

## Lead Zirconate Titanate Film Synthesized from Sulfate Slurry

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A lead zirconate titanate (PZT) film was formed on a titanium plate in a hydrothermal slurry contains  $\text{PbSO}_4$ ,  $\text{Zr}(\text{SO}_4)_2$  and  $\text{KOH}$ . The PZT film was composed of particles with cubic shape. The size of particle and the yield of product were smaller and lower, respectively, than a PZT film [1] formed in  $\text{Pb}(\text{NO}_3)_2$ ,  $\text{ZrOCl}_2$  and  $\text{KOH}$  solution with the same conditions. The difference can be explained based on the nucleation process of PZT crystal. In the solution contains sulfate, the amount of dissolution of Ti substrate is larger. The resulting high concentration of Ti increases the number of PZT nuclei. Most of the nuclei of PZT crystal was precipitated not on the substrate but in the solution as powder, which reduced the size of particle in the film and the yield of product.

### 1. INTRODUCTION

A porous crystalline film made of cubic lead zirconate titanate (PZT) crystal was synthesized on a titanium plate from a mixed solution of  $\text{Pb}(\text{NO}_3)_2$ ,  $\text{ZrOCl}_2$  and  $\text{KOH}$ , under hydrothermal condition [2]. The temperature of synthesis was around  $150^\circ\text{C}$ . Any heat treatments over curie point of PZT were not made. The piezoelectric constant ( $d_{31}$ ) of the film was comparable to that of well-sintered and electrically polarized PZT, however the relative density of the film was about 60 % of a well-sintered PZT [3]. The Young's modulus of the film was also 60% of the PZT. The film was rough and its thickness was not controllable because the growth rate of the film was large. In this study we tried to synthesize films composed of fine crystals with low roughness on the surface using sulfate in starting materials.

### 2. EXPERIMENTAL

A slurry containing powders of  $\text{PbSO}_4$ ,  $\text{Zr}(\text{SO}_4)_2$  and  $\text{KOH}$  solution were used as starting materials in order to deposit PZT crystals on a

titanium substrate. The molar ratio of  $\text{Pb}/\text{Zr}$  was 2.12 and the charged concentrations of  $\text{Pb}$  was  $0.33\text{mol}\cdot\text{dm}^{-3}$ . The charged volume and the concentrations of  $\text{KOH}$  solution were  $21\text{cm}^3$  and  $2.5\text{-}6.0\text{mol}\cdot\text{dm}^{-3}$ , respectively. The slurry and the titanium substrate (sized  $10\text{mm}\times 50\text{mm}\times 0.05\text{mm}$ ) were put into a Teflon lined stainless autoclave. The reactor heated and rotated in a oil bath at  $150^\circ\text{C}$ , for 4-48h. After the reaction, the substrate was separated from the residual slurry and washed with distilled water. As a control experiment, the Ti substrate was treated in  $\text{KOH}$  solution or a solution containing  $\text{KOH}$  and  $\text{K}_2\text{SO}_4$ , without  $\text{PbSO}_4$  and  $\text{Zr}(\text{SO}_4)_2$  powder, where the dissolution rate of the substrate was measured.

The Ti substrates were weighed before and after the PZT formation or dissolution experiment. Phases of the product on the substrate were identified by X-ray diffractometry (XRD), the morphology of films was observed by scanning electric microscopy (SEM), and the distribution of elements in the films along the depth were determined by the energy dispersive spectroscopy (EDS).

### 3. RESULTS AND DISCUSSION

### 3.1. PRECIPITATION ON TITANIUM SUBSTRATE

A crystal layer precipitated on the Ti substrate was identified as perovskite-type crystals by XRD. Figure 1 shows the change in the weight of Ti substrate by the reaction with  $\text{PbSO}_4$  and  $\text{Zr}(\text{SO}_4)_2$  (open circle), and the reaction with  $\text{Pb}(\text{NO}_3)_2$  and  $\text{ZrOCl}_2$  (closed circle). The concentration of KOH was  $4.6 \text{ mol} \cdot \text{dm}^{-3}$ . Although no increase is seen at 8h in the curve of  $\text{PbSO}_4 + \text{Zr}(\text{SO}_4)_2$ , a PZT layer had been formed (Fig. 4-c). On the other hand,  $\text{Pb}(\text{NO}_3)_2$  and  $\text{ZrOCl}_2$  requires at least 12.5h to form a PZT layer [4]. Sudden increase after 12h are significant for both reactions. The change in the weight at this time is much larger in the  $\text{Pb}(\text{NO}_3)_2 + \text{ZrOCl}_2$  solution than the  $\text{PbSO}_4 + \text{Zr}(\text{SO}_4)_2$  slurry.

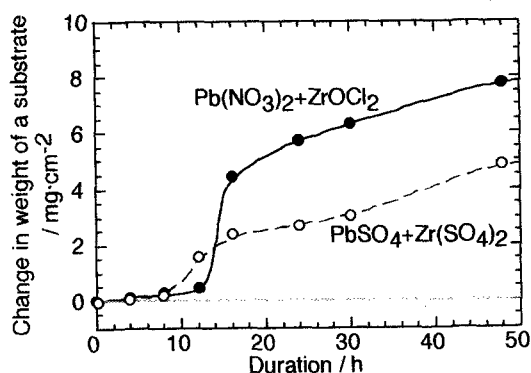


Fig. 1 Change in the weight of Ti substrate after the reaction with  $\text{PbSO}_4 + \text{Zr}(\text{SO}_4)_2$  (open circle) and  $\text{Pb}(\text{NO}_3)_2 + \text{ZrOCl}_2$  (closed circle) at  $150^\circ\text{C}$  for 48 h.

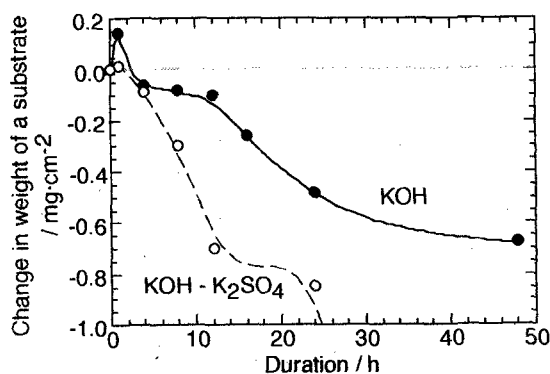


Fig. 2 Change in the weight of Ti substrate by the reaction with KOH (closed circle) or KOH -  $\text{K}_2\text{SO}_4$  (open circle) solution.

The change in the weight of Ti substrate by the reaction with KOH or KOH -  $\text{K}_2\text{SO}_4$  solution is shown in Fig. 2. KOH concentration was  $3.6 \text{ mol} \cdot \text{dm}^{-3}$  and  $\text{K}_2\text{SO}_4$  concentration was  $0.66 \text{ mol} \cdot \text{dm}^{-3}$ . The weight of the Ti substrates shows a small increase prior to the monotonous decrease.

In the process of PZT formation, Pb, Zr and Ti must be supplied from liquid phase [5]. A dissolution of the titanium substrate was necessary for precipitation of PZT film on the substrate [1]. In Fig. 2, the rate of dissolution in the KOH- $\text{K}_2\text{SO}_4$  solution is larger than KOH solution until 10h, suggesting an effects of  $\text{SO}_4^{2-}$  anion for the enhancement of Ti dissolution. During the period 8 to 10h, the rate of PZT formation in  $\text{PbSO}_4 + \text{Zr}(\text{SO}_4)_2$  slurry is larger than that in  $\text{Pb}(\text{NO}_3)_2 + \text{ZrOCl}_2$ . The difference may be due to the difference in the Ti dissolution at the early stage of the reaction.

### 3.2. MORPHOLOGY OF FILM

Figure 3 shows the increase in the weight of the substrate brought by the change in KOH concentration at the PZT formation. The experimental duration was 48h at  $150^\circ\text{C}$ . At least  $1.6 \text{ mol} \cdot \text{dm}^{-3}$  is necessary in the KOH concentration. The yield of the product increases with KOH concentration. In a solution of  $\text{Pb}(\text{NO}_3)_2$  and  $\text{ZrOCl}_2$ , at least  $3 \text{ mol} \cdot \text{dm}^{-3}$  in KOH concentration was necessary for the formation of PZT film [5]. At  $4.6 \text{ mol} \cdot \text{dm}^{-3}$ , the yield of PZT was almost same as that by the reaction in  $\text{Pb}(\text{NO}_3)_2$  and  $\text{ZrOCl}_2$  solution.

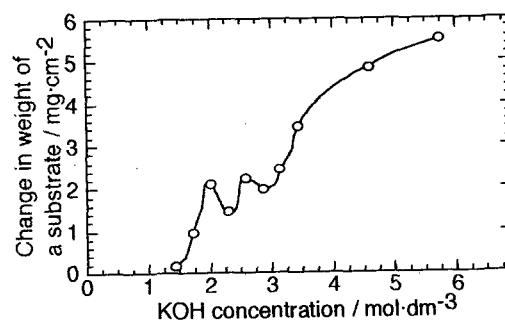


Fig. 3 Change in the weight of the substrate brought by the change in KOH concentration at the PZT formation.

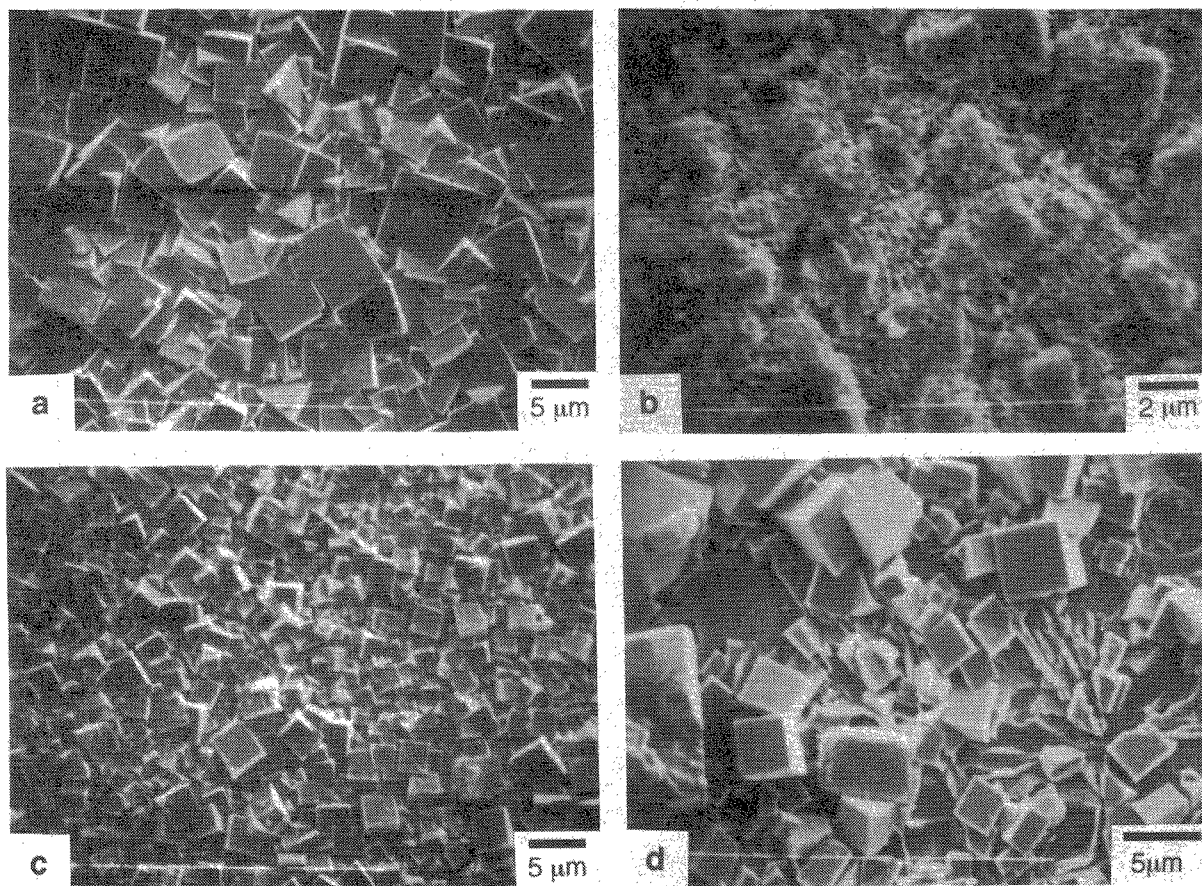


Fig. 4 SEM photographs of the PZT films; (a)  $\text{Pb}(\text{NO}_3)_2 + \text{ZrOCl}_2$ ,  $\text{KOH}=4.6 \text{ mol}\cdot\text{dm}^{-3}$ , 48 h, (b)  $\text{PbSO}_4 + \text{Zr}(\text{SO}_4)_2$ ,  $\text{KOH}=4.6 \text{ mol}\cdot\text{dm}^{-3}$ , 48 h, (c)  $\text{PbSO}_4 + \text{Zr}(\text{SO}_4)_2$ ,  $\text{KOH}=4.6 \text{ mol}\cdot\text{dm}^{-3}$ , 8 h, (d)  $\text{PbSO}_4 + \text{Zr}(\text{SO}_4)_2$ ,  $\text{KOH}=3.2 \text{ mol}\cdot\text{dm}^{-3}$ , 48 h.

SEM photographs of PZT films are shown in Fig. 4. The PZT films from a  $\text{Pb}(\text{NO}_3)_2$  and  $\text{ZrOCl}_2$  solution [2] are shown for comparison (Fig. 4a). In Figs. 4(b), (c) and (d), PZT films from  $\text{PbSO}_4$  and  $\text{Zr}(\text{SO}_4)_2$  slurry are shown. The duration of the reaction was 48 h for (a), (b) and (d), while (c) was 8 h. The KOH concentration was  $4.6 \text{ mol}\cdot\text{dm}^{-3}$  for (a), (b) and (c), and  $3.2 \text{ mol}\cdot\text{dm}^{-3}$  for (d). The film from  $\text{Pb}(\text{NO}_3)_2$  and  $\text{ZrOCl}_2$  solution was covered with euhedral particles (a). The surface of the film from  $\text{PbSO}_4$  and  $\text{Zr}(\text{SO}_4)_2$  slurry was covered with agglomerated fine particles (b) at the conditions same as the PZT in (a). Shortening the duration (c) or decreasing the KOH concentration (d) made the PZT film euhedral.

The reaction in the slurry are thought to proceed at first via a dissolution reaction with slow rate,  $\text{PbSO}_4 \rightarrow \text{Pb}^{2+} + \text{SO}_4^{2-}$ , then a hydroxylation,  $\text{Pb}^{2+} + 2\text{OH}^- \rightarrow \text{HPbO}_2^-$  [6]. In the solution, the dehydration,  $\text{HPbO}_2^- + \text{Zr}(\text{OH})_5^- \rightarrow \text{PbZrO}_3 + 2\text{H}_2\text{O} + 2\text{OH}^-$  [7], produces a precipitate of  $\text{PbZrO}_3$ . As Ti ion is supplied from the Ti substrate and the concentration is negligible in the solution, PZT crystals precipitates on the Ti substrate exclusively. Because of a limited rate of  $\text{PbSO}_4$  dissolution the effective  $\text{OH}^-$  concentration is higher in the sulfate slurry than the solution contains  $\text{Pb}(\text{NO}_3)_2$  and  $\text{ZrOCl}_2$ . The higher  $\text{OH}^-$  concentration and the presence of sulfate anion raises Ti concentration near the Ti substrate and the

number of nuclei of PZT, and the higher OH<sup>-</sup> concentration produces a larger amount of PbZrO<sub>3</sub> precipitate and a reduced Pb and Zr concentrations, which results in the formation of a thin PZT layer composed of fine crystals.

#### 4. CONCLUSION

PZT films can be hydrothermally precipitated on a titanium substrate from the PbSO<sub>4</sub> and Zr(SO<sub>4</sub>)<sub>2</sub> slurry as same as the previous study from the Pb(NO<sub>3</sub>)<sub>2</sub> and ZrOCl<sub>2</sub> solution. In the reaction with PbSO<sub>4</sub> and Zr(SO<sub>4</sub>)<sub>2</sub>, the rate of PZT formation was fast as early stage and gradual after that, making the morphology and thickness of the PZT film controllable. The fast formation at early stage is due to the effective high OH<sup>-</sup> concentration in the solution or the dissolution of Ti substrate enhanced by SO<sub>4</sub><sup>2-</sup> anion.

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