Effect of mental oxide on the structure and property of rare earth doped glass

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Abstract. Glass fiber reinforced concrete (GFRC) is a very widely used material. However, the highly alkaline environment in concrete will erode and destroy the glass fiber therein, so it is particularly important to improve the corrosion resistance of glass. In this study, ZrO₂ and TiO₂ were introduced into the La₂O₃-CaO-Al₂O₃-P₂O₅ system glass and their effects on the structure and properties of the glass were systematically studied. The results show that the introduction of ZrO₂ and TiO₂ has a similar effect on rare earth doped glass. For one thing, it will increase the density of the glass and make the structure of the glass dense. For another, it can improve the water resistance and alkali corrosion resistance of the glass. SEM images showed that after the glass was immersed in the alkali solution, a protective CaO film was formed on the surface of the glass sample. As the etching time increases, the protective film on the glass surface peels off in a sheet shape, and the skeleton of the glass peels off in a lump shape.

1. Introduction

Concrete materials have the characteristics of convenient material, good plasticity and high durability. But the concrete itself has a large weight and low tensile strength, which prevents its wide application. By adding glass fiber to the concrete material to form glass fiber reinforced concrete (GFRC) can greatly improve its overall performance and expand its scope of application[1].

The structure, composition and properties of aluminum phosphate and calcium phosphate determine that it is an ideal biological material, which can be used for human teeth and bones[2]. But because of the double bond in the structure of phosphate, it is different from silicate in structure, phosphate glass has lower water resistance and chemical stability than silicate glass.

Glass fiber is usually added to concrete as a reinforcing material[3], and there is a high alkali environment in the cement, which contains MgO, CaO, Al₂O₃, K₂O, SiO₂. The hardening process of cement is accompanied by the production of by-products such as KOH, Ca(OH)₂, NaOH, which hardens into gelatinous substances that cause the pH of the cement to rise significantly[4]. The OH⁻ in the base destroys the skeleton of the [PO₄] tetrahedron, and destroys Si-O-Si to form Si-O group, which causes SiO₂ to dissolve in the lye, thus alkali corrosion of silicate glass is generated[5].

When rare earth ions enter the glass structure as network exosomes[6], they will affect the glass structure and performance[7]. Since rare earth ions have a high dissolution rate in phosphate glass, they have been widely concerned[8]. Compared with silicate glass, the price of phosphate raw materials is relatively low[9], the melting temperature required in the manufacturing process is also low, and it can have properties comparable to silicate glass[10,11]. Since ZrO₂ and TiO₂ have excellent corrosion resistance, it is meaningful to study the effect of the introduction of ZrO₂ and TiO₂ on rare earth doped...
aluminum phosphate glass, and it is expected to obtain materials with excellent performance and low cost.

2. Experimental

2.1. Materials
The specific components of the glass are shown in Table 1 and Table 2.

| Table 1. Main components of ZrO2-added aluminophosphate glass (mol%) |
|---|
| **Number** | **P2O5** | **CaO** | **Al2O3** | **La2O3** | **ZrO2** |
| LZ0 | 57 | 30 | 12 | 1.00 | 0 |
| LZ0.3 | 57 | 30 | 12 | 1.00 | 0.3 |
| LZ0.6 | 57 | 30 | 12 | 1.00 | 0.6 |
| LZ0.9 | 57 | 30 | 12 | 1.00 | 0.9 |
| LZ1.2 | 57 | 30 | 12 | 1.00 | 1.2 |
| LZ1.5 | 57 | 30 | 12 | 1.00 | 1.5 |

| Table 2. Main components of TiO2-added aluminophosphate glass (mol%) |
|---|
| **Number** | **P2O5** | **CaO** | **Al2O3** | **La2O3** | **TiO2** |
| LT0 | 57 | 30 | 12 | 1.00 | 0 |
| LT0.3 | 57 | 30 | 12 | 1.00 | 0.3 |
| LT0.6 | 57 | 30 | 12 | 1.00 | 0.6 |
| LT0.9 | 57 | 30 | 12 | 1.00 | 0.9 |
| LT1.2 | 57 | 30 | 12 | 1.00 | 1.2 |
| LT1.5 | 57 | 30 | 12 | 1.00 | 1.5 |

2.2. Experiment Process
The required raw materials were accurately weighed using the analytical balance (FA2004, Shanghai Yuheng Electronic Instrument Co., Ltd., China). Put the weighed ingredients into the mixing bottle, and the mixing bottle was shaken to uniformly mixed the batch materials. After mixing uniformly, the batch materials were placed in an alumina crucible, then set the resistance furnace (SG-G06163, Jiangxi Sanxing Instrument Co., Ltd., China) program and placed the crucible in a resistance furnace for glass melting. The raw material will be heated from 50°C to 1350°C, and then heated at 1350°C for 3 h to remove bubbles in the melt.

After the heat preservation, a uniform bubble-free melt was obtained, the crucible was taken out, tilted, and the glass melt was poured onto a graphite plate, quenched and cast, then placed in air to be naturally cooled to room temperature. When the sample was cooled, it was taken out with a pliers, part of the glass was broken into small pieces, and then the crushed sample was ground by a dimple grinder (RM-200, Germany NETZSCH). After grinding, use 60 mesh, 80 mesh, 200 mesh sieve to sieve the glass powder. In this study, six different metal oxide doping levels (0, 0.3, 0.6, 0.9, 1.2 and 1.5 mol%) of rare earth aluminum phosphate glass were studied, and their corresponding glass samples were referred to as LZ-X and LT-X (Z stands for ZrO2, T stands for TiO2, X is the mole percent of metal oxide).

According to Archimedes' principle, a density analyzer (AR233CN, Ohaus Instruments, Inc., America) was used to measure the density of the sample. After grinding the sample and sieving, select 60 to 80 mesh small glass particles for chemical stability test. The appropriate amount of sample was weighed and placed in a centrifuge tube, and deionized water or alkali solution was injected. After sealing, the centrifuge tube was placed in a constant temperature water bath (HH-S8, Jiangsu Jintan Medical Instrument Factory, China). The sample was taken out at intervals, washed and dried, and the weight loss was calculated. Infrared spectrometer (Nicolet-380, Thermol Fisher) was used to detect the internal structure of the sample and the wavelength was 400–4000 cm⁻¹. Scanning electron microscopy...
3. Results and Discussion

3.1. Effect of adding metal oxides on the density of aluminophosphate glass

It can be seen in Figure 1 that as the amount of added ZrO$_2$ increases, the density of the LZ series samples tends to increase gradually. It is related to the relative molecular mass of the atom and the density of the network structure. As the content of ZrO$_2$ is gradually added, the bonds P=O and P-O-P in the glass network structure are gradually reduced to produce P-O-Zr, which makes the network structure of the glass more dense, and strengthen the network structure of glass, which increases the density of the glass\cite{12}; the relative molecular mass of ZrO$_2$ is larger, with the gradual increase of the content of ZrO$_2$ incorporated, the density of the sample will show an upward trend. As can be seen from the above figure, as the amount of TiO$_2$ incorporation increases, the density of the LT series shows a gradual increase, because when the titanium ions acquire the free oxygen in the glass network structure, they can enter into the glass network structure in the form of [TiO$_4$] tetracoordinate, which can connect the broken P-O network. Moreover, titanium ions have a high field strength and can play a role in accumulation, which makes the accumulating force of the glass network structure continuously increase, thereby increasing the bulk density of the glass and the packing density of oxygen atoms. At the same time, as the content of TiO$_2$ incorporated is gradually increased, the network density of the glass matrix and the cohesive force of the glass structure are continuously increased, thereby improving the stability of the glass structure\cite{13}.

![Figure 1. Comparison of density change of LZ and LT series.](image)

3.2. Effect of metal oxide doping on structure of aluminophosphate glass

It can be seen in Figure 2 there are mainly the following characteristic peaks. Around 1626 cm$^{-1}$ is the H-O-H bond bending vibration; near to 1282 cm$^{-1}$, it represents the stretching vibration of the P=O bond and the [PO$_3$] group\cite{14}; the vicinity of 1124 cm$^{-1}$ represents the asymmetric stretching vibration

![Figure 2. Infrared spectrum of (a) the LZ, (b) the LT series.](image)
of (PO₃)²⁻ in Q² group; the peak near 928 cm⁻¹ represents the asymmetric stretching vibration of P-O-P; the peak near 756 cm⁻¹ represents the bending vibration of P-O-P[15]. From the infrared spectrum of the LZ series of samples, it can be seen that the symmetrical stretching vibration of P-O-P bond near 756 cm⁻¹ increases first and then decreases, this is because the addition of zirconium ions decreases the number of P-O-P bonds in the network structure of glass, P-O-P in the network structure is replaced by P-O-Zr, and the bond strength of P-O-Zr is stronger than P-O-P, so it enhances the network structure of glass. The vicinity of 928 cm⁻¹ is the asymmetric stretching vibration of the P-O-P bond. The stretching vibration of the [PO₂] group and the P=O bond is in the range of 1282 cm⁻¹, and the intensity of the peak is gradually decreased because the added ZrO₂ breaks the P=O and the P-O-P bond in the glass network structure and generates P-O-Zr, which strengthens the network structure of the glass. When the number of P=O bonds in the structure is reduced, the glass network structure will become more compact. The vicinity of 1626 cm⁻¹ is the bending vibration of the H-O-H bond. The possible reason is that the powder sample absorbs free water in the air during production[16]. But for the LT series, the P-O-P in the network structure is replaced by P-O-Ca or P-O-Al. The bond strength of P-O-Ca or P-O-Al is stronger than that of P-O-P, so the network structure of the glass can be made closer. The combination of titanium ions and oxygen to form [TiO₄] also contributes to a reduction in the number of P-O-P bonds. The intensity of the peak shows a decreasing trend because the titanium ions in the glass system break the P=O bond in the glass network structure and causes it to break, P-O-Ca or P-O-Al is formed. Meanwhile the titanium ions are combined with oxygen to form [TiO₄], when the number of P=O bonds is reduced, the glass network structure becomes more compact.

3.3. Addition of metal oxides on chemical stability of aluminophosphate glass

Figure 3 shows the trend of mass loss rate per 5h of LZ series glass in alkali resistance test. As the corrosion time increases, the weight loss rate of the LZ series glass shows a trend of rapidly increasing and then stabilizing. The main reason for this result is that when the sample is immersed in the alkali solution, the skeleton of the glass is eroded by the alkali solution, so that the alkali-loss weight loss rate of the glass gradually increases. As the time of corrosion of the sample in the lye increases, a layer of CaO film is formed on the surface of the glass sample. This film can prevent the lye from further erosion, thereby reducing the weight loss rate of the glass and slowly tending to be flat. In the alkali resistance experiment, the weight loss rate of LT series glass shows an overall increasing trend with the increase of corrosion time. This is the skeleton of the glass is attacked by the alkali solution, the network structure is attacked by OH⁻, resulting in an uneven surface to make the alkali resistance worse, and the alkali-resistant weight loss rate of the glass gradually increase. The addition of metal oxides leads to P=O fracture in the glass structure and the formation of new P-O-M (M represents Zr or Ti), thereby enhancing the density of the glass network structure. The alkali-resistant weight loss of the glass sample is lowered. However, when more metal oxides are added, the oxygen supplied by the oxide damages the network structure of the glass, resulting in a weak network structure of the glass, thereby reducing the alkali resistance of the sample and causing the weight loss rate of the sample to gradual increase. It can be found that the incorporation of a certain amount of ZrO₂ and TiO₂ can improve the alkali resistance of the glass, when the doping amount of TiO₂ is 0.9% (LT0.9), the sample has the lowest alkali-loss weight loss rate, indicating that it has good alkali resistance.

Figure 4 is a plot of the mass loss rate per 17 h in the LZ and LT series glass water resistance test. It can be seen that as the corrosion time increases, the weight loss rate of the glass sample shows a trend of increasing first and then decreasing. The main reason for this result is that the erosion of water on the glass at the beginning causes the weight loss rate of the glass to increase. However, as the corrosion time becomes longer, the hydration product produced by the corrosion of the phosphate glass fails to dissolve in the solution, but adheres to the upper layer of the glass, thereby forming a protective film, which hinders further erosion of the glass by water. When the amount of ZrO₂ is 1.2%, the sample weight loss rate is the smallest, indicating that when the blending amount is 1.2%, the water corrosion resistance of the glass is relatively good, when the amount of TiO₂ is 0.6%, the weight loss rate of the sample is the smallest, indicating that the water corrosion resistance of the glass is
relatively good when the blending amount is 0.6%. The surface of the glass sample is attacked by the aqueous solution, which causes the weight loss rate of the sample to increase. However, as the oxide content increases, ion exchange occurs on the surface of the glass, and the metal ions exchange with ions of relatively small molecular mass, the weight loss rate decreases. And then as the content of the incorporated oxide increases, because the molecular weight of the metal ions is larger, so that the macromolecules are eluted from the glass structure, and the weight loss rate of the sample is increased.

![Figure 3. Trend of weight loss rate per 5 h of (a) LZ and (b) LT series glass in alkali resistance test.](image)

![Figure 4. Trend rate of mass loss rate per 17 h in (a) LZ and (b) LT series glass water resistance test](image)

![Figure 5. SEM image of alkali-resistant glass samples before and after experiment, a) the original sample, b-f) alkali-resistant after 5h, 10h, 15h, 20h, 25h sample morphology](image)

3.4. *Surface morphology of aluminophosphate glass*

SEM image of the corrosion process of glass by alkali is shown in Figure 5. As can be seen from Figure 5a, the surface of the sample is very smooth before the alkali resistance test, it can be seen from
Figure 5b, when the sample is eroded by the lye, a protective film is formed on the surface of the sample to protect the sample, it is shown in Figure 5c that as the lye further erodes the sample, the protective film on the surface of the sample is eroded by the lye and form a lot of cracks, and begins to fall off in the form of a sheet, with the further increase of erosion time, the large protective film on the surface of the sample in Figure 5d falls off from the surface of the glass in the form of sheets. At the same time, the skeleton of the glass is corroded by alkali solution, which results in obvious cracks. From Figure 5e, it can be seen that the surface of the glass is already very rough, and there are obvious and numerous cracks in the interior of the glass, as can be seen in Figure 5f, the surface of the glass has fallen off in a block and the glass has broken into many small pieces.

4. Conclusion
The performance of rare earth dropped aluminophosphate glass, especially the chemical stability, can be improved by externally doping different content and different kinds of metal oxides. The incorporation of different amounts of ZrO₂ into the aluminophosphate glass causes the P=O and P-O-P bonds in the aluminophosphate glass system to be destroyed, and the glass network structure becomes more compact. The results of chemical stability study show that the addition of ZrO₂ and TiO₂ can make the network structure of the glass tight. The addition of a certain amount of ZrO₂ and TiO₂ can improve the water and alkali resistance of the glass. Compared with ZrO₂, doped TiO₂ has better water resistance than ZrO₂. The doping metal oxides in rare earth dropped aluminophosphate glass can significantly optimize the chemical stability of glass, the optimal doping amount of metal oxide can be used as the next research direction.

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