Recovery of lead from lead-based electronic ceramics by wet ball-mill treatment with acidic solution and the effective use of metals in the wastewater

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Abstract

Selective Pb recovery as a solid state PbSO₄ from lead-based electronic ceramics, such as Pb(Zr₀.₅₂Ti₀.₄₈)O₃ (abbreviated as PZT), PbTiO₃ (PT) and PbZrO₃ (PZ), was investigated by wet ball-mill treatment with H₂SO₄ solution. The treatment was performed using a pot mill apparatus in air at room temperature for 0-72 h with the rotational speed fixed at 300 rpm. A sample dipped in H₂SO₄ solution was prepared in order for the comparison with the above milled sample. The ball-mill treatment resulted in pulverization and destabilization of the PZT ceramic particles, and then both the dissolution into the H₂SO₄ solution and the precipitation of PbSO₄ were efficiently progressed by combining mechanical activation and chemical reaction. More than 99 mass% of Pb in the ceramics was recovered as PbSO₄ form with a purity of about 98 mass%.

Subsequently, an effective use of Zr and Ti in the wastewater generated after the ball-mill treatment was attempted. Crystalline α-Zr(HPO₄)₂·H₂O (abbreviated as α-ZrP) and α-Ti(HPO₄)₂·H₂O (α-TiP) were prepared by hydrothermal treatment using the metals in the wastewater. The phosphates were characterized by X-ray diffraction (XRD) analysis, scanning electron microscopy (SEM), cation exchange capacity (CEC) measurement and leaching test of lead.

Keywords: lead-based electronic ceramics, lead recovery, ball-mill treatment, hydrothermal synthesis, ion exchanger.
1 Introduction

In recent years, electronics industries have an effort to minimize the use of lead in electrical and electronic products, for example Pb solders [1-3] because of the concern for the environment. However, most piezoelectric materials are still lead-based ferroelectrics with perovskite structure such as Pb(Zr, Ti)O₃ and Pb(Mg, Nb)O₃. In addition, eco-friendly lead-free or lower-lead-content ferroelectrics, which possess the properties identical to the lead-based one and are applicable in the specific appliances with high electromechanical coupling factor and high piezoelectric constant, have not been developed as yet. Therefore, it is very important to establish the technique to control the lead discharge and recover the solid lead in a safe state.

The mechanochemical process has been used to fabricate a wide variety of engineering materials [4-9]. In recent years, it is reported that the mechanochemical technique is effective to extract precious and rare metals from wastes [10, 11], and to detoxify and decompose hazardous organic compounds like dioxins [12, 13]. We reported that wet ball-mill treatment of PZT and PLZT ceramics was effective to recover lead from these ceramics [14, 15]. In the present study, Pb(Zr₀.₅₂Ti₀.₄₈)O₃, PbTiO₃ and PbZrO₃ ceramics (abbreviated as PZT, PT and PZ, respectively) were treated by wet ball-mill with H₂SO₄ solution at room temperature, and the selective recovery of lead as its sulfate form was investigated. Subsequently, the hydrothermal synthesis of cation exchangers, i.e., crystalline α-Zr(HPO₄)₂·H₂O (abbreviated as α-ZrP) and α-Ti(HPO₄)₂·H₂O (α-TiP) was also investigated for the effective use of the metals (Zr and Ti) in the acidic wastewater after the wet ball-mill treatment. In addition, the cation exchange capacities of these phosphates and the leaching behavior of lead contained in the phosphates were examined.

2 Experimental

2.1 Samples and wet ball-mill treatment

Commercially available sintered PZT, PZ or PT (KOJUNDO CHEMICAL LAB Co., Ltd.) was used as a sample. A sintered compact was roughly precrushed in agate mortar by hand. The wet ball-mill treatment was carried out using a pot mill apparatus in air for 0–72 h at room temperature, and the rotational speed was fixed at 300 rpm. The precrushed samples were placed in a polypropylene container with inner volume 50ml together with ZrO₂ balls (diameter: 5 mm, weight ratio of the sample / ZrO₂ = 1/50), and then 4 ml of 4.5 M H₂SO₄ was added into the container. A sample only dipped in H₂SO₄ solution was prepared in order to compare with the above milled sample. Approximately 7.7 mmol of PZT was used to compare the wet ball-mill treatment and dip treatment. The milled and dipped samples were sonicated in 100 ml of 0.5 M H₂SO₄ for 15 min, after which solid constituents in the solution were separated by filtration, and they were washed by the filtrate again. Finally, solid constituents on the filter were dried at 50 °C in an oven for 24 h.
2.2 Hydrothermal synthesis of crystalline phosphates

The acidic wastewater generated after the ball-mill treatment of lead-based ceramics (5.6 mmol) for 24 h was used for the synthesis of crystalline phosphates. H₃PO₄ solution was added into the 100 mL of wastewater stirring vigorously to form gelatinous white precipitates. After stirring for 1 h, the precipitates were collected by filtration, washed with a plenty of water and dried at 110 °C for 24 h. Approximately 0.3 g of dried sample was charged into the 34 washed with water, and finally dried at 50 °C for 24 h.

2.3 Characterization

The constituent phases of the samples were identified by X-ray diffraction (XRD; Rigaku, RINT2500H) analysis using CuKα X-ray radiation filtered by Ni, and the morphology was characterized using a scanning electron microscopy (SEM; JEOL, JSM-6330F). The metals dissolved in the solution were analyzed quantitatively by the inductively coupled-plasma atomic-emission spectroscopy (ICP-AES; Perkin Elmer Japan, 3300DV). The thermal behaviors of the synthesized phosphates were examined by thermogravimetric analysis (TG) and differential thermal analysis (DTA) under O₂/N₂ atmosphere of the ratio 1/4 (total flow rate of 100 mL/min) at the heating rate 10 K/min.

Cation exchange capacity of the phosphate was estimated from titration curve. The titration was carried out in a thermostatic water bath regulated at 27°C. In each measurement, approximately 0.1 g of the phosphate was dispersed in the 50 mL of 0.1 M NaCl solution with stirring until the pH value became constant. After the equilibrium, pH of the solution was measured by a digital pH meter (HORIBA, D-21) and then a standard 0.01 M NaOH solution was added by a micropipette. Subsequently, the pH of the solution was recorded when the pH drift was less than 0.01 /min.

Leaching test of lead was performed, i.e., firstly the sample of 0.1 g was dispersed stirring for 3 h in HCl solution with various pH values. NaOH+NaCl solution was used for pH adjustment. The amounts of lead in the solution and contained in the residues were quantified by ICP-AES.

3 Results and discussion

3.1 Wet ball-mill treatment

No significant difference in disintegration and dissolution behavior among the PZT, PZ and PT can be seen, so that the data on ball-mill treatment of PZT are shown below as a typical example.

3.1.1 Disintegration behavior of PZT

Figure 1 shows the XRD profiles of the wet ball-milled samples for (a) 4, (b) 12, (c) 48 and (d) 96 h. The peaks of PbSO₄ were confirmed in all the wet ball-
milled samples as in the case of the dipped ones. The same trend of the intensity change in PZT and PbSO₄ peaks in both milled and dipped samples was observed, i.e., with an increase in milling time, the intensity of the PZT peaks gradually decreased while the intensity of the PbSO₄ peaks gradually increased. In the case of a milling time of more than 48 h, the PZT peaks completely disappeared, as seen in Figs. 1(c) and (d).

Figure 1: XRD profiles of the samples obtained after the wet ball-mill for (a) 4, (b) 12, (c) 48 and (d) 96 h. Symbols show PZT (▼) and PbSO₄ (●).

Figure 2: The dependence of the XRD intensity ratio for the wet ball-milled (■) and dipped (□) samples on treatment time.
Figure 2 shows the dependence of XRD intensity ratio $[I_{\text{PbSO}_4}/(I_{\text{PZT}}+I_{\text{PbSO}_4})]$ on the treatment time for the wet ball-milled ($\blacksquare$) and dipped samples ($\square$). Peak intensities of PZT and PbSO$_4$ species were measured from the diffraction lines at 30.9° and 29.7°, respectively. The XRD intensity ratio for the milled samples increased markedly compared with that for the dipped sample. This is not only because the PZT particles are finely ground, but also because PbSO$_4$ particles precipitated on the PZT surface are detached and well dispersed during the milling process. Preliminary experiments revealed that the perfect conversion of lead in the PZT sintered compact to PbSO$_4$ was not attained by hydrothermal treatment with aqueous H$_2$SO$_4$ solution. Thus, milling of the PZT plays a significant role in accelerating the reaction rate by enlarging the fresh surface area of the PZT particles. A few milligrams (1-3 mg) of weight loss of ZrO$_2$ balls were observed after the wet ball-mill with H$_2$SO$_4$ solution.

![Graph showing treatment time dependence of dissolution amount of Pb, Zr, Ti](image)

Figure 3: Treatment time dependence of the dissolution amount of Pb ($\blacksquare$, $\square$), Zr ($\bullet$, $\circ$) and Ti ($\blacktriangle$, $\triangle$) in the H$_2$SO$_4$ filtrate. Filled symbols and open symbols indicate ball-milled and dipped samples, respectively.

### 3.1.2 Dissolution behavior of PZT

Figure 3 shows the dependence of the dissolution amount of Pb, Zr and Ti in the H$_2$SO$_4$ on treatment time. In all cases of ball milling and dipping, the dissolution amount of Zr and Ti was found to increase with treatment time. No remarkable difference in dissolution amount between Zr and Ti can be observed in all the samples. Zr and Ti are transition elements of the same group, so that both elements seem to exhibit a similar dissolution behavior under this condition. It is considered by comparing Fig. 2 with Fig. 3 that the leaching behavior of both components (Fig. 3) is closely related to the disintegration behavior of the PZT crystal structure (Fig. 2). These results indicate, therefore, that the dissolution of Zr and Ti in the PZT crystal structure and the disintegration of the PZT crystal structure took place almost simultaneously.
On the other hand, the dissolution amount of Pb was less than 0.1 % compared with the initial Pb content in PZT under all the ball-mill conditions. This small dissolution amount of Pb came from the dissociation of PbSO₄ according to

\[
PbSO_4(s) \leftrightarrow Pb^{2+} + SO_4^{2-}. \tag{1}
\]

The amount of Pb was less than that of Pb calculated from the solubility product constant. The dissociation of PbSO₄ was significantly suppressed using H₂SO₄ solution in the milling and rinsing process, because the excess sulfate ions acted as shifting the equilibrium to the left side of equation (1). These results lead to the conclusion that most of the Pb exists either as PZT or as precipitated PbSO₄, as supported by the previous XRD analysis. Therefore, it can be said that more than 99.9 % of Pb in PZT was transformed into solid PbSO₄ by the ball-mill for more than 48 h, when the diffraction line of the PZT completely disappeared.

### 3.1.3 Purity of PbSO₄ recovered

The remaining amount of Pb, Zr and Ti in the recovered powder obtained after the wet ball-mill for various milling times was calculated using the ICP results. Here, the remaining amount of each element was defined as

\[
\text{(Remaining amount)} = (\text{Initial content in PZT}) - (\text{Dissolution amount}). \tag{2}
\]

The purity of recovered PbSO₄ was also calculated by converting the masses of the remaining Pb, Zr and Ti into those of PbSO₄, ZrO₂ and TiO₂. These results are summarized in Table 1. About 98 mass% of PbSO₄ was recovered by the wet ball-mill treatment for more than 48 h.

#### Table 1: Purity of PbSO₄ recovered after the ball-mill treatment.

<table>
<thead>
<tr>
<th>Milling time / h</th>
<th>Sample / mg</th>
<th>Remaining amount / mg</th>
<th>Converted mass / mg</th>
<th>PbSO₄ / mass%</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Pb</td>
<td>Zr</td>
<td>Ti</td>
<td>PbSO₄</td>
</tr>
<tr>
<td>48</td>
<td>2503.2</td>
<td>1592.5</td>
<td>10.0</td>
<td>23.5</td>
</tr>
<tr>
<td>72</td>
<td>2501.6</td>
<td>1591.4</td>
<td>14.0</td>
<td>16.4</td>
</tr>
<tr>
<td>96</td>
<td>2502.4</td>
<td>1591.5</td>
<td>24.6</td>
<td>6.6</td>
</tr>
</tbody>
</table>

### 3.2 The effective use of metals in the wastewater

#### 3.2.1 Hydrothermal synthesis of crystalline phosphates

Crystalline phosphates were prepared by hydrothermal treatment of the precipitates, which were obtained by H₃PO₄ addition to the PZT, PZ and PT treated wastewater. Figure 4 shows the XRD profiles of the phosphates prepared by the hydrothermal treatment in 6.2 M H₃PO₄ at 200°C for 72 h. It is expected that monolithic α-ZrP and α-TiP particles with high purity and crystallinity can be obtained from PZ and PT treated wastewaters, since only sharp diffraction peaks are seen with no impurity precipitated, as seen in Fig. 4(a) and (b). On the other hand, the phosphate prepared from PZT treated wastewater was found to be a mixture of α-ZrP and α-TiP. In addition, the detailed observation of the XRD
profile of the mixture (Fig. 4(2)) revealed that the peaks of the $\alpha$-ZrP and $\alpha$-TiP were shifted to higher angle value and lower angle value, respectively. In order to clarify the above findings, elemental distribution on the phosphate particles was examined by EDS.

Figure 4: XRD profiles of the phosphates prepared by hydrothermal treatment from (a) PT, (b) PZ and (c) PZT treated wastewater. Left (1) and right (2) profiles are wide- and narrow-range profiles, respectively. Symbols show (○) $\alpha$-Ti(HPO$_4$)$_2$·H$_2$O and (●) $\alpha$-Zr(HPO$_4$)$_2$·H$_2$O.

Figure 5: (a) Secondary electron image, and elemental images of (b) Ti and (c) Zr on the phosphate prepared by hydrothermal treatment from PZT treated wastewater.

Figure 5 shows the (a) secondary electron image, and elemental maps of (b) Ti and (c) Zr on the phosphate prepared by hydrothermal treatment from PZT treated wastewater. EDS images show Ti and Zr atoms exist in all the particles seen in Fig. 5(b) and (c). Therefore, peak shift observed in XRD profile (Fig. 4(c))
would come from the formation of solid solution by replacement of Zr by Ti, and vice versa.

### 3.2.2 Thermogravimetric (TG) analysis of the synthesized phosphates

Generally, weight loss of α-ZrP and α-TiP proceed firstly to form anhydrous phase (Zr(HPO$_4$)$_2$ and Ti(HPO$_4$)$_2$), and then further heating leads to the formation of ZrP$_2$O$_7$ and TiP$_2$O$_7$ with the loss of constituent water [16,17], according to

\[
\text{Zr(HPO}_4\text{)}_2\text{H}_2\text{O} \rightarrow \text{Zr(HPO}_4\text{)}_2 \rightarrow \text{ZrP}_2\text{O}_7 \ (-11.96\%) \ \text{and} \ \text{Ti(HPO}_4\text{)}_2\text{H}_2\text{O} \rightarrow \text{Ti(HPO}_4\text{)}_2 \rightarrow \text{TiP}_2\text{O}_7 \ (-13.97\%).
\]

Typical TG curves of the synthesized phosphates are shown in Figure 6. α-ZrP and α-TiP prepared from PZ and PT treated wastewater lose weight approximately 11.8 and 14.1 %, respectively. These values were almost equal to the theoretical ones, as described in the equation (4) and (5), indicating that α-ZrP and α-TiP with high purity and crystallinity could be synthesized as supported by the XRD result in Fig. 4. According to the TG analysis, weight loss of the phosphate prepared from PZT wastewater was approximately 13.1 %. The ratio of α-ZrP/α-TiP in the mixture was calculated as 0.43/0.57 by weight from the TG weight loss.

![Figure 6: TG curves of the phosphates synthesized hydrothermally from various wastewaters.](image)

### 3.2.3 Cation exchange capacity (CEC) measurement of the synthesized phosphates

In order to evaluate the properties of the synthesized phosphates, cation exchange capacity was measured by titration method [18]. Table 2 shows the theoretical CEC values and experimentally measured ones of the phosphates.
CEC value of $\alpha$-ZrP prepared from PZ treated wastewater was identical to that of theoretical CEC. The CEC values of $\alpha$-TiP and a mixture of $\alpha$-ZrP/$\alpha$-TiP, however, showed smaller values compared with theoretical ones, due to the hydrolysis of the phosphates [19].

Table 2: Cation exchange capacities of theoretical $\alpha$-ZrP and $\alpha$-TiP, and the phosphates prepared by hydrothermal method.

<table>
<thead>
<tr>
<th>Wastewater Phase</th>
<th>CEC, meq/g</th>
</tr>
</thead>
<tbody>
<tr>
<td>Theoretical value</td>
<td>$\alpha$-ZrP 6.6</td>
</tr>
<tr>
<td>PZ</td>
<td>$\alpha$-ZrP 6.5</td>
</tr>
<tr>
<td>PT</td>
<td>$\alpha$-TiP 7.0</td>
</tr>
<tr>
<td>PZT</td>
<td>$\alpha$-ZrP/$\alpha$-TiP 5.7</td>
</tr>
</tbody>
</table>

3.2.4 Leaching test of lead from the phosphate

Table 3 shows the result of the leaching test of Pb for the phosphates prepared from PZT treated wastewater. No leaching of Pb, Ti and Zr can be observed in the pH range from 3.7-8.6. However, the dissolution amount of Pb, Ti and Zr tended to increase with decreasing pH value, due to the dissolution of the phosphate.

Table 3: Result of the leaching test of lead.

<table>
<thead>
<tr>
<th>pH</th>
<th>Dissolution amount, mg/g</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Pb</td>
</tr>
<tr>
<td>8.6</td>
<td>N.D.</td>
</tr>
<tr>
<td>4.7</td>
<td>N.D.</td>
</tr>
<tr>
<td>3.7</td>
<td>N.D.</td>
</tr>
<tr>
<td>3.1</td>
<td>0.008</td>
</tr>
<tr>
<td>2.3</td>
<td>0.030</td>
</tr>
<tr>
<td>1.2</td>
<td>0.041</td>
</tr>
</tbody>
</table>

4 Conclusions

The selective recovery of Pb from lead-based electronic ceramics was achieved by the wet ball-mill treatment with $\text{H}_2\text{SO}_4$ solution. The ball-mill treatment of PZT demonstrated that PZT particles were pulverized and activated, and both the dissolution into the $\text{H}_2\text{SO}_4$ solution and the precipitation of PbSO$_4$ were progressed significantly by combining mechanical activation and chemical reaction. More than 99 mass% of Pb in the ceramics was recovered as PbSO$_4$ form with a purity of 98 mass%.

Effective use of Zr and Ti in the wastewater generated after the ball-mill treatment was examined. Crystalline $\alpha$-Zr(HPO$_4$)$_2 \cdot \text{H}_2\text{O}$ and $\alpha$-Ti(HPO$_4$)$_2 \cdot \text{H}_2\text{O}$ were prepared by hydrothermal method using the metals in the wastewater. The phosphates prepared from PZT treated wastewater were mixtures of plate-like $\alpha$-
ZrP and α-TiP. The CEC of the obtained phosphates showed almost the same value as the theoretical one.

References