Effect of Silica Surface Area on Molecular Structures of Lead in Thermally Treated Mixtures of Lead Acetate and Silica Oxide

Yu-Ling Wei¹,*, Kai-Wen Cheng¹, Nicky Cheng¹, H. Paul Wang²

¹Department of Environmental Science and Engineering, Tunghai University, Taichung City, 407 Taiwan
²Department of Environmental Engineering, National Cheng-Kung University, Tainan City, 700 Taiwan

Abstract. The extent of lead dispersion can affect lead molecular environment in lead silicate. Mixtures of lead acetate and silica oxide were heated at 500 and 1100 °C for two hours. Two silica oxides (a quartz, syn and an amorphous SiO₂) of different surface areas were used in this study. The final products were investigated with X-ray absorption spectroscopy, X-ray diffraction, BET surface meter, and scanning electron microscopy. The XRD results observe the existence of PbSiO₃, Pb(0), and PbO (litharge, syn) only in the mixture of lead acetate and quartz heated at 1100 °C, as well as SiO₂ (cristobalite, syn). The mixture of lead acetate and the amorphous SiO₂ heated at 1100 °C basically remains as amorphous although its XRD patterns do show some low-intensity peaks of SiO₂ (cristobalite, syn). Both BET and SEM results indicate that sintering occurs at 1100 °C. Results from the fitting of Fourier transformed Pb L III-edge EXAFS spectra from the heated mixtures shows that both first-shell (Pb-O) interatomic distance and coordination number depend on the type of starting materials and the thermal treatment temperature. Pb first-shell coordination number decreases with increasing temperature for both low-surface area and high-surface area mixtures. The high-surface area mixture after heating at 500 °C have greater first-shell coordination number than the corresponding low-surface area sample. However, after thermal treatment at 1100 °C, both mixtures have similar first-shell coordination number. The interatomic distance for the first shell for all thermally treated mixtures is 2.18-2.28 Å. The high-surface area mixture treated at 1100 °C has the shortest first-shell interatomic distance (2.18 Å).

Keywords: sintering, lead silicate, Pb coordination number
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INTRODUCTION

Lead silicate glass has important application in manufacturing image amplifiers and scintillators in industry and recently its structure has been intensively studied [1-7]. The structure of the lead silicate glass that was partially chemically reduced in hydrogen atmosphere was studied with X-ray absorption spectroscopy (XAS) techniques [1,2]. The Pb environment in the pre-reduced lead silicate glass is similar to that of the red PbO [1] and the XAS analysis can give an estimate of the extent of chemical reduction and the average granule size [2]. X-ray diffraction (XRD) was used to study the environments of lead in various oxide glasses including SiO₂; the number of oxygen in the nearest shell is three and the interatomic distance is 2.30 Å [3]. The structures of lead environment in lead silicate glasses were examined using both XAS techniques and molecular dynamics simulations and the results are in good agreement [5]. Silicon is determined to be the main glass former at low lead content [6].

The objective of this study is to investigate how the extent of lead dispersion on silica oxide affects the lead molecular environment in lead silicate. Mixtures of lead acetate and silica oxide were heated at 500 and 1100 °C for two hours. The thermally reacted Pb-doped silicon oxides were investigated, at room temperature, with BET surface analyzer, field emission scanning electron microscope (FE-SEM), X-ray diffractometer (XRD), and synchrotron-based X-ray absorption spectroscopy (XAS).

EXPERIMENTAL

Two types of silicon oxide are used in this study. The first one is quartz that has a BET surface area of 5.6 m²/g (GR grade, Alfa Aesar, USA). The other is amorphous and has a BET surface area of 180.6 m²/g (GR grade, Alfa Aesar, USA). The procedure of
doping Pb onto silicon oxides in aqueous solution was as follows. In a 2-L polyethylene bottle, 0.5 kg quartz powder or 0.1 kg amorphous SiO₂ powder was mixed with 1.5 L of de-ionized water that contains either 36.616 g or 7.3232 g of Pb(CH₃COO)₂·3H₂O. These slurry mixtures were end-to-end rotated at 30 rev/min for 2 days. Then it was oven-dried at 105 °C, and ground to serve as the raw materials for further thermal treatment. Both types of Pb-doped silicon oxide were allowed to thermally react at 500 and 1100 °C for 2 hours (i.e., these four samples are denoted as LB-500 °C, LB-1100 °C, HB-500 °C, and HB-1100 °C for the low surface area samples and high surface area samples, respectively). The thermally reacted Pb-doped silicon oxides were investigated with BET surface analyzer, field emission scanning electron microscope, X-ray diffractometer, and X-ray absorption spectroscopy (XAS) at room temperature.

The Pb-L₃ XAS spectra were recorded on the wiggler C (BL-17C) beam line at the National Synchrotron Radiation Research Center (NSRRC) of Taiwan. During the XAS experiment, the facility had a storage ring energy of 1.5 GeV, and a beam current of 120—200 mA. XAS spectra at the Pb-L₃ edge (13055 eV) were collected at room temperature in transmission mode for all reference compounds and fluorescence mode for the previously heated samples. Data reduction was carried out using WinXAS software [8]. Phase shifts and backscattering amplitudes for specific atom pairs, based on the crystallographic data for red PbO, were theoretically calculated with the FEFF software [9].

RESULTS AND DISCUSSION

TABLE 1. BET surface area of lead-containing SiO₂ samples heated at 500-1100 °C for 2 hours.

<table>
<thead>
<tr>
<th>Sample identity</th>
<th>BET surface area (m² g⁻¹)</th>
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<tbody>
<tr>
<td>LB-500 °C</td>
<td>3.8</td>
</tr>
<tr>
<td>LB-1100 °C</td>
<td>1.5</td>
</tr>
<tr>
<td>HB-500 °C</td>
<td>155.9</td>
</tr>
<tr>
<td>HB-1100 °C</td>
<td>5.1</td>
</tr>
</tbody>
</table>

Table 1 shows that the BET surface area decreases as the thermal treatment temperature increases. It changes from 3.8 m² g⁻¹ for the LB-500 °C sample to 1.5 m² g⁻¹ for the LB-1100 °C, and from 155.9 m² g⁻¹ for the HB-500 °C sample to 5.1 m² g⁻¹ for the HB-1100 °C. This decrease in surface area results from the sintering of samples heated at 1100 °C.

Figure 1 shows the surface morphology from all heated samples. Sintering reaction is clearly evidenced in the SEM images of the samples that have been heated at 1100 °C. The results of the SEM images are consistent with the results of the BET surface areas presented in Table 1.

Figure 2 presents the XRD patterns from the low-surface-area samples (LB-500 °C and LB-1100 °C) and high-surface-area samples (HB-500 °C and HB-1100 °C). Figure 2 shows that no diffraction patterns associated with lead species is observed in the LB-500 °C sample. The JCPDS data base identifies the diffraction pattern as characteristics of quartz, syn. However the XRD pattern from the HB-1100 °C sample shows the presence of other phases.
sample reveals the existence of lead silicate, elemental lead, and yellow PbO. We infer the following possible transformation of lead species during heating at 1100 °C. First, lead acetate decomposes to red PbO upon heating. Red PbO then further decomposes into Pb(0) and oxygen, or it chemically reacts with SiO2 to form lead silicate. However, no definite XRD pattern attributed to lead species is observed for the high-surface-area samples (HB-500 °C and HB-1100 °C); these two samples are mainly in amorphous form. It is noted that both XRD patterns from LB-1100 °C and HB-1100 °C samples indicate the existence of SiO2 (Cristobalite, syn) that is formed from quartz and amorphous SiO2 in the LB-1100 °C and HB-1100 °C samples, respectively.

![FIGURE 3. Fourier transforms of sample EXAFS spectra fit with red PbO crystallographic data.](image)

Figure 3 shows the Fourier transforms of the sample EXAFS spectra fit with a model based on crystallographic data for red PbO. The spectra are quite complex up to 8 Å, thereby indicating great long-range structure order. The structural results of the first shell derived from fitting are listed in Table 2. The Debye-Waller factor is set as 0.01 in deriving the structural parameters. The first-shell coordination numbers decrease with increasing thermal treatment temperature. The high BET-surface-area samples have greater first-shell coordination numbers than the corresponding low BET-surface-area samples. The interatomic distance for the first shell for all samples is 2.18-2.28 Å. The high-surface area mixture heated at 1100 °C (HB-1100 °C sample) has the shortest first-shell interatomic distance, 2.18 Å.

### CONCLUSIONS

Both BET surface area of silica oxide and heating temperature affect lead molecular environment in the mixtures of lead acetate and silica oxide; the mixtures were previously heated at 500 and 1100 °C for two hours. Pb first-shell coordination number decreases with the temperature for both low-surface area mixture and high-surface area one. The interatomic distance for the first shell for all samples heated at 500 or 1100 °C is 2.18-2.28 Å. The XRD results indicate the existence of PbSiO3, Pb(0), and PbO (litharge, syn) only in the mixture of lead acetate and quartz heated at 1100 °C. The mixture of lead acetate and the amorphous SiO2 heated at 1100 °C basically remains as amorphous although its XRD patterns do show some low-intensity peaks of SiO2 (cristobalite, syn). Both BET and SEM results indicate that sintering occurs at 1100 °C.

### ACKNOWLEDGMENTS

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### REFERENCES


### TABLE 2. Pb structural results in mixtures of lead acetate and SiO2 heated at 500 and 1100 °C for 2 hours

<table>
<thead>
<tr>
<th>Sample identity</th>
<th>N type at R (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>LB-500 °C</td>
<td>2.63 Pb-O at 2.22</td>
</tr>
<tr>
<td>LB-1100 °C</td>
<td>2.22 Pb-O at 2.28</td>
</tr>
<tr>
<td>HB-500 °C</td>
<td>3.01 Pb-O at 2.26</td>
</tr>
<tr>
<td>HB-1100 °C</td>
<td>2.25 Pb-O at 2.18</td>
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