A Novel Process Utilizing Subcritical Water to Remove Lead from Wasted Lead Silicate Glass

Hiroshi Miyoshi,[†] Danping Chen,[†] and Tomoko Akai*[†,††]
[†]*PRESTO, JST, 1-8-31 Midorigaoka, Ikeda, 5638577, Osaka*
[††]*AIST, 1-8-31 Midorigaoka, Ikeda, 5638577, Osaka*

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Lead was removed from lead silicate glass 7.3Na_2O–6.4K_2O–3.7MgO–5.4CaO–66.4SiO_2–7.8PbO–3Al_2O_3 (mol %), used in color television CRT funnel, utilizing a subcritical hydrothermal treatment at 628 K and 24 MPa followed by acid leaching at 373 K. This process may be used to prevent disposal of lead containing waste glass wares to landfills, reduce environmental risks in future.

Lead has been widely used, such as alloy solder, ceramics, water pipes, and fuels. However, because of its possible environmental risks, major countries imposed legal controls for using lead. Efforts to substitute lead to non-toxic element have been recently made, and a number of lead-free products have been newly developed. However, huge amount of alkali lead silicate glasses are still used in CRTs in color television sets, since no alternative materials are practically available. When these television sets are disused, CRTs are decomposed into each parts-panels (alkali–alkaline-earth silicate glass with strontium and barium) funnels (lead silicate glass).[1] The glass thus collected is recycled as a cullet and introduced into batch on the production of new CRTs. However, it may not be possible to use all the cullet collected from the waste, because maximum cullet content cannot be very high from the standpoint of quality control. Furthermore, rapid development of flat display panels, such as LCD and PDP inevitably leads the reduction in the production of CRT. So, unused cullet may aggravate shortage of “secure” landfills for hazardous waste. Therefore, a method to extract lead from the glass is highly in demand.[2] However, owing to the high chemical durability of the lead silicate glasses, it is generally accepted that it is impossible to remove large portion of lead from the glass without decomposing glass matrix.

We have recently proposed several new processes to recycle colored soda–lime–silicate glass bottles, utilizing several phenomena in glass such as diffusion,[3] phase separation,[4] and crystallization.[5] Among them, subcritical hydrothermal treatment is one of the best methods because of its relatively low energy consumption without using environmentally unacceptable chemicals such as hydrofluoric acid.[5] Since this process employs fundamental reaction between silicate glass network and water, and succeeding crystallization, it is highly expected that this process successfully used to remove lead from lead silicate glasses. In this paper we report a novel method to remove lead from lead silicate glass of waste CRT funnel.

The glass composition of 6Na_2O–8K_2O–2MgO–4CaO–53SiO_2–23PbO–4Al_2O_3 (wt %), namely 7.3Na_2O–6.4K_2O–3.7MgO–5.4CaO–66.4SiO_2–7.8PbO–3Al_2O_3 (mol %), was obtained by two step melting to reduce vaporization of volatile PbO, as described follows. At first, 7.3Na_2O–6.4K_2O–3.7MgO–5.4CaO–66.4SiO_2–3Al_2O_3 glass was prepared by melting mixture of stoichiometric amount of Na_2CO_3, K_2CO_3, $MgCO_3$, $CaCO_3$, SiO_2, and $Al(OH)_3$ in an electric furnace with an alumina crucible at 1673 K for 3 h, then at 1873 K for 5 min. The glass was crushed and mixed with stoichiometric amount of PbO_2, and the mixture was melted at 1373 K for 30 min and 1573 K for 30 min, then poured to graphite plate, and finally stretched to form rods. 2.56 g of glass rods with a diameter of approximately 0.5 mm are placed in an SUS-316L flow type autoclave with inner diameter of 14.3 mm, and heated to 628 K. Temperature was measured by use of a thermocouple, sealed in an SUS-316 tube and placed in the autoclave. Pressure was kept 24 MPa by a back pressure regulator and subcritical water was continuously introduced by a high pressure pump at about 0.5–2 mL/min to keep pressure constant. After 3–7 h, pressure was removed and, the autoclave was cooled in air. After this operation, 2.46 g of white porous rod was obtained. It was crushed, soaked in 1.55 N nitric acid at 373 K for 15 h, and washed by water. Powder X-Ray diffraction (XRD) measurements were made with a Shimazu XRD-6000 diffractometer using Cu Kα radiation. Chemical analysis was made according to standardized methods (JIS R3101) utilizing atomic absorption spectroscopy. SEM observation and EDS analysis were made with JEOL JSM-5900 LVS.

After hydrothermal treatment, lead silicate glass changed to crystalline compound as evidenced by the XRD pattern in Figure 1. Some diffraction peaks were attributed to orthoclase (PDF 31-966). The others were not assigned, but diffraction peak at $2\theta = 8.82$ degrees ($d = 1.00$ nm) may correspond to that of inter-layer distances, frequently observed in layered silicate

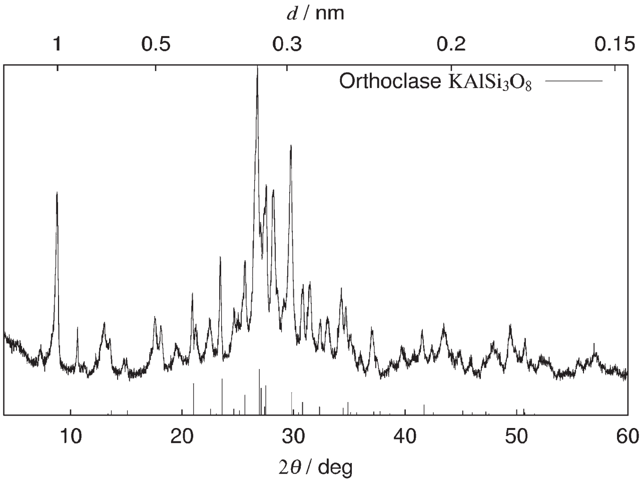

Figure 1. XRD pattern after hydrothermal treatment at 628 K and 24 MPa for 7 h.

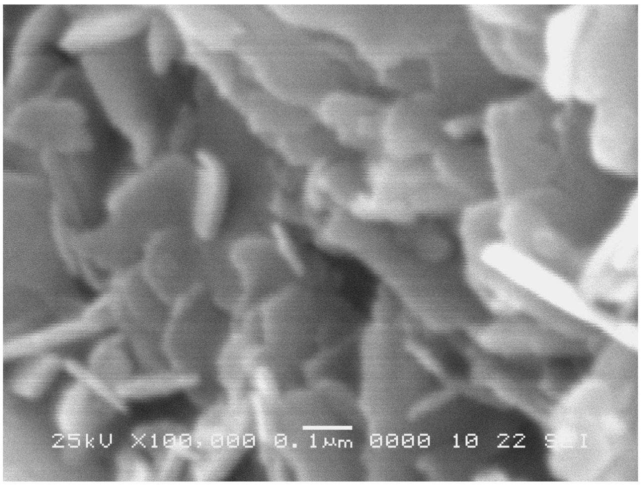

Figure 2. SEM image after hydrothermal treatment at 628 K and 24 MPa for 3 h.

compounds such as clay minerals and calcium silicate hydrate systems.[6] The formation of layered silicate was also supported by the observed SEM image as shown in Figure 2. Planer crystals, which are likely to occur when the crystals have layered structure, are clearly observed. Randomly oriented crystals probably indicate that homogeneous nucleation and crystal growth occur during the hydrothermal treatment because aligned crystals should be formed if the crystallization occurs from the surface. Surely, randomly oriented crystals can also be formed by the deposition from the water phase since some portion of the glass should dissolved in water. However, this possibility should be excluded because the crystals with similar size were formed even though the glass was treated in super critical water in which solubility of the glass should be greatly different because of the reduced dielectric constant of water. Additionally, if the deposition from the water phase was important, crystal size would be larger as lower supersaturation was expected when dissolution process was involved. Although composition of the glass in this study is quite different from the soda–lime–silicate glass, the shape and arrangement of obtained crystals were very similar to the poor tobermorite crystals obtained from soda–lime–silicate glass.[5]

The cations in this crystals are easily removed by immersing it in the nitric acid as shown in Table 1. It is seen that Ca, Pb, and Na are successfully extracted. The result of chemical analysis indicates that Pb in the material was as low as 2.38 wt %. Assuming that solubility of SiO_2 in subcritical water and nitric acid are negligible, fraction of removed lead was 93%.

Reaction of glassy silicate network and water molecule is generally explained as follows. When the glass is exposed to water at high temperature and pressure, water molecule can easily diffuse into glass and react with alkali metal oxide(Si–O$^-$–Na$^+$) to form hydroxy ions (Si–OH + Na$^+$ + OH$^-$). Hydroxy ions attack ≡Si–O–Si≡ bonding in silicate network and break it (Si–OH + Na$^+$O$^-$–Si).[7] Once silicate network is broken, glass transition temperature is drastically decreased down to the temperature where hydrothermal treatment temperature is carried out.[8] In addition, it is well known that nucleation and crystal growth are accelerated near the glass transition temperature.[9] Therefore, crystalline alkaline-earth lead silicate and orthoclase are easily formed when the incorporation of the water proceeds to a certain extent.

Table 1. Result of EDS analysis after hydrothermal treatment at 628 K and 24 MPa for 7 h and 1.55 N nitric acid treatment at 373 K for 15 h. We note that EDS analysis is not so reliable, especially at low concentration (i.e. <2%, but differ with samples and elements)

	SiO_2	Al_2O_3	K_2O	MgO	Na_2O	CaO	PbO
wt %	86.4	7.7	5.3	0.4	0.2	0	0

After leaching in acid, Mg, Na, Ca, and Pb are mostly removed, while Si, Al, and K are not. The reason why the potassium was not removed may be attributed to the structure of silicate crystals. In orthoclase crystal, each tetrahedral SiO_2 (partially occupied by aluminum atom) are three-dimensionally bonded. When orthoclase is soaked in acid, only potassium atoms existing at the surface of the crystal can be immediately removed, but other potassium atoms are hardly removed as surrounded by silicate tetrahedrons. Thus it dissolves in acid solution very slowly from surface, by layer-by-layer process.[10] On the other hand, each silicate layer in layered silicate such as tobermorite and clays are separated by cation layer and/or inter-layer spacing. Thus, cation in layered silicate compounds, such as Ca, Pb, Mg, and Na, can be easily replaced by proton in nitric acid, through the space between silicate layer.

The use of unique property of subcritical water may be essential to promote such reaction. We tried hydrothermal treatment at lower temperature such as 523 K, but only surface leaching was observed and all the glass remains amorphous. Probably, the use of subcritical water with lower dielectric constant prevents ions in the glass from being solved in water phase, and as a result, crystallization becomes dominant.

Lead silicate glass having the composition used in CRT's is treated in subcritical water. With the subcritical hydrothermal treatment the glass is converted to chemically active layered silicate compound. Finally, 93% of lead was removed by immersing this compound in the dilute nitric acid. unlike in the treatment at lower temperature.

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