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The Crystallization of $Pb_5Si_3O_{11}$ from the Glass in the PbO-SiO_2 System

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Synopsis. A new compound, $Pb_5Si_3O_{11}$, is prepared by the crystallization of the glass in the PbO–SiO_2 system. $Pb_5Si_3O_{11}$ has an orthorhombic symmetry, and its lattice parameters are determined to be a_0=9.93 Å, b_0=8.31 Å, and c_0=34.4 Å.

During the course of a systematic study of the crystallizing phenomena of lead germanate glasses and of lead germanosilicate glasses,[1,2] it was found that a ferroelectric crystalline phase, $Pb_5Ge_3O_{11}$, was easily obtained from the $5PbO \cdot 3GeO_2$ glass, that the glass-ceramic product was transparent, and that a ferroelectric solid solution, $Pb_5Ge_{3-x}Si_xO_{11}$ ($0 \leq x \leq 2$), was precipitated from the $5PbO \cdot (3-X)GeO_2 \cdot XSiO_2$ glass ($0 \leq X \leq 2$).

Eysel *et al.*[3] reported that the single crystals of the $Pb_5(Ge, Si)_3O_{11}$ solid solution, containing up to 62% of Si replacing Ge, were prepared from the melt. Assuming that Si can be completely substituted for Ge in a nearly ideal fashion, the presence of $Pb_5Si_3O_{11}$ can be expected. As to the PbO–SiO_2 system, Ott and McLaren[4] obtained a corrected phase diagram by means of the crystallization of lead silicate glasses and suggested the existence of five compounds: Pb_4SiO_6, Pb_3SiO_5, Pb_2SiO_4, $Pb_3Si_2O_7$, and $PbSiO_3$. More recently, Smart and Glasser[5] studied the phase equilibria in this system and reported the existence of six compounds: Pb_4SiO_6, Pb_3SiO_5, Pb_2SiO_4, $Pb_3Si_2O_7$, $PbSiO_3$ and $Pb_5Si_8O_{21}$. However, the existence of the $Pb_5Si_3O_{11}$ compound has not been reported.

The purpose of this research is to ascertain the existence of $Pb_5Si_3O_{11}$ by using the crystallization of lead silicate glasses.

Experimental

Pure lead monoxide and silicic acid were carefully mixed. About 50 g of the mixture was preheated at 550 °C for 10 h, and then melted in a platinum crucible at 800 °C. After the melting has been completed, the melt was poured onto a steel mould and formed into a plate glass. The compositon of the glass was checked by chemical analysis. The specimen prepared in this way was placed in a platinum basket, heated in an electric furnace at temperatures from 350 to 650 °C for 1 to 340 h, and then quickly cooled to room temperature. The crystallized phases after the heat-treatment were identified by powder X-ray diffraction analysis.

Results and Discussion

A microcrystalline phase, denoted as "Phase X," was precipitated in the $5PbO \cdot 3SiO_2$ glass by heating at about 400 °C. This phase was stable up to 600 °C, but decomposed at a higher temperature into Pb_2SiO_4 and $PbSiO_3$. According to the phase diagram of this system reported by Ott and McLaren, the major crystalline phase precipitated from the $5PbO \cdot 3SiO_2$ glass might be $Pb_3Si_2O_7$. However, the powder X-ray diffraction pattern of Phase X was similar not to that of lead-barysilite, $Pb_3Si_2O_7$, reported by Billhardt,[6] but to that of ferroelectric $Pb_5Ge_3O_{11}$ as shown in Fig. 1.

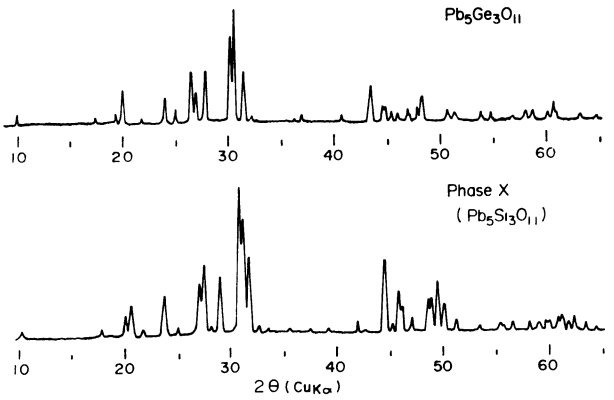

Fig. 1. X-Ray diffraction patterns of Phase X and $Pb_5Ge_3O_{11}$.

On the basis of the crystal structure of $Pb_5Ge_3O_{11}$, the crystal structure of Phase X was determined to be pseud-hexagonal and orthorhombic. Its lattice parameters were calculated to be a_0=9.93 Å, b_0=8.31 Å. and c_0=34.4 Å. The X-ray diffraction data of Phase X are tabulated in Table 1.

TABLE 1. X-RAY DIFFRACTION DATA OF PHASE X

(h k l)	I/I_0	d_{obsd}	d_{calcd}	(h k l)	I/I_0	d_{obsd}	d_{calcd}
1 0 2	5	8.616	8.600	3 2 4	2	2.480	2.479
1 0 6	10	4.962	4.965	3 0 10	2	2.384	2.385
1 0 7	15	4.410	4.404	1 2 12	2	2.300	2.296
2 0 4	30	4.300	4.300	4 0 8	5	2.149	2.150
2 1 2	5	4.111	4.117	1 1 16	40	2.037	2.037
0 2 4	30	3.738	3.741	5 0 0	15	1.982	1.986
1 1 8	10	3.564	3.564	2 0 16	10	1.976	1.973
3 0 0	30	3.294	3.301	5 0 4	10	1.932	1.935
2 0 8	45	3.250	3.250	5 0 6	20	1.877	1.877
1 2 6	2	3.169	3.168	0 1 18	15	1.864	1.862
3 0 4	40	3.076	3.079	4 3 2	30	1.840	1.838
3 1 4	100	2.896	2.896	2 0 18	10	1.783	1.784
3 0 6	75	2.867	2.867	6 0 2	2	1.646	1.647
2 0 10	45	2.821	2.818	6 0 4	5	1.625	1.625
3 0 7	2	2.744	2.745	6 0 6	2	1.589	1.590
0 3 3	2	2.696	2.693	0 0 22	5	1.562	1.562

Orthorhombic; a_0=9.93Å
b_0=8.31Å
c_0=34.4Å ($2\sqrt{3} \cdot a_0$)

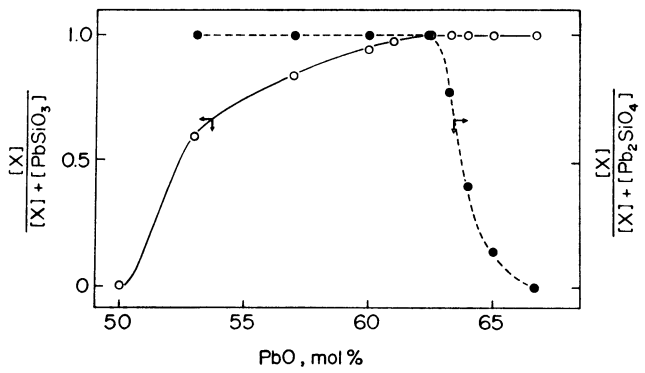

Fig. 2. Relative amounts of products after the crystallization of the glasses as functions of the PbO content of the glass.

Phase X was obtained only through the crystallization of glass. All the attempts to synthesize Phase X by the usual solid-state-reaction methods and by the solidification of the melts failed.

The chemical composition of Phase X was determined by using the following process. Powder glass samples with ten compositions, ranging from 50.1%PbO·49.9%SiO_2 to 66.7%PbO·33.3%SiO_2 in mol, were heat-treated at about 550 °C for 340 h, and the amounts of crystallized products were estimated from the intensities of the most intense peaks of Phase X, Pb_2SiO_4 and $PbSiO_3$. The crystallization of the glasses investigated was completed within about 5 h at 550 °C, so that our experimental conditions—at 550 °C for 340 h—are sufficient to reach the equilibrium state. A microscopic examination of crystallized products showed that the sample was completely crystalline. The relation between the amounts of each phase and the PbO contents of the glass is illustrated in Fig. 2. As is shown in this figure, in the range where the PbO content is less than 62.5%, the yield of Phase X increased with an increase in the PbO content, and in the range where the PbO content is more than 62.5%, mixtures of Phase X and Pb_2SiO_4 were observed. From these results, the chemical composition and the chemical formula of Phase X were determined to be 62.5%PbO·37.5%SiO_2 and $Pb_5Si_3O_{11}$.

In conclusion, in the present research the existence of a new crystalline phase, $Pb_5Si_3O_{11}$, has been confirmed by using the crystallization of lead silicate glasses.

References

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