Material Conversion of Waste Aluminoborosilicate Glass into Faujasite-type Zeolite using Alkali Fusion

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***Abstract*—*A large amount of liquid crystal display (LCD) television becomes popular for the last decades, and the amount of waste LCD panels will increase soon. LCD panels mainly consist of aluminoborosilicate glass, and it is difficult to recycle aluminoborosilicate glass using the same recycling method of soda-lime glass, due to the high strain point. Therefore, a novel recycling method for aluminoborosilicate is desired. In this study, we attempted to convert waste aluminoborosilicate glass powder into faujasite-type zeolite using alkali fusion method. Waste aluminoborosilicate glass powder (< 300 μm) were mixed with NaOH powder (the weight ratio of NaOH / aluminoborosilicate = 1.0 - 2.0), and then heated at 100 – 800 ^oC for 0.5 - 7 h to make a fused material with high solubility. This fused material was agitated in distilled water for one day, then heated at 80 ^oC for 24 hours to synthesize zeolite product. Most of the aluminoborosilicate glass were converted into soluble phases by alkali fusion with NaOH (NaOH / sample = 1.5) at 400 ^oC for 0.5 h, and could be transformed into faujasite-type zeolite. The cation exchange capacity (CEC) of the zeolite product is 1.9 mmol/g, which is 31 times higher than that of raw glass powder, and is 59% of CEC for commercial faujasite-type zeolite 13X (3.2 mmol/g). Zeolitization process from agitated material can be explained by theconcentrations of Si, Al and B in the product and the crystallinity of faujasite-typezeolite in the product.*

Keywords*—*Waste aluminoborosilicate glass, Faujasite-type zeolite, Alkali fusion, Recycle.

I. INTRODUCTION

In recent years, home appliance recycling law was established to promote the recycling society in Japan. Therefore, a novel recycling technology for typical home appliance, such as televisions (TVs), refrigerators and washing machines were developed to recycle. TV is a typical home appliance. In Japan, liquid crystal display (LCD) TVs began to popular since 2000, and demands for TV change from Cathode Ray Tube TV to LCD TV. LCD mainly consists of aluminoborosilicate glass. Therefore, in the future, a large amount of waste aluminoborosilicate glass will discharge in Japan [1-2]. Aluminoborosilicate glass mainly consists of SiO_2 and Al_2O_3,and is difficult to recycle by the typical method of soda lime glass because strain point of aluminoborosilicate glass (650 ^oC) is higher than that of soda lime glass (550 ^oC). Aluminoborosilicate glass also has high heat and chemical-resistance, and has various composition in each product. Therefore, it is difficult to recycle LCD again. From these background, new utilization of waste LCD is desired.

In recent years, researches have also been made to synthesize zeolite from industrial wastes, such as coal fly ash [3-6], papermaking sludge incineration ash [7-16], rice husk ash [17], waste ceramics [18, 19], stone cake [20, 21] and so on using hydrothermal reaction, andthere is possibility to convert a part of aluminoborosilicate glass waste into zeolite materialsby hydrothermal treatmentvia pretreatment, e.g. acid leaching [22-24]. Zeolite is microporous aluminoborosilicate minerals with regularly arrange pores, and can use as catalyst and ion-exchanger for cleaning polluted environment [25]. Zeolite has a structure in which tetrahedrons share the oxygen located at the apexes of the tetrahedral unit and are regularly bonded three-dimensionally [26]. Furthermore, since aluminoborosilicate glass contains boron, it would be possible to synthesize a boron-containing zeolite having high heat resistance and hydrophobicity by incorporating this boron into the structure of the zeolite [27-29].

In our previous studies,stable minerals, such as quartz, were converted into soluble alkali salts to synthesize zeolite using alkali fusion [30-35], and it would be possible to covert a large part of aluminoborosilicate to zeolite crystals via alkali fusion.

In this study, we tried to convert the aluminoborosilicate glass into zeolite using alkali fusion. For conversion of aluminoborosilicate into zeolite, alkali fusion was applied to convert insoluble oxide into soluble alkali salt to convert aluminoborsilicate glass powder into faujasite-type zeolite including boron.

II. MATERIALS AND METHODS

2.1 Raw material

In this study, we used powder of aluminoiborosilicate glass discharged from one of the company in Japan. Particle size of this sample is under 300 μm and the color is grey. The sample mainly consists of SiO_2 (66 %), Al_2O_3 (22 %), B_2O_3 (10%) and others.

2.2 Experimental procedure

Experiments are two steps. 1st step is alkali fusion. Aluminoborosilicate glass is fused with NaOH on various conditions; temperature, the ratio of NaOH to aluminoborosilicate glass and heating time are parameters. 5 g of aluminoborosilicate powder and 5 - 12.5 g of NaOH were mixed and the mixture was added into nickel crucible. The crucible set in the electric furnace, and then heated at 100 - 800 ^oC for 0.5 - 7 h. After heating, the crucible was cooled to room temperature naturally outside the electric furnace, then fused material were taken out and crashed.

Mineral phases in raw and fused material were analyzed by powder X-ray diffraction apparatus (XRD, Rigaku MiniFlex600). The solubility of Si, Al and B in raw and fused materials (meaning that reactivity of fused material to be converted into zeolite,) were investigated as follows. 0.1g of sample was added into 20 mL of 1 mol/L HCl solution and shaken for 24 hours. After shaking, filtration was carried out, and the concentrations of Si and Al in the filtrate were measured by atomic absorption spectrometer (AAS, Perkin Elmer, AAnalyst200) and that of B was measured by inductirely coupled plasma method (ICP, ICP-7500, Shimadzu) to calculate the solubility of fused material.

2nd step is zeolite synthesis. Fused material was converted into the precursor by shaking in distilled water, and then heated to synthesize zeolite crystals. 1 g of fused material was added into 5 mL of distilled water in 10 mL tube, and the tube was shaken for 24 hours to prepare the precursor. The precursor was heated to be converted into faujasite-type zeolite. The precursor was heated at 80^{o}C for various times in oil bath. After heating, the solid was filtered and washed with distilled water, and dried at 80^{o}C to obtain the product. Mineral phases in the product were analyzed by XRD and the concentrations of Si, Al, and B in the solid were measured by AAS and ICP as mentioned above for the solubility measurement. The cation exchange capacity (CEC) of raw material and the product were examined by modified shöllenberger method [7]. The specific surface area of the product was measured by specific surface area meter (Mascorb HM model-1208/1210, Mountech).

III. RESULTS AND DISCUSSION

Effect of heating temperature on the property of fused material was examined. Heating time was 3 hours, the ratio of NaOH to aluminoborosilicate glass was 2, and heating temperature was changed between 200^{o}C and 800^{o}C.

Figure 1 shows XRD patterns of fused materials heated at various temperatures. While the peak of the liquid crystal glass is broad, the peaks of alkali salts, such as Na_4SiO_4, $NaAlSiO_4$ and Na_2SiO_3, in the glass via alkali fusion at each temperature was confirmed. It was found that alkali fusion can be applied for the conversion of aluminoborosilicate glass with high chemical stability into alkali salts.

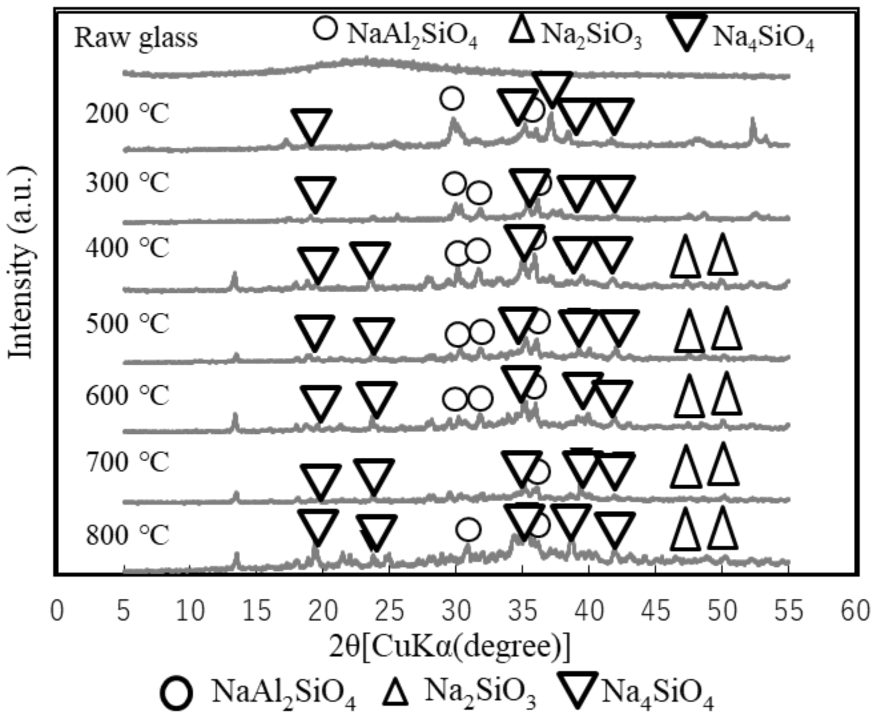

FIGURE 1: XRD patterns of fused materials at various temperatures.

Figure 2 shows the solubility of Si, Al and B from fused materials obtained at various temperatures. Before the alkali fusion treatment, solubilities of Si, Al and B from raw glass are 1.36 mmol/g, 0.028 mmol/g, and 0.022 mmol/g, respectively. With increasing the fused temperature, solubilities of these elements increased, and were almost constant (Si = 4.74 mmol/g, Al= 1.41 mmol/g, B= 1.04 mmol/g) above 400^{o}C. Therefore, the fused materials with high reactivity were obtained by alkali fusion above 400^{o}C.

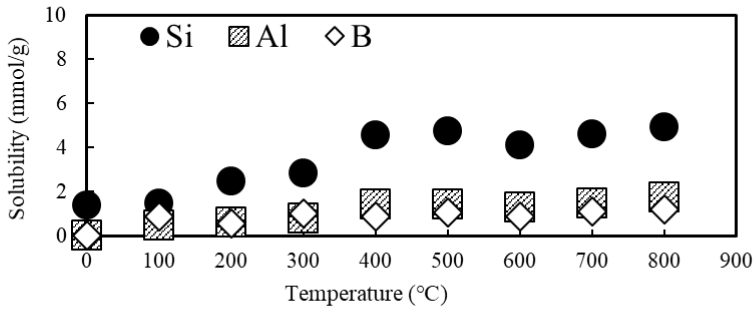

FIGURE 2: Solubility of the aluminoborosilicate glass fused with NaOH at various temperatures.

The effect of NaOH addition on the property of fused material was examined. Heating time was 3 hours, heating temperature was 400^{o}C, and the ratio of NaOH to aluminoborosilicate glass was changed between 1 and 2.5.

Figure 3 shows the XRD patterns of fused material with various amounts of NaOH addition. Alkali salts such as Na_4SiO_4, $NaAlSiO_4$ and Na_2SiO_3, were confirmed in all fused materials. With increasing the NaOH addition peaks of Na_4SiO_4 and $NaAlSiO_4$ appeared at the additional ratio of NaOH per raw glass = 1, their peaks increased, and peaks of Na_2SiO_3 appeared at the ratio of 1.5. Above the ratio of more than 2.0, the peak intensities decreased. The fused material obtained at the additional ratio of NaOH per raw glass = 1.5 has the highest intensity of alkali salts.

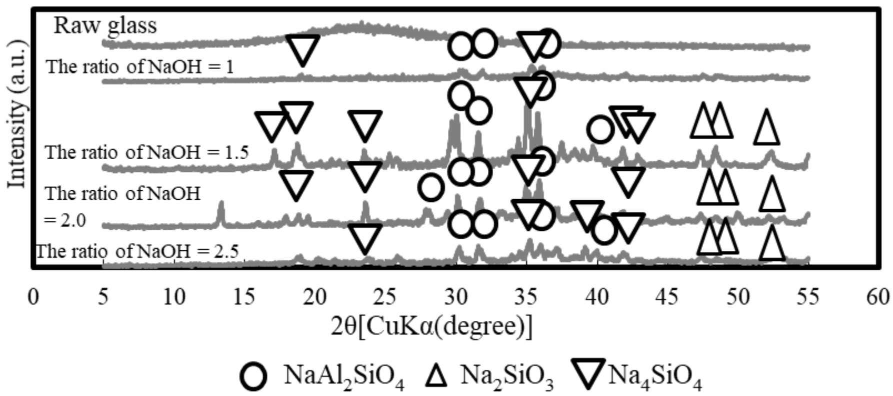

FIGURE 3: XRD patterns of fused material at various amount of NaOH.

Figure 4 shows the solubilities of Si, Al and B from fused material with various amount of NaOH addition. With increasing the addition amount of sodium hydroxide, solubility of Si, Al and B increased, and were almost constant (Si = 4.37 mmol/g, Al= 1.25 mmol/g, B=0.62 mmol/g) above the additional ratio of the 1.5. Therefore, fused materials with high reactivity were obtained above the ratio of 1.5 of NaOH per aluminoborosilicate glass.

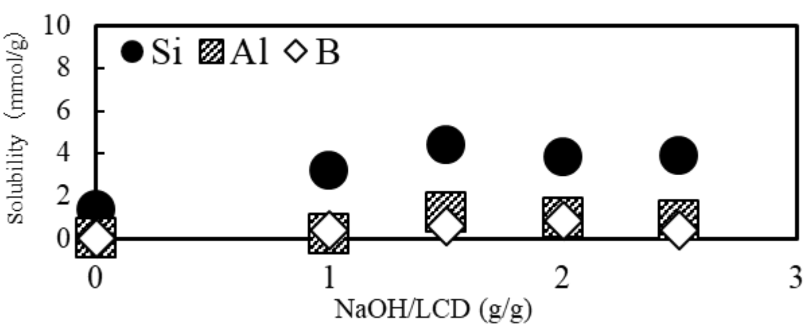

FIGURE 4: Solubility of the LCD fused with various weight of NaOH.

Effect of reaction time on the property of fused material was examined. The ratio of NaOH was 1.5, heating temperature was 400^{o}C, and heating time was changed between 0.5 and 7.

Figure 5 shows the XRD patterns of fused material during the alkali fusion reaction. It was confirmed that alkali salts were rapidly formed in fused material after 0.5-h reaction.

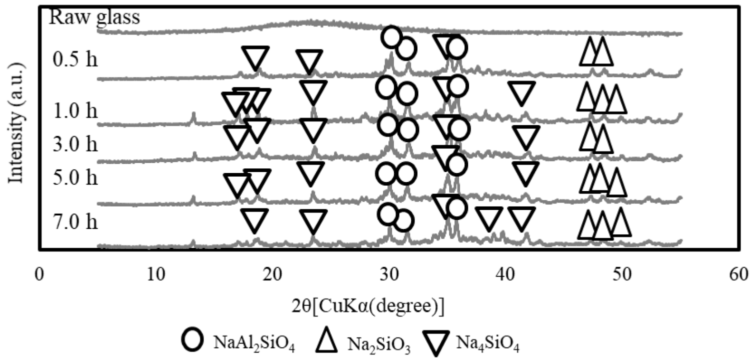

FIGURE 5: XRD patterns of fused material heated at various heating time.

Figure. 6 shows the solubilities of Si, Al and B from fused materials during the alkali fusion reaction. The solubilities of Si, Al and B rapidly increased at the initial stage of 30 min, and were almost constant (Si = 3.50 mmol/g, Al= 1.17 mmol/g, B=0.42 mmol/g) above 0.5 h. Therefore, high reactivity fused materials were obtained rapidly after 0.5-h heating.

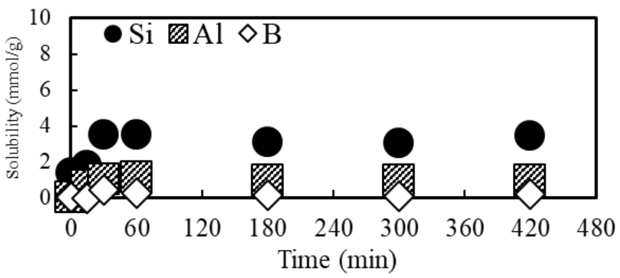

FIGURE 6: Solubility of the LCD fused with NaOH for various heating time.

From these results, we converted waste aluminoborosilicate glass into fused materials with high reactivity in the condition that heating condition is above 400^{o}C, the weight of NaOH/aluminoborosilicate glass is above 1.5, and heating time is above 0.5 h.

We attempted to synthesize zeolite from fused material obtained on the condition mentioned above.

Figure 7 shows the XRD patterns of the products. The precursor indicates broad peaks, which means that the precursor is formed as amorphousmaterials. During the reaction, the peaks of faujasite-type zeolite increase in the products, and is constant after 8 hours.

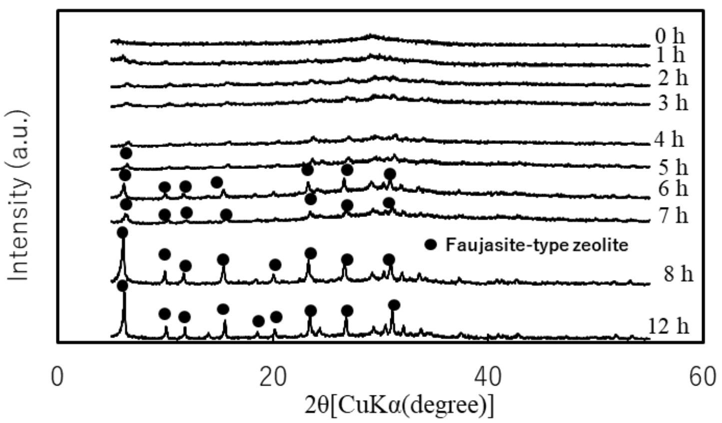

FIGURE 7: XRD patterns of the products during heating at 80^{o}C.

Figure 8 shows the contents of each element in the product. The contents of Si, Al and B in the product increase in the initial stage for 3 h, and then be almost constant (Si=2.95 mmol/g, Al=1.84 mmol/g, B=0.26 mmol/g,), which are good accordance with XRD patterns as shown in Fig. 8. It would be considered that the reaction between the solution and the solid mainly occurs for 4 h, and crystallization of the solid mainly occurs after 4 h. It is noted that the Si/Al molar ratio of the product after 8 h is 1.89, which is almost same as that of faujasite-type zeolite X, and the boron content of the product was about 3 wt%.

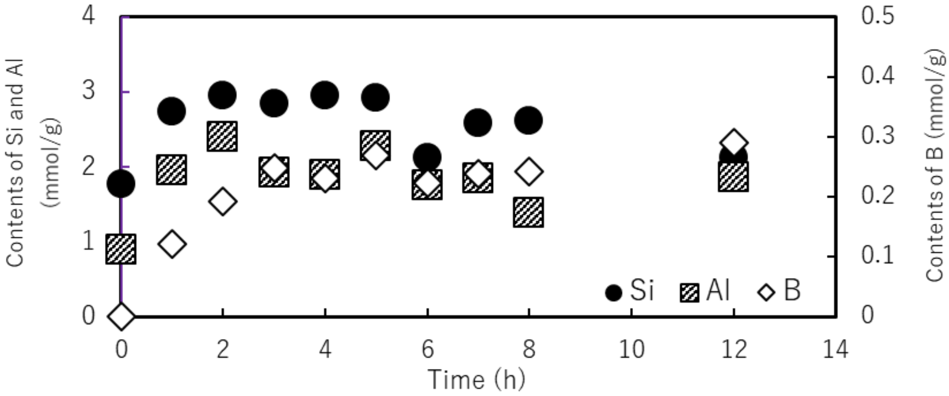

FIGURE 8. The contents of Si, Al and B in the product during the reaction.

Figure 9 shows SEM images of (a) aluminoborosilicate glass, (b) fused material, (c) the precursor and (d) the product. Raw glass was particle like amorphous glass pieces, and fused material was particle with melted surface like alkali salts. The precursor was amorphous gel particles, and the product has faujasite-type zeolite octahedral crystals.

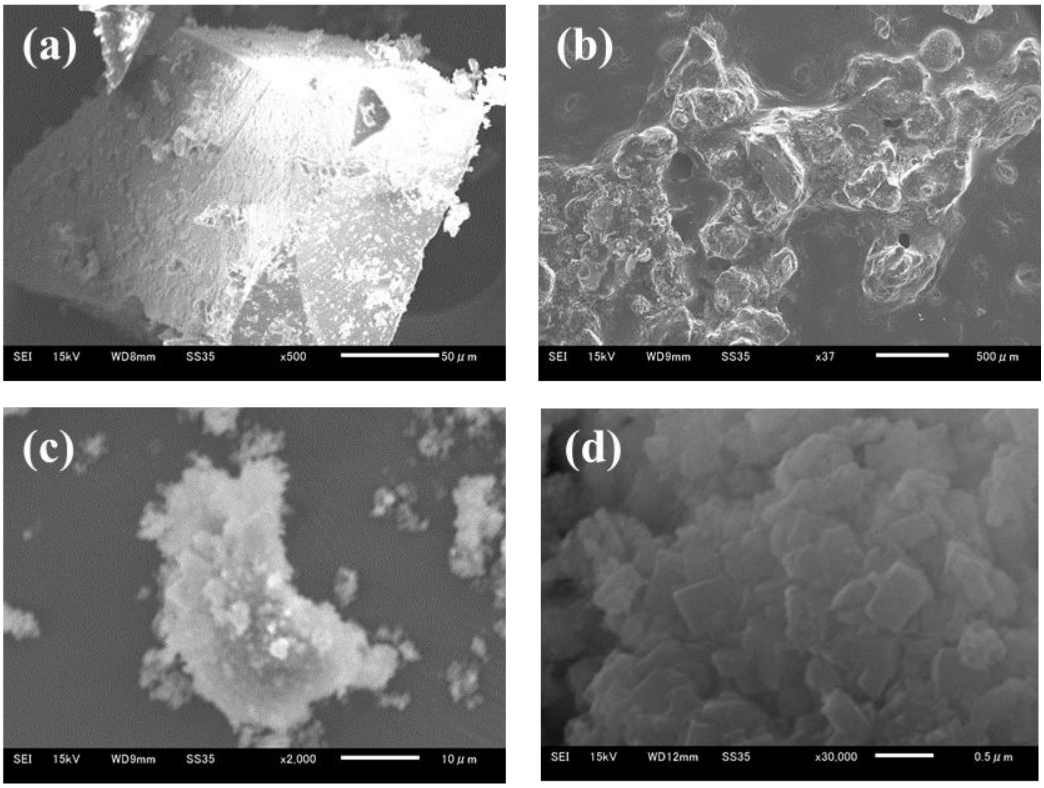

FIGURE 9: SEM image of (a) aluminoborosilicate glass, (b) fused material, (c) the precursor and (d) the product.

The CEC of the product was 1.9 mmol/g, which is 31 times higher than that of raw glass powder. It is noted that the CEC of commercial faujasite-type zeolite was 3.2 mmol/g. The specific surface area of the product was 201 m^2/g, which is 55 % of the commercial molecular sheives 13X (365 m^2/g).

These results indicate that waste aluminoborosilicate glass can be converted into faujasite-type zeolite containing 3 % boron using alkali fusion.

IV. CONCLUSION

We attempted to synthesize faujasite-type zeolite from waste aluminoborosilicate glass using alkali fusion. The processing conditions to obtain fused material with sufficiently high reactivity for zeolite formation was investigated. By alkali fusion, we converted waste aluminoborosilicate glass into fused materials with high reactivity on the condition that heating condition is above 400^{o}C, the weight of NaOH/aluminoborosilicate glass is above 1.5 and heating time is above 0.5 h. Faujasite-type zeolite can be synthesized from aluminoborosilicate glass using alkali fusion, and the CEC of the product with 3 wt% boron content is CEC of 1.9 mmol/g and specific surface area of 201 m^2/g.

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