Phase Relation in the System PbO–$PbGeO_3$

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Phase relations in the system PbO–$PbGeO_3$ were determined using both the quenching and DTA techniques. Two new lead germanate phases Pb_5GeO_7 and $Pb_{11}Ge_3O_{17}$ were found to be stable. It was found that the Pb_5GeO_7 melts incongruently at 738 °C to PbO plus liquid, whereas the $Pb_{11}Ge_3O_{17}$ decomposes into Pb_5GeO_7 plus Pb_3GeO_5 at 728 °C. The compounds Pb_3GeO_5, $Pb_5Ge_3O_{11}$, and $PbGeO_3$ were identified as congruently melting compounds, in accordance with previous investigations. Some other compounds, such as Pb_6GeO_8, Pb_4GeO_6, and $Pb_3Ge_2O_7$, which have been reported previously could not be confirmed as stable phases.

The PbO–GeO_2 binary system has been studied by Speranskaya,[1] Phillips and Scroger,[2] and Gouju *et al.*[3] There is an almost total disagreement regarding intermediate phases. Speranskaya reports Pb_6GeO_8, Pb_3GeO_5, $Pb_5Ge_3O_{11}$, $PbGeO_3$, and $PbGe_3O_7$ as stable compounds, while Phillips and Scroger list Pb_4GeO_6, $Pb_3Ge_2O_7$, $PbGeO_3$, $PbGe_2O_5$, and $PbGe_4O_9$. Only the compound $PbGeO_3$ is common to the two diagrams. Gouju *et al.* report Pb_3GeO_5, $Pb_3Ge_2O_7$, $PbGeO_3$, and $PbGe_4O_9$ in their phase diagram.

Sugii, *et al.*[4] grew crystals of $PbGeO_3$, and $Pb_5Ge_3O_{11}$ successfully by means of the Czochralski method, but were unable to confirm the existence of $Pb_3Ge_2O_7$. Zwicker *et al.*[5,6] also grew crystals of $Pb_5Ge_3O_{11}$ by the Czochralski method. The prototype structures of $Pb_5Ge_3O_{11}$ and Pb_3GeO_5 were described by Newnham *et al.*[7] and Neurgaonkar *et al.*[8] respectively. These studies on single crystals of $Pb_5Ge_3O_{11}$ and Pb_3GeO_5 agree with Speranskaya's data, but disagree with those of Phillips *et al.* and Gouju *et al.* Contrary to Speranskaya's phase diagram, Pentegova *et al.*[9] have concluded that the $Pb_3Ge_2O_7$ is a stable phase.

The aim of the present study is to examine the discrepancies among these phase diagrams and to establish the phase relations of intermediate compounds in the system PbO–$PbGeO_3$.

Experimental

General Procedure. Two different experimental methods were used in the present investigation: quenching and differential thermal analysis (DTA). In the quenching method, samples were heated at given temperatures until an equilibrium was attained among stable phases. The samples were then quenched rapidly to room temperature and the phases present were determined by electron probe microanalysis, X-ray diffraction, and microscopic examination.

Melting and crystallization temperatures were obtained by means of DTA. Melting temperature of each compound obtained was also ascertained by the quenching method.

Starting Materials. Commercial GeO_2 of purity 99.99% and a purified PbO were used as starting materials. The PbO was prepared from basic lead carbonate. A raw basic lead carbonate was brought into a lead nitrate solution by treating with an equivalent nitric acid. The solution was added with aqueous ammonia to form a small amount of lead hydroxide precipitate. After standing in a water bath for about 10 h, the solution was filtered. The solution was then heated again in a water bath, and an equivalent sulfuric acid was added to it. The precipitate with its mother liquid was heated in a water bath for a day and the volume of the precipitate was allowed to decrease. The precipitate was filtered, washed, and mixed with an excess of ammonium carbonate to bring the precipitate into lead carbonate. The mixture was heated overnight in a water bath, filtered, and washed. The washed precipitate was treated with nitric acid to bring the carbonate into a solution of lead nitrate. The solution was kept again in a water bath for a day and filtered. After that, lead nitrate crystals were allowed to deposit from the filtrate. The lead nitrate was heated at 420 °C in air, and PbO was obtained as product. Only about 10 ppm of Al and Ni were detected in the PbO by means of spectroscopic analysis.

Furnace and Temperature Control. A vertical-tube quench furnace with three heating zones was used for the equilibration runs. About 10 cm length of even heating zone reduced the total variation of temperature of the sample to less than ±0.5 °C. The actual temperature in the furnace was measured with a Pt–PtRh (13%) thermocouple which was calibrated against the melting point of gold. Frequent calibration was necessary because a decrease in emf of the thermocouple was found after a series of runs.

Checking of Equilibration and Quenching Procedures. The approach to equilibrium was studied by X-ray diffraction and microscopy. The quenched samples in the equilibration runs were examined as a function of time. Starting from a mixture of PbO and GeO_2, a complex mixture of more than 3 phases of intermediate compounds was obtained for short runs. Two phases or a single phase was found at equilibrium. The equilibrium was approached closely, for example, after several hundred hours of reaction poriod at about 650 °C. Starting from glasses, metastable crystalline phases were found after short runs.

Liquids of high PbO concentrations could not be quenched to glasses. The presence of a liquid phase, therefore, was evidenced by meniscus formation from the powdered compound in question.

Differential Thermal Analysis. About 2 g of PbO and GeO_2 were mixed and enclosed by welding in a platinum capsule, 6 mm in diameter and 35 mm long. The platinum capsule was mounted in a silver block and heated. The use of the silver block, which resulted in a long zone of even heating, reduced the total variation of temperature within the lead germanate sample to less than 2 °C.

Electron Probe Microanalysis. A mixture of PbO and GeO_2, mixed thoroughly in an agate mortar, was enclosed in a platinum tube by welding and kept at 800 °C for several hours in a vertical tube furnace, and allowed to fall into chilled water. Three kinds of glasses thus obtained and the two pure oxides were used as standards of known compositions to determine the correction factor. The oxide binary has been known to have the following linear relationship for C/K *vs.* C:

$$C/K = \alpha + (1-\alpha)C,$$

Table 1. Analytical results by electron probe microanalysis

Starting materials		Temp	Duration	Products						
				Phase 1			Phase 2			
Phase	Composition mol %PbO	°C	h	GeO_2/wt %	PbO/wt %	Pb/Ge	GeO_2/wt %	PbO/wt %	Pb/Ge	Phases
PbO+GeO_2	85.7	730	130	8.6	92.6	5.05	0	100	—	Pb_5GeO_7+PbO
PbO+GeG_2	86.0	660	290	8.9	92.7	4.88	0	100	—	Pb_5GeO_7+PbO
PbO+GeO_2	83.4	717	250	8.8	91.7	4.89	—	—	—	Pb_5GeO_7
Glass	82.0	636	288	8.8	92.2	4.91	11.0	89.6	3.82	Pb_5GeO_7+$Pb_{11}Ge_3O_{17}$
PbO+GeO_2	81.0	660	290	8.9	92.1	4.85	11.3	89.7	3.72	Pb_5GeO_7+$Pb_{11}Ge_3O_{17}$
Glass	80.0	726	200	9.0	90.2	4.70	11.6	87.9	3.50	Pb_5GeO_7+$Pb_{11}Ge_3O_{17}$
				av 8.8	91.9	4.88				
				(calcd 8.57	91.4	5.00)				(Pb_5GeO_7)
PbO+GeO_2	90.0	602	1840	0	100	—	11.5	89.6	3.65	PbO+$Pb_{11}Ge_3O_{17}$
Glass	77.7	603	520	13.9	84.3	2.84	11.8	86.3	3.42	Pb_3GeO_5+$Pb_{11}Ge_3O_{17}$
Glass	76.0	706	530	13.8	85.1	2.89	11.5	86.8	3.54	Pb_3GeO_5+$Pb_{11}Ge_3O_{17}$
							av 11.4	88.5	3.62	
							(calcd 11.33	88.67	3.67)	($Pb_{11}Ge_3O_{17}$)
PbO+GeO_2	75.0	730	100	13.6	84.2	2.90	—	—	—	Pb_3GeO_5
PbO+GeO_2	70.0	701	350	13.7	85.5	2.92	21.2	77.4	1.71	Pb_3GeO_5+$Pb_5Ge_3O_{11}$
Glass	67.0	603	520	13.7	84.8	2.90	21.6	79.4	1.72	Pb_3GeO_5+$Pb_5Ge_3O_{11}$
				av 13.7	84.7	2.89				
				(calcd 13.51	86.49	3.00)				(Pb_3GeO_5)
PbO+GeO_2	62.5	730	130	—	—	—	22.3	77.2	1.62	$Pb_5Ge_3O_{11}$
Glass	55.0	706	530	31.7	67.8	1.00	22.1	76.2	1.62	$PbGeO_3$+$Pb_5Ge_3O_{11}$
				(calcd 31.91	68.09	1.00	av 21.8	77.6	1.67	($PbGeO_3$)
							(calcd 21.95	78.05	1.67)	($Pb_5Ge_3O_{11}$)

where C is the concentration of oxide in weight, K is the background-corrected intensity of characteristic radiation relative to that of the element in the pure oxide, and α is the constant introduced by Bence and Albee.[10] Under the present experimental conditions, *i.e.*, 20 kV accelerating potential and 40° take-off angle, the correction factor α was determined as follows: $\alpha^{Pb}_{GeO_2}=1.50$ and $\alpha^{Ge}_{PbO}=1.54$. Relative deviations of the analysis were determined by replicate analysis and are within ±2% for PbO and GeO_2 respectively.

Results and Discussion

Identification of Phases. The phases present in quenched samples were identified by X-ray diffraction and electron probe microanalysis. Selected results are summarized in Table 1.

Four phases with intermediate compositions were detected between PbO and $PbGeO_3$. These compositions of intermediate phases can be represented approximately by the following formulae: Pb_5GeO_7, $Pb_{11}Ge_3O_{17}$, Pb_3GeO_5, and $Pb_5Ge_3O_{11}$. The latter two, Pb_3GeO_5 and $Pb_5Ge_3O_{11}$ have been reported by Speranskaya. But the former two phases, Pb_5GeO_7 and $Pb_{11}Ge_3O_{17}$, have not been reported yet.

Equilibrium relations are illustrated in Fig. 1. The Pb_5GeO_7 was determined to be stable only between 738 °C and 632±7 °C. The composition of this phase was determined to be 4.9±0.2 in atomic ratio of Pb/Ge. The crystal structure determined by Kato indicates that the site ratio of Pb to Ge in the crystal lattice is equal to 5.[11] These results are consistent with each other within the experimental errors.

The phase $Pb_{11}Ge_3O_{17}$ seems the same compound as "Pb_4GeO_6" reported by Phillips and Scroger. X-Ray diffraction data on Pb_4GeO_6 shown by them could be indexed assuming that the sample was mainly $Pb_{11}Ge_3O_{17}$ mixed with a small amount of Pb_5GeO_7.

The analytical results of this phase ranged from 79.3 to 77.4 mol % PbO; this variation is considered to be within analytical errors. This phase is not regarded as a solid solution but as a compound with a constant composition. Preliminary study of the crystal structure of this compound indicates that there are 14 metal sites in a subunit cell, after Kato.[14] The average atomic ratio Pb/Ge=3.62 and the number of metal sites for this compound indicate the formula of $Pb_{11}Ge_3O_{17}$ (Pb/Ge=3.67) to be the compound with the simplest integral ratio.

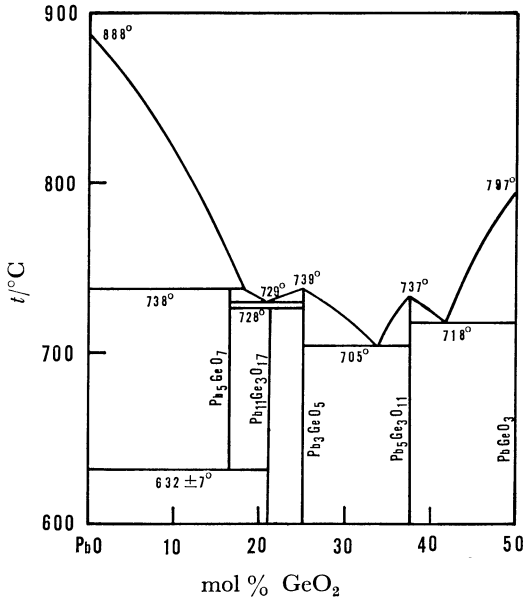

Fig. 1. Phase relations in the system PbO–$PbGeO_3$.

TABLE 2. X-RAY DIFFRACTION DATA OF POWDER SAMPLES

Pb_5GeO_7		$Pb_{11}Ge_3O_{17}$	
d spacing Å	Relative intensity	d spacing Å	Relative insensity
6.70	2	7.35	11
5.78	6	3.534	3
4.082	6	3.286	6
3.715	16	3.268	4
3.341	15	3.188	13
3.290	13	3.159	67
3.064	100	3.122	10
2.950	19	3.054	100
2.885	57	2.951	29
2.848	28	2.763	64
2.776	13	2.668	22
2.756	26	2.576	16
2.327	13	2.499	12
2.260	6	2.333	3
2.216	9	1.983	4
2.041	10	1.928	10
1.907	17	1.879	14
1.877	5	1.851	13
1.842	5	1.838	12
1.811	13	1.796	4
1.800	4	1.591	10
1.752	2	1.580	10
1.742	7		
1.698	24		
1.645	10		
1.562	10		
1.556	11		

Not Substantiated Compounds. No evidence for the existence of the compounds Pb_6GeO_8 and Pb_2GeO_4 was obtained in this work. Speranskaya has reported Pb_6GeO_8 as stable. It is difficult to determine the chemical composition by means of DTA only, when a compound melts incongruently. The phase Pb_5GeO_7, found in the present investigation, melts incongruently at 738±2 °C, while the Pb_6GeO_8 also has been reported to melt incongruently at 740 °C. It is noteworthy that the temperatures of incongruent melting of the two are in good agreement with each other within experimental errors. The methods adopted to determine the chemical composition of the phase Pb_6GeO_8 were not given.

The phase Pb_2GeO_4 has been reported by Merker *et al.*[12] An X-ray diffraction pattern has been given. But Hasegawa *et al.*[13] have pointed out that this diffraction pattern can be completely indexed by as-

suming that the phase is a mixture of $Pb_5Ge_3O_{11}$ and Pb_3GeO_5.

The stability of a $Pb_3Ge_2O_{11}$ compound could not be substantiated at the temperature range in our experiment. The result is in accordance with Zwicker *et al.* and Sugii *et al.* The congruently melting phase in question is not $Pb_3Ge_2O_7$ but $Pb_5Ge_3O_{11}$. Hasegawa *et al.* have reported that $Pb_3Ge_2O_7$ crystallized from a glass at lower temperatures and transformed to $Pb_5Ge_3O_{11}$ at 489 °C. In the present investigation the presence of a phase with composition $Pb_3Ge_2O_7$ could not be verified at 600 °C, the lowest temperature in our experiment; the product after 1600 h of reaction period was a mixture of $Pb_5Ge_3O_{11}$ and $PbGeO_3$.

It may seem surprising that the three published phase diagrams in the system $PbO-GeO_2$ disagree with one another, and that the existence of compounds such as $Pb_5Ge_3O_{11}$ or Pb_3GeO_5 has been questioned several times. One of the reasons for this is probably due to the presence of metastable phases. Slow cooling of melts tried by Pentegova *et al.*, is not necessarily adequate to investigate the phase relations in the system $PbO-GeO_2$. For example, Zwicker *et al.* have shown that, in the system $PbO-GeO_2$, slow cooling can substantially bring about super-cooling of the melt, and rapid crystallization may form metastable crystalline phases.

In order to assure the equilibrium state in this system, therefore, it is essential to keep the sample at constant temperature and composition for a sufficiently long time, this was tried in the present investigation.

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