Effect of Glass Composition on Chemical Reaction between Lead Zirconate Titanate and Glasses (Part 2)

—Lead-silicate and Lead-borosilicate Glasses—

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ジルコン酸チタン酸鉛とガラスの化学反応に及ぼすガラス組成の影響 (第2報)

—ケイ酸鉛ガラスとホウケイ酸鉛ガラス—

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The products of reaction between $\text{Pb}(\text{Zr}_{0.53}\text{Ti}_{0.47})\text{O}_3$ (PZT) and glasses in the PbO-SiO_2 and $\text{PbO-B}_2\text{O}_3\text{-SiO}_2$ systems at 850°C were studied using powder and bulk PZT samples. A reaction zone was formed between bulk PZT and the glass. The microstructure of the reaction zone changed with the amount of PZT dissolved in the glass phase, which was dependent on the activity of PbO in both the glass phase and PZT. When the amount of dissolved PZT was small, as in the reaction between PZT and 60 mol% $\text{PbO} \cdot 40$ mol% SiO_2 glass, the glass phase penetrated into grain boundaries of PZT, and no solid reaction product was formed. When the amount of dissolved PZT was intermediate, as in that between PZT and 40 mol% $\text{PbO} \cdot 60$ mol% SiO_2 glass, the glass phase penetrated into the PZT pellet and ZrO_2 particles were precipitated in the glass phase. When the amount of dissolved PZT was large, as in those between PZT and 60 mol% $\text{PbO} \cdot 20$ mol% $\text{B}_2\text{O}_3 \cdot 20$ mol% SiO_2 glass and 40 mol% $\text{PbO} \cdot 30$ mol% $\text{B}_2\text{O}_3 \cdot 30$ mol% SiO_2 glass, the reaction zone was formed, which was composed of Ti-rich PZT and ZrO_2 particles dispersed in the glass phase.

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1. Introduction

Glasses are an important material in the application of dielectric and piezoelectric ceramics, and the chemical interaction between ceramics and glasses must be understood to design the ceramic devices. In the preceding paper (Part 1),¹⁾ we examined the chemical reaction between $\text{Pb}(\text{Zr}_{0.53}\text{Ti}_{0.47})\text{O}_3$ (PZT) and $\text{PbO-B}_2\text{O}_3$ glasses. In this paper, we used the glasses in the PbO-SiO_2 and $\text{PbO-B}_2\text{O}_3\text{-SiO}_2$ systems. The same experimental methods as those used in Part 1, using powder and bulk PZT, were employed in this work. We will mainly deal with the reaction products and microstructure of the reaction zone between bulk PZT and glasses.

2. Experimental procedures

The detailed experimental procedures were described in the preceding paper.¹⁾ Here, the procedures are briefly described. PZT powder was prepared by heating the mixture of PbO , TiO_2 , and ZrO_2 (1.00 : 0.53 : 0.47 in the molar ratio) at 885°C for 4 h. Part of the resultant PZT powder was used in the powder reaction experiment. The remaining powder was used to prepare sintered disks by heating at 1100°C for 1.5 h. Lead-silicate and lead-borosilicate glass powders were prepared by melting the mixtures of PbO , SiO_2 , and B_2O_3 powders in platinum crucibles at 1200°C for 1.5 h, quenching, and stamp-milling. The nominal composition is expressed in mol%; 40% $\text{PbO} \cdot 60$ % SiO_2 (PS40), 60% $\text{PbO} \cdot 40$ % SiO_2 (PS60), 40% $\text{PbO} \cdot 30$ % $\text{B}_2\text{O}_3 \cdot 30$ % SiO_2 (PBS40), and 60% $\text{PbO} \cdot 20$ % $\text{B}_2\text{O}_3 \cdot 20$ % SiO_2 (PBS60).

Green compacts of the mixtures of PZT and glass powders (PZT : glass = 1 : 1 by weight unless otherwise stated) and PZT pellets buried in the glass powder were heated in a furnace kept at 850°C. The glasses used in this experiment must be completely melted at this temperature, as judged

from the phase diagrams.^{2),3)} After heating for 30 min, the samples were cooled slowly in the furnace or quickly by quenching in air. In some experiments, PbZrO_3 and PbTiO_3 powders were used in the powder reaction. The phases present were identified by the X-ray diffraction (XRD) analysis, and microstructure and distribution of elements were observed with a scanning electron microscope (SEM) and electron-probe X-ray microanalyzer (EPMA), respectively.

3. Results and discussion

3.1 Lead-silicate glasses

The microstructure of interfacial region between the PZT pellet and glass was changed with the glass composition and cooling rate. Figure 1 shows the microstructure of interfacial regions of PZT pellet-PS40 glass and PZT pellet-PS60 glass. The microstructure shown in Fig. 1(a) is PZT/PS40 cooled quickly. The same microstructure was obtained by slow-cooling, indicating that the cooling rate gave a small effect on the microstructure in this sample. The glass dissolved PZT grains and penetrated into the PZT pellet. The penetration of glass was not uniform. Probably, the PZT pellet was not completely homogeneous, and the dissolution rate was dependent on the position. In the glass phase penetrating into the PZT pellet, small black particles are observed.

The PS60 glass gave different microstructure and the microstructure was influenced by a cooling rate. The glass penetrated into the PZT pellet by dissolving grain boundaries. No solid product formed in the sample cooled quickly (Fig. 1(b)), but black materials were present at the interfacial region between PZT and the glass phase in the sample cooled slowly (Fig. 1(c)); the black materials precipitated during cooling.

The mechanisms of formation of the interfacial micro-

Fig. 1. SEM microphotographs of the PZT/PS40 (a) and PZT/PS60 (b) samples cooled quickly and the PZT/PS60 sample (c) cooled slowly, obtained by the reaction between PZT pellet and glass. The left- and right-hand sides are PZT and glass, respectively.

structure were examined from the EPMA and XRD results using bulk and powder PZT, respectively.

PZT/PS40: Figure 2 shows the EPMA result of the PZT/PS40 sample obtained by the reaction between the PZT pellet and glass. The areas with the presence of Si and absence of Ti in the PZT pellet indicate the penetrating glass phase. The Si concentration decreased as the depth of penetration increased, for which the dissolution of PZT was responsible. Zr-rich and Pb-, Ti- and Si-poor areas are present in the penetrating glass phase, indicating that the black particles in Fig. 1(a) are mainly composed of ZrO_2 .

Figure 3(a) shows the XRD pattern of the PZT/PS40 powder mixture (1 : 1 by weight) heated at 850°C for 30 min and cooled quickly. Several new diffraction lines in addition to those of PZT were present, indicating the formation of a new compound. The same new lines were observed in the XRD pattern (Fig. 3(b)) of the PbZrO_3 /PS40 powder mixture (1 : 1 by weight) treated by the same heating program, but they were not observed in the PbTiO_3 /PS40 powder mixture (1 : 1 by weight) (Fig. 3(c)). No compounds having the same diffraction lines as this reaction product were found in the JCPDS data files. Probably, the reaction product is a compound in the $\text{PbO-SiO}_2\text{-ZrO}_2$ system. This compound will be referred to as phase X.

The product of powder reaction was dependent on the mixing ratio of PZT or PbZrO_3 to PS40. Figure 3(d) shows the XRD pattern of the PbZrO_3 /PS40 powder mixture (2 : 1 by weight) heated at 850°C for 30 min and cooled quickly. In this case, the reaction product was ZrO_2 as well as phase X.

Phase X and ZrO_2 were formed in the PbZrO_3 /PS40 powder mixtures. However, it is impossible for both of these two phases to be stable phases in equilibrium with PbZrO_3 and glass melt, as judged from the phase rule. The degree of freedom (F) available to the system under constant pressure is determined by $F = C - P + 1$, where C is the number of components and P is the number of equilibrium phases. For the present system ($\text{PbZrO}_3\text{-PbO-SiO}_2$), $C = 3$. When PbZrO_3 , glass melt, ZrO_2 , and phase X are equilibrium phases and coexist as in the sample shown in Fig. 3(d), the degree of freedom is zero. However, the coexistence of four phases (PbZrO_3 , glass melt, ZrO_2 , and phase X) was observed in the PbZrO_3 /PS40 samples heated between 800° and 850°C and quenched. Therefore, both phase X and ZrO_2 are not the stable phases in equilibrium with PbZrO_3 and glass melt.

Fig. 2. Microstructure (a) and distribution of Pb (b), Zr (c), Ti (d), and Si (e) in the PZT/PS40 sample cooled quickly, obtained by the reaction between PZT pellet and glass. The left- and right-hand sides are PZT and glass, respectively.

Fig. 3. XRD patterns of products in the powder reaction between PS40 and PZT (a), PbZrO_3 (b), and PbTiO_3 (c) with the mixing ratio 1 : 1 by weight and between PS40 and PbZrO_3 (d) with the mixing ratio 1 : 2. All samples were cooled quickly.

ZrO_2 is probably metastable as compared with phase X. When PZT or PbZrO_3 dissolves in the glass melt, the con-

stituent oxides dissolve completely and the ZrO_2 concentration exceeds the solubility limit. In general, the solubility of metastable phase is larger than that of stable phase. Therefore, at small supersaturation, the concentration of a precipitating component exceeds the solubility limit with respect to the stable phase but stays within the solubility limit with respect to the metastable phase. In the present case, the ZrO_2 concentration is smaller in the $\text{PbZrO}_3/\text{PS40}$ mixture with the ratio 1 : 1 than that with the ratio 2 : 1. Phase X precipitated in the former mixture. Thus, phase X is judged to be more stable phase.

From above discussion, it is possible that ZrO_2 and phase X are precipitated from glass melt with high and low ZrO_2 concentration, respectively. However, the supersaturation, not the ZrO_2 concentration, determines the precipitation behavior. Therefore, we will use the degree of supersaturation, instead of the ZrO_2 concentration, in the explanation of the precipitation of reaction products.

The mechanism of formation of the interfacial microstructure (Fig. 1(a)) can be explained as follows. PZT dissolves in the PS40 glass melt, but the dissolution rate is dependent on the characteristics of PZT grains. The glass melt penetrates into PZT by dissolving grain boundaries. In the penetrating glass melt, the concentration of PbO , ZrO_2 , and TiO_2 increases. The solubility of ZrO_2 and TiO_2 in the glass melt is estimated from the glass-forming regions in the $\text{PbO-SiO}_2\text{-ZrO}_2$ and $\text{PbO-SiO}_2\text{-TiO}_2$ systems (Fig. 4);⁴⁾ TiO_2 has larger solubility than ZrO_2 . Thus, while TiO_2 can continue to dissolve in the glass melt but the ZrO_2 concentration exceeds the solubility limit. In the penetrating glass melt, the relative amount of PZT to PS40 is large and therefore the degree of supersaturation is large, resulting in the precipitation of ZrO_2 particles.

PZT/PS60: Figure 5 shows the EPMA result of the slowly-cooled PZT/PS60 sample obtained by the reaction between the PZT pellet and glass. The black materials were composed of Pb, Zr, and Si.

Figure 6 shows the XRD patterns of the products of powder reaction at 850°C for 30 min. In the sample cooled quickly (Fig. 6(a)), no crystalline phase except for PZT was

present, indicating that no reaction product was precipitated at 850°C . The different behavior compared with the PZT/PS40 mixture is explained by the amount of dissolved PZT. The amount of dissolved PZT is expected to be smaller in the PZT/PS60 mixture than in the PZT/PS40 mixture, because the PbO content and the activity of PbO are higher in the PS60 glass than in the PS40 glass.¹⁾ Therefore, the concentration of ZrO_2 and TiO_2 does not exceed the solubility limit, and no solid product forms in the PZT/PS60 mixture

Fig. 5. Microstructure (a) and distribution of Pb (b), Zr (c), Ti (d), and Si (e) in the PZT/PS60 sample cooled slowly, obtained by the reaction between PZT pellet and glass. The left- and right-hand sides are PZT and glass, respectively.

Fig. 4. Glass-forming regions in the $\text{PbO-SiO}_2\text{-TiO}_2$ and $\text{PbO-SiO}_2\text{-ZrO}_2$ systems.

Fig. 6. XRD patterns of products in the powder reaction between PS60 and PZT (1 : 1 by weight) cooled quickly (a) and slowly (b).

at 850°C.

In the slowly-cooled sample obtained by the powder reaction (Fig. 6(b)), new diffraction lines appeared. These lines belong to Pb_2SiO_4 ,⁵⁾ indicating that a small amount of Pb_2SiO_4 crystallizes during cooling.⁶⁾ This compound is not the black materials observed in the sample obtained by the reaction of bulk PZT (Fig. 1(c)), because the black materials contain Zr and the concentration of Pb and Si in the black materials is lower and higher than that in the glass phase (60 mol% PbO), as judged from Fig. 5. The black materials may be phase X, even though it is not detected by XRD in the product of powder reaction (Fig. 6(b)). The constituent oxides of PZT completely dissolve in the glass melt at 850°C until the activity of PbO in the glass melt reaches that in PZT. During cooling, the solubility of ZrO_2 decreases as the temperature decreases, and phase X precipitates under the small degree of supersaturation.

The concentration of the constituent oxides of PZT dissolved in the glass melt probably determines the solid product in the slowly-cooled samples. In the sample obtained by the reaction of bulk PZT, the relative amount of PZT to PS60 is large and the concentration of ZrO_2 is high as compared with that in the sample obtained by the powder reaction, resulting in the formation of phase X during cooling. In the sample obtained by the powder reaction, on the other hand, the relative amount of PZT to PS60 is small and the concentration of ZrO_2 is low. Thus, the rate of precipitation of phase X is small. The rate of crystallization might be increased by the introduction of TiO_2 and/or ZrO_2 , and Pb_2SiO_4 forms in the sample obtained by the powder reaction (the PS60 glass itself did not crystallize by slow-cooling).

3.2 Lead-borosilicate glasses

Figure 7 shows the microstructure of interfacial region of the PZT/PBS40 and PZT/PBS60 samples obtained by the reaction between the PZT pellet and glass.

PZT/PBS40: The microstructure shown in Fig. 7(a) is PZT/PBS40 cooled quickly. The same microstructure was obtained by slow-cooling, indicating that the cooling rate gave a small effect on the microstructure. The reaction zone similar to that observed between PZT and the 40 mol% PbO ·60 mol% B_2O_3 glass (PB40) (Fig. 8 of Part 1¹⁾) developed between PZT and the glass phase. The reaction zone was composed of two layers; layer I contained white and

Fig. 7. SEM microphotographs of the PZT/PBS40 (a) and PZT/PBS60 (b) samples cooled quickly and the PZT/PBS60 sample (c) cooled slowly, obtained by the reaction between PZT pellet and glass. The left- and right-hand sides are PZT and glass, respectively.

black particles and layer II contained black particles. The white and black particles are Ti-rich PZT and ZrO_2 , respectively, as in the case of the PZT/PB40 sample (the EPMA result is not shown here). The formation mechanism of the zone is the same as that of PZT/PB40.¹⁾

PZT/PBS60: The microstructure of the PZT/PBS60 sample obtained by the reaction between the PZT pellet and glass was dependent on the cooling rate. The glass melt dissolved PZT and penetrated into grain boundaries of PZT and black particles were formed in the sample cooled quickly (Fig. 7(b)). Figure 8 shows the EPMA result, indicating that the black particles are ZrO_2 particles. Figure 9 shows the XRD pattern of the product of powder reaction between PZT and PBS 60 heated at 850°C for 30 min and cooled quickly. The diffraction lines of ZrO_2 were confirmed. Furthermore, the comparison between Figs. 9 and 6(a) indicates that the c/a ratio of PZT in the PZT/PBS60 mixture is larger than that of PZT in the PZT/PS60 mixture. These

Fig. 8. Microstructure (a) and distribution of Pb (b), Zr (c), Ti (d), and Si (e) in the PZT/PBS60 sample cooled quickly, obtained by the reaction between PZT pellet and glass. The left- and right-hand sides are PZT and glass, respectively.

Fig. 9. XRD pattern of product in the powder reaction between PBS60 and PZT (1:1 by weight) cooled quickly.

Fig. 10. Microstructure (a) and distribution of Pb (b), Zr (c), Ti (d), and Si (e) in the PZT/PBS60 sample cooled slowly, obtained by the reaction between PZT pellet and glass. The left- and right-hand sides are PZT and glass, respectively.

results indicate that the solid reaction products are Ti-rich PZT and ZrO_2 . The PBS60 melt dissolves grain boundaries of PZT and penetrated into the PZT pellet. The concentration of the constituent oxides of PZT increases in the glass melt, and Ti-rich PZT and ZrO_2 precipitate, as in the case of PZT/PBS40 sample.

In the slowly-cooled PZT/PBS60 sample (Fig. 7(c)), dark gray particles were formed in the glasses penetrated into PZT and adjacent to the reaction zone. Figure 10 shows the EPMA result. The dark gray particles contain Pb, Si, and Zr, and are judged to be phase X. Phase X precipitates during cooling, as in the case of the slowly-cooled PZT/PS60 sample.

3.3 Effect of glass composition

The phase relation and interfacial microstructure are affected by the amount of PbO dissolved in the glass melt from PZT, and this amount of PbO is determined by the activity of PbO in the glass melt and PZT, as explained in Part 1 of the present paper.¹⁾ The activity of PbO in the glass melt is determined by the PbO concentration and the B_2O_3/SiO_2 ratio.⁷⁾ The activity of PbO is higher and the amount of PbO dissolved in the glass phase is smaller in the melt containing 60 mol% of PbO than in that containing 40 mol% of PbO. Thus, the concentration of the constituent oxides of PZT does not exceed the solubility limit in the PZT/PS60 sample, and no solid product forms at 850°C. In the PBS60 glass melt, the activity of PbO is reduced by substituting B_2O_3 for SiO_2 ,⁷⁾ and the amount of PbO dissolved in the glass melt is larger than that in the PZT/PS60 sample. The concentration of the constituent oxides of PZT exceeds the solubility limit and Ti-rich PZT and ZrO_2 particles form.

In the PZT/PS40 sample, the amount of PbO dissolved in the glass melt is larger than that in the PZT/PS60 sample.

The ZrO_2 concentration exceeds the solubility limit and ZrO_2 particles precipitate. In the PBS40 glass melt, the activity of PbO in the glass melt is much reduced from that in the PS40 glass melt by substituting B_2O_3 for SiO_2 . Thus, the amount of PbO dissolved in the glass melt from PZT is large, resulting in the formation of the thick reaction zone composed of Ti-rich PZT and ZrO_2 particles.

The shape of phase X was different in the PZT/PS60 and PZT/PBS60 samples cooled slowly (Figs. 1(c) and 8(c)). This compound precipitates from the melt during cooling from 850°C to room temperature. The difference in the shape might be caused by the viscosity of the melt; the PBS60 glass has smaller viscosity than the PS60 glass.⁸⁾ When the viscosity is small, the diffusion rate is large and ions can easily move in the melt and also along the interface between a precipitated particle and melt. In this case, the particle surface with low interfacial energy can easily develop. Thus, the particles with habit form in the PZT/PBS60 sample.

4. Conclusions

The chemical reaction between $Pb(Zr_{0.53}Ti_{0.47})O_3$ and the glasses in the $PbO-SiO_2$ and $PbO-B_2O_3-SiO_2$ systems was studied for powder and bulk PZT samples at 850°C. The amount of PZT dissolved in the glass was smaller in the $PbO-SiO_2$ glasses than in the $PbO-B_2O_3$ glasses (Part 1¹⁾) with the same PbO content, resulting in the formation of thin reaction zone between PZT and the glass phase, for which the higher activity of PbO in the $PbO-SiO_2$ glasses than in the $PbO-B_2O_3$ glasses was responsible. The solid reaction products were a compound in the $PbO-SiO_2-ZrO_2$ system (phase X) and ZrO_2 in the PZT/PS40 samples obtained for powder and bulk PZT, respectively. The degree of supersaturation of ZrO_2 determined the phase of solid product. In the PZT/PS60 sample obtained by the reaction of bulk PZT, no solid reaction product formed at 850°C, and phase X precipitated during cooling to room temperature.

The substitution of B_2O_3 for SiO_2 in the glass melt increased the amount of PZT dissolved in the glass, for which a decrease in the activity of PbO in the glass melt is responsible. Ti-rich PZT and ZrO_2 particles formed in the reaction zone in the PZT/PBS40 and PZT/PBS60 samples. The PBS40 glass formed the thicker reaction zone than the PBS60 glass. In the PZT/PBS60 sample, phase X precipitated during cooling.

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