Changes of Alkali Metal Ions and Alkaline Earth Metal Ions on The Surface of Lead Silicate Glasses

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Abstract. Lead silicate glasses are currently the most employed glasses for micro-channel plates (MCP) and other applications. X-ray photoelectron spectroscopy was used to determine the changes of alkali metal ions and alkaline earth metal ions on glasses surface during hydrogen reduction. The results showed that the chemical states of alkali metal ions and alkaline earth metal ions did not change. However, the content of these metal ions increases, which is beneficial to secondary electron emission yield of lead silicate glasses and the gain of MCPs.

1. Introduction

Lead silicate glasses based on R$_2$O-PbO-SiO$_2$ system are currently the most employed glasses for micro-channel plates (MCP) [1-4]. They are also used for other applications: electrical vacuum devices, sealing glasses, radiation protection, optical glasses, for example. In the temperature field, the migration of ions, especially alkali metal ions and alkaline earth metal ions, has an important influence on the properties of lead silicate glass. Knowledge of ionic mobility in these glasses is of great importance for a proper understanding of these materials and their applications.

Hydrogen reduction is an important chemical reaction in the preparation of MCP based on lead silicate glasses. After this process, lead silicate glasses have higher secondary electron emission coefficient and conductivity. As the study by A M Then et al [5] showed, alkali metal ions migrate in lead silicate glasses, meanwhile, the migration rates of different alkali metal ions are different. However, some studies have shown that alkali metal ions (Na$^+$, for example) do not migrate to the surface of lead silicate glass during hydrogen reduction [6].

In order to clarify the migration of metal ions on the surface of lead silicate glasses, we investigated the changes of metal ions (including alkali metal ions and alkaline earth metal ions) on the surface of lead silicate glasses by X-ray photoelectron spectroscopy method.
2. Experimental

Lead silicate glasses were synthesized in 500g batches in a corundum crucible using reagent-grade silica, lead oxide and sodium, potassium, cesium, magnesium, calcium, barium carbonate powders or nitrate powders. The mixture with 66% of SiO$_2$, 18% of PbO, 8% of R$_2$O, 5% of RO and other oxide was melted at 1450°C, and refined for 2h at the same temperature. It was quenched by pouring onto a stainless steel plate, and annealed at 500°C for 4h to reduce the thermal stress. Finally, flake glass samples were prepared for hydrogen reduction treatment and performance testing.

The glass samples were reduced in hydrogen atmosphere by a furnace. The reduced temperature was as follows, non-reduction, 300°C, 400°C, 500°C, 600°C, and the reaction time was as follows, 0h, 0.5h, 2h, and 3.5h, respectively.

After hydrogen reduction, all samples were measured by XPS (ESCALAB 250, Thermo Fisher Scientific, USA) with Al Kα radiation (1486.6 eV). The test conditions were as follows: pass energy of 30 eV, analyzed area diameter of 500 μm, and energy resolution of 0.80 eV. The neutralization was used to correct the shift of binding energy caused by charge accumulation, and the energy shift was compensated by the binding energy of C 1s (284.8 eV). Atomic concentrations of alkali metal ions and alkaline earth metal ions were calculated from the relative area of photoelectron peaks.

3. Results and Discussion

3.1. The changes of alkali metal ions on the surface of lead silicate glasses

As the XPS spectra showed in Figure 1, there is no change in the binding energy of Na 1s at 1071 eV, the binding energy of K 2p3/2 and Cs 3d5/2 maintain at 293.4 eV and 724.5eV, respectively. This indicates that the chemical state of alkali metal ions has not changed during the hydrogen reduction. However, the relative content of alkali metal ions on the surface of lead silicate glasses calculated by XPS peak area changes significantly, as shown in Figure 2(a). The content of alkali metal ions increases with the increase of reduction temperature. The higher the temperature is, the more alkali metal content in the surface layer. This is because the thermal motion of ions is enhanced at high temperature, while the free energy of the new surface after reduction is generally higher, so that the ions tend to segregate towards the surface. It is obvious from the figure that the migration of sodium ions is much higher than that of potassium ions and cesium ions. According to the ion diffusion equation, the faster the ion with small radius diffuses. According to the ion diffusion equation, ions with small radius are easier to diffuse from the inside of glass to the surface.

The glass samples at different reduction time were tested, and found that there are no changes in binding energies and chemical states of alkali metal ions, consistent with the experimental results of reduction temperature. The calculation results of XPS spectra show that the mobility of alkali metal ions increases with time. Moreover, the migration rate of sodium ion and potassium ion is similar, and higher than that of cesium ions.
Figure 1. XPS spectra of sodium ions (a) and cesium ions (b) at different temperature

Figure 2. Relationship between content of alkali ions in glass surface with reduction temperature (a) and time (b)

3.2. The changes of alkaline earth metal ions on the surface of lead silicate glasses

Further, we studied the migration of alkaline earth metal ions on the surface of lead silicate glass during hydrogen reduction. The results are shown in Figure 3 and Figure 4. With the increase of reduction temperature or time, the chemical states of alkaline earth metal ions on glass surface did not change. As shown, the binding energy of Mg 1s is 1038.5 eV, and the binding energy of Ba 3d5/2 is 779.8 eV. Alkaline earth metal ions segregate on the surface of lead silicate glass just like alkali metal ions, and the migration speed slows down with the increase of ion radius. On the whole, the rate and amount of the migration of alkaline earth metal ions are less than that of alkali metal ions. Therefore, it can be considered that the migration of alkali metal ions on glass surface is more prominent, and it will also have a greater impact on the chemical state and properties of glass surface.
3.3. Effects of metal ions migration on secondary electron emission coefficient of glasses

Lead silicate glass has a high secondary electron emission coefficient, so it is often used as a basic material for the preparation of MCPs. Segregation of alkali metal ions on glasses surface can reduce the surface potential barrier, which is conducive to the escape of secondary electrons, can increase the yield of secondary electrons, and improve the electronic gain of MCPs. Moreover, both MgO and BaO have high secondary electron yields. The secondary electron yields of lead silicate glass after reduction increased significantly compared with that before reduction [6-7], which was expected, as Figure 5 shown. According to the addition rule, the secondary electron emission coefficients of glass samples treated by different reduction processes are calculated, as shown in Figure 6. With the increase of reduction temperature or time, the secondary electron yield increases rapidly at first, then stabilizes gradually, and finally decreases slightly, which coincides with the results of MCP electronic gain measurement [3].
Figure 5. Secondary electron emission yield of glasses before and after reduction

Figure 6. Effects of reduction process on second electron yield of glasses

4. Conclusion
The changes of metal ions (including alkali metal ions and alkaline earth metal ions) on the surface of lead silicate glasses were studied by XPS method. With the increase of reduction temperature or time, the chemical states of alkali metal ions and alkaline earth metal ions on glass surface did not change. However, the content of these metal ions increases, and the migration of sodium ions is much higher than that of potassium ions and cesium ions. The migration rate of alkaline earth metal ions is slower than that of alkali metal ions. The increase of alkali metal ions and alkaline earth metal ions on glass surface is beneficial to secondary electron emission yield of lead silicate glasses and the gain of MCPs.
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