, a yellowish glass was formed. From the DTA trace indicated in Fig. 1, the glass transition temperature was determined to be 337°C. At a temperature in the range of 372 to 403°C, crystallization took place. This crystalline phase denoted as "phase A" had a hexagonal crystal structure with $a = 10.16$Å and $c = 19.37$Å. The X-ray diffraction data of phase A are given in Table III. This phase melted at 733°C congruently.

3.2. PG-62.5 glass

The PG-62.5 glass was easily formed by quenching of the melt. As indicated in Fig. 1, there are three exotherms and one endotherm in the DTA trace. Among them, the first exothermal step at 334°C corresponded to the glass transition. Both sharp exothermal steps at 372 to 403°C and 482 to 514°C were owing to crystallization and recrystallization respectively. From the results of X-ray diffraction analysis on these two crystalline phases, the crystalline phase

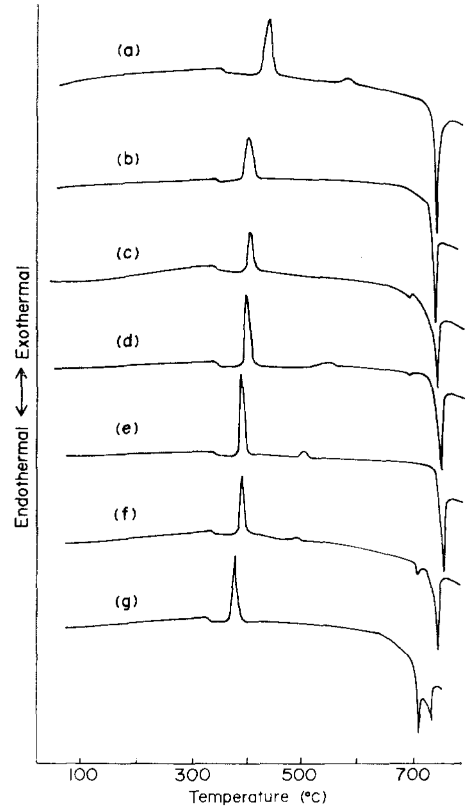

Figure 1 DTA traces of glasses, (a) PG-58, (b) PG-60, (c) PG-61, (d) PG-62, (e) PG-62.5, (f) PG-63, and (g) PG-65, at the heating rate of 10°C min^{-1}.

which appeared at a temperature in the range from 403 to 480°C was identified as phase A, and the X-ray diffraction pattern for the product which was recrystallized above 483°C agreed with that of $Pb_5Ge_3O_{11}$ single crystal reported by Sugii [2]. Therefore, the third exothermal step was assigned to the formation of $Pb_5Ge_3O_{11}$ by the reaction between $Pb_3Ge_2O_7$ and residual glass matrix. $Pb_5Ge_3O_{11}$ denoted as "phase B" melted at 737°C congruently.

3.3. PG-65 glass

In this case, when the melt with the glass composition was rapidly cooled, partial devitrification was observed. As seen in the DTA trace of Fig. 1, the glass transition and crystallization occurred at 325°C and 367 to 395°C respectively. The results of X-ray diffraction analysis indicated that after crystallization the mixture of phase B and a new crystalline phase denoted as "phase C" appeared. It was considered that the two endothermal steps of DTA trace were attributed to the melting of these two crystalline phases.

An attempt was made to determine the chemical composition and crystal structure of phase C using a solid reaction process. The amounts of products as a function of PbO mol % were estimated by the measurement of the area of the most intense peaks which correspond to those of phase B, phase C and yellow PbO in the X-ray diffraction pattern.

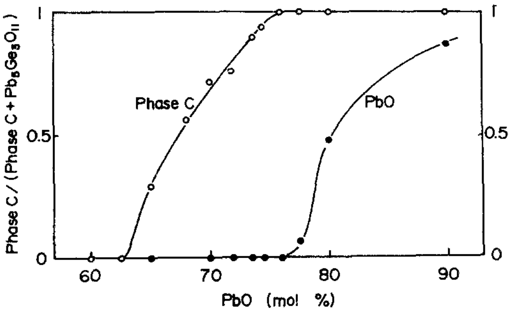

Figure 2 Relative amounts of products after the reaction between PbO and GeO_2 at 700°C for 24 h as a function of PbO mol %. ($[Pb_5Ge_3O_{11}] = I_{2\theta = 30.6}$, $[\text{Phase C}] = I_{2\theta = 28.6}$, $[PbO] = I_{2\theta = 29.2}$.)

As shown in Fig. 2, in the range where the PbO content is less than 76 mol % the yield of phase C increases with increasing PbO content, and in the range over this composition the yield is saturated and yellow PbO appears. Therefore, the chemical composition and chemical formula were determined to be $75PbO{\cdot}25GeO_2$ by mol % and Pb_3GeO_5. The melting point of this phase is 731°C.

4. Discussion

Phase relations in the system of PbO-GeO_2 reported by previous investigators are given in Fig. 3.

Speranskaya [5] studied the phase relations by the DTA method as shown in Fig. 3a, and reported the existence of several compounds with different chemical formulas 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 in this binary system, Phillips and Scroger [6] obtained five compounds of Pb_4GeO_6, $Pb_3Ge_2O_7$, $PbGeO_3$, $PbGe_2O_5$ and $PbGe_4O_9$ as indicated in Fig. 3b. From the results of solid reactions between PbO and GeO_2, Gouju [7] suggested that compounds obtained in this system were

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

Phase A; ($Pb_3Ge_2O_7$) hex. a = 10.16 Å c = 19.37 Å			Phase B; ($Pb_5Ge_3O_{11}$) hex. a = 10.23 Å c = 10.54 Å			Phase C; (Pb_3GeO_5) ortho. a = 4.85 Å b = 15.52 Å c = 11.77 Å		
d	(hkl)	I/I_0	d	(hkl)	I/I_0	d	(hkl)	I/I_0
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

Pb_3GeO_5, $Pb_3Ge_2O_7$, $PbGeO_3$ and $PbGe_4O_9$. It is obvious from Fig. 3 that there are some disagreements in phase relation between these diagrams.

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

The existence of $Pb_3Ge_2O_7$ ($3PbO{\cdot}2GeO_2$) was recognized by Phillips and Gouju. From the results of i.r. measurements on lead germanate glasses, Morozov [10] intimated the presence of $Pb_3Ge_2O_7$, but the crystal data were not given in detail. In our results, this 3:2 compound denoted as "phase A" appeared as a stable phase during crystallization of the PG-60 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 = 10.16 Å and c = 19.37 Å. These lattice parameters however, did not agree with those of $Pb_3Ge_2O_7$ reported by Phillips which was quite similar to that of $Pb_5Ge_3O_{11}$.

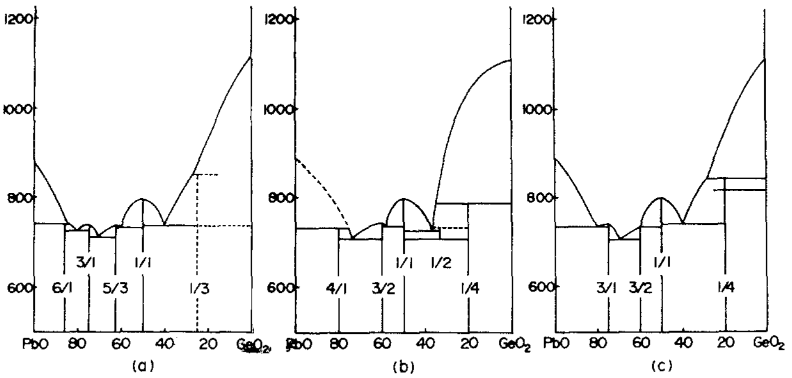

Figure 3 Phase relations in the system of PbO-GeO$_2$ proposed by (a) Speranskaya, by (b) Phillips and by c) Gouju.

$Pb_5Ge_3O_{11}$ ($5PbO{\cdot}3GeO_2$) crystallized from the PG-62.5 glass after the heat-treatment at the temperature range from 489 to 737°C. In the PG-62.5 glass, during heating, $Pb_3Ge_2O_7$ precipitated at lower temperatures and this phase easily transformed to the 5:3 phase denoted as "phase B" at 489°C. The X-ray diffraction data of phase B in this study precisely agreed with those of single crystals of $Pb_5Ge_3O_{11}$ reported by Sugii [2]. $Pb_5Ge_3O_{11}$ was very stable and no transformation was recognized during the heating up to the melting point. When the PG-65 glass, with PbO content in excess compared to that of the PG-62.5 glass, was heated at a temperature above 373°C, phases of B and C were obtained.

The 3:1 compound ($3PbO{\cdot}GeO_2$) denoted as "phase C" mentioned above was formed as a single phase after solidification of melt or solid reaction between PbO and GeO$_2$ as shown in Fig. 2. Although the existence of Pb_3GeO_5 was suggested by Speranskaya [5], Gouju [7] and Morozov [11], there was no description about X-ray diffraction data. Our data are given in Table III.

As illustrated in Fig. 2, the presence of yellow PbO was recognized in cases when the specimen with a high PbO content melted and then cooled below a liquidus temperature. Therefore there is little probability for the existence of the compound with a PbO content higher than that of Pb_3GeO_5 in the system of PbO-GeO$_2$.

A phase of Pb_2GeO_4 reported by Eulenberger *et al* [12] could not be detected in this study. Although the existence of the same phase has already been reported by Merker [4], the X-ray diffraction pattern given by him was completely indexed assuming that the phase is the mixture of $Pb_5Ge_3O_{11}$ and Pb_3GeO_5. If this procedure is reasonable, the presence of Pb_2GeO_4 would be very doubtful.

The phase relations in the chemical compositions around $5PbO{\cdot}3GeO_2$ determined using the above mentioned data are shown in Fig. 4.

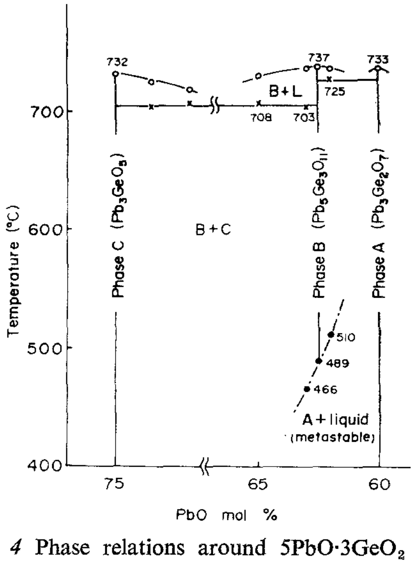

Figure 4 Phase relations around $5PbO{\cdot}3GeO_2$ in the system of PbO-GeO$_2$ determined from our work.

The characteristic temperature with transformations during the heating of each glass presented in Table II was determined as the result of the average of three measurements, and an experimental error for each measurement was at most ± 2°C. The glass transition temperature T_g decreased with increase of lead oxide content. However, the change of T_g was not so much.

Two step crystallization seen in the PG-62.5 glass were also observed in the case of glasses whose PbO content were less than 63 mol %. Below the transformation temperature from $Pb_3Ge_2O_7$ to $Pb_5Ge_3O_{11}$, co-existence of $Pb_3Ge_2O_7$ and glassy phase was confirmed as shown in Fig. 4. Assuming that the assemblage of $Pb_3Ge_2O_7$ and liquid is metastable in this region, the boundary curve joining solid circles given in Fig. 4 would be tied with the stable liquidus of $Pb_3Ge_2O_7$. The existence of metastable region of $Pb_3Ge_2O_7$ may be attributed to the structural similarity between crystalline and glass phases.

In the PG-65 glass, both phases of Pb_3GeO_5 and $Pb_5Ge_3O_{11}$ were precipitated simultaneously. Since, in this chemical composition, it is considered that the temperature region where the assemblage of $Pb_3Ge_2O_7$ and liquid existed as metastable was lower than the glass transition temperature T_g, $Pb_3Ge_2O_7$ did not crystallize. If $Pb_5Ge_3O_{11}$ appeared as a primary crystalline phase, the residual glassy phase became richer in PbO content and glassy state could not exist as a stable phase, but crystallization of Pb_3GeO_5 would occur at once.

Ferro-electric $Pb_5Ge_3O_{11}$ was easily obtained from lead germanate glasses without any deformation of the original shapes of the glass samples. From the result of dielectric measurement, the value of dielectric constant of the glass-ceramics was determined to be 23 at room temperature. This value was quite equal to that of single crystals of $Pb_5Ge_3O_{11}$. Details of dielectrical properties for glass-ceramics in this system will be presented elsewhere in future.

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