Effect of CaO on Phase Separation and Properties in Na$_2$O-CaO-SiO$_2$-P$_2$O$_5$ Opaque Glass

Lida Luo$^{1,2}$, Zihao Li$^{1,3}$, Qingwei Wang$^{1,2*}$, Kaidong Lan$^3$ and Weizhong Jiang$^1$

$^1$State Key Laboratory for Modification of Chemical Fibers and Polymer Materials, Donghua University, Shanghai 201620, People’s Republic of China
$^2$Engineering Research Center of Advanced Glass Manufacturing Technology, Ministry of Education, Shanghai 201620, People’s Republic of China
$^3$.Shanghai Jingcai New Materials Co.Ltd, Shanghai, 201800, China
*Corresponding author: wqwq888@dhu.edu.cn

Abstract. In the Na$_2$O-CaO-SiO$_2$-P$_2$O$_5$ opaque glass system, the effects of CaO on the phase separation and properties were investigated by means of SEM, XRD, UV-VIS Spectrophotometer, Thermal dilatometer, etc. The results showed the size of the second phases enriched with phosphate became smaller from 200nm to 80nm with the increase of CaO concentration. CaO had clear influence on the transmittance of opal glass, and the glass was changed into semi opaque when the amount of CaO was 12%. It also affected the crystallization of the glass samples, especially in crystal peak intensity of the Na$_3$Ca$_6$(PO$_4$)$_5$ and Zn$_2$P$_2$O$_7$, the coefficient of thermal expansion of sample was reduced but the density increased with the increase of CaO concentration. Results showed that Calcium ions in Na$_2$O-CaO-SiO$_2$-P$_2$O$_5$ system was good to bind with the P ions and boost the separation of the second phase and the crystallization.

1. Introduction
With the rapid development of society, the demand of people for material life is getting higher and higher. Opal glass is widely used in architecture[1], decoration[2], containers[3], lamps[4,5] and other fields[6], due to its soft color and delicate appearance. However, the volatilization of fluoride in opal glass is not only harmful to the environment and the human body, but causes huge economic losses by fluoride erosion in the furnace during production, so the study of fluorine-free opal glass has been concerned in the world. Phosphate opal glass uses phosphate as an emulsion, which can avoid volatilization of fluoride, save costs, and reduce pollution, which is one of the important development directions of opal glass. As a network modifier of glass, Ca$^{2+}$ does not participate in the network, and belongs to an external ion of the network. Calcium ions have very little activity in the structure and are not easily precipitated from glass can reduce viscosity of high temperature glass, it is because Ca$^{2+}$ can polarize bridge oxygen and weaken the silicon oxygen bond force.

At present, the influence of CaO on glass has been studied[7-12]. Research shows that: in CaO-Al$_2$O$_3$-SiO$_2$ microcrystalline glass, the increasing of CaO is beneficial to the crystallization of microcrystalline glass, and can reduce the crystallization temperature[8]. Moreover, with the increase of CaO and the decrease of Al$_2$O$_3$, the precipitation of calcium silicate crystals is promoted, and the dielectric constant and thermal expansion coefficient of the sample are increased. The increase of the proportion of CaO/SiO$_2$ in the sample can reduce the sintering temperature and increase the dielectric constant, dielectric loss, and thermal expansion coefficient of the sample[11].
Although CaO has many studies on the performance of glass, there are fewer studies on the influence of changing CaO on the phase separation and performance of Na₂O-CaO-SiO₂-P₂O₅ opal glass.

In this paper we presented comprehensive study on the Na₂O-CaO-SiO₂-P₂O₅ opaque glass system with different concentrations of CaO, and the effects of CaO on the phase separation and properties were discussed and investigated by means of SEM, XRD, UV-VIS Spectro Photometer, Thermal dilatometer, etc.

2. Experimental

2.1. Sample Preparation
The opal glass samples were made according to the mass ratio of 69SiO₂ – xCaO-12Na₂O-6B₂O₃-4P₂O₅-3ZnO (x=6, 8, 10, 12, 14) using reagent grade silica, calcium carbonate, sodium carbonate, boric acid, sodium phosphate and were noted as C6, C8, C10, C12 and C14 respectively. The homogenized mixture of raw ingredients about 1000 g was melted at 1530 °C for 2 h with a 90Pt/10Rh crucible, the melt was cast into a steel mold to form glass block of 50 mm×50 mm×10mm, which were annealed at 600 °C for 2 h.

2.2. Sample Characterization
The microstructure of the opal glass specimens was observed using a field emission scanning electron microscope (JSM5600 LV, JEOL, Japan) before which the section was broken. From crystallized and powdered samples, X-ray diffraction patterns were recorded using CuKa radiation in a 2θ ranging from 10° to 70° (RAX-10, RIGAKU, Tokyo, Japan). The samples were cut into the block of 10mm×30mm×30mm, and the surface was polished. The whiteness test was carried out by the WSB2 whiteness meter. The transmittance of glass samples was measured using a Ultraviolet visible spectrophotometer (solid) (Lambda 950, Perkin Elmer) before which the samples were cut into blocks of 5mm×5mm×25mm and polished. Meanwhile, the samples were cut into 4mm×4mm×25mm blocks and polished, the density was tested by ZMD-1 solid densitometer, and the coefficient of thermal expansion was tested by a relaxation thermal dilatometer (DIL402C), and which test temperature region was 50~300 °C, and the heating rate was 5 C/min.

3. Result and Discussion

3.1. Microstructure and Phase Separation
Field emission scanning electron (FESEM) images of the glass samples with different concentrations of CaO were shown in Figure 1. With increasing CaO content from 6wt.% to 14wt.%, the phosphorus rich glass phase became gradually dispersed, phosphorus rich phase changes from rounded to plum blossom shape, and then by the plum blossom shape into a dispersed state. In sample C6, as shown in Fig.1(a), the separated droplet was round and the diameter is about 200nm, and in sample C14, the plum blossom shape gradually separated into dispersed droplets, and the diameter of the split phase is about 80nm.
3.2. Crystallization

Figure 2 showed the XRD patterns of the samples C6, C8, C10, C12 and C14. All samples in the figure exhibited half opacifying phase. The main crystalline phase was Na$_3$Ca$_6$(PO$_4$)$_5$ crystal and Zn$_2$P$_2$O$_7$ crystal in the glass samples from C6 to C14, which indicated that CaO did not affect the type of the crystalline phase of the samples, but the intensity of the diffraction peak was different. With the increase of CaO content, the intensity of Na$_3$Ca$_6$(PO$_4$)$_5$ crystal peak and Zn$_2$P$_2$O$_7$ crystal peak increased gradually.

3.3. Transmittance and Whiteness

The transmittance of the glass samples C6, C8, C10, C12 and C14 were shown in Figure 3. All samples in the figure exhibited the increase of the transmittance of samples with the concentration of CaO from 6wt.% to 14wt.%. As shown in Figure 3, the samples with 14wt.% CaO content had a transmittance of more than 10%, and exhibited semi opaque state. However, when the CaO content
decreased to 6wt.%, the transmittance of the opacifying sample was lower to about 5%, but showed the highest whiteness up to 89% shown in Figure 4. This indicated that CaO in glass network was good to the reduction of the phase separation of samples. From the FESEM pictures, it could be seen that the increase of CaO made the internal phase size smaller and cause more phosphorus rich phase separated, which would weaken the scattering phenomenon, and better the transparency of the glass samples.

![Transmittance image of samples with different contents of CaO](image1)

![Whiteness of samples with different contents of CaO](image2)

Figure 3. Transmittance image of samples with different contents of CaO

Figure 4. Whiteness of samples with different contents of CaO

Figure 4 showed the whiteness of the glass samples, which of the samples decreased gradually with the change of the concentration of CaO. The maximum whiteness of the sample with the 14wt.% CaO content was as high as 88.89% shown in Figure 4, but it reduced to 78.01% when the content of CaO was 6wt.%.

The whiteness of the opaque glass is related to the size and the number of the phase separation. As the addition of CaO is 6%, the size of phosphorus rich phase is around 200nm, which is close to the half wavelength of the visible light. Therefore, more scattering are produced under light irradiation, so the whiteness is higher. As the addition of CaO, the phosphorus rich phase size becomes smaller and smaller. When the addition of CaO is 14%, the phase size is around 80nm, far less than the half wavelength of visible light. Under light, the scattering effect of the samples becomes weaker, so the whiteness becomes smaller.

3.4. Coefficient of Thermal Expansion and Bulk Density

The linear thermal expansion coefficient(50–300°C) of the glass samples were shown in Figure 5, and the results showed that the thermal expansion coefficient of the opaque glass decreased from 8.4432×10⁻⁶/°C to 8.1580×10⁻⁶/°C with the increase of CaO concentrations. As we know, to be a network modifier, Ca²⁺ did not participate in the formation of glass network, but existed in the gap of glass network.
The bulk density of the glass for different CaO mass fraction were showed in Figure 6. It was noticed that the bulk density of the glass increased with increasing CaO content from C6 to C14. It seemed the CaO was good to the density of the glass network. As we knew, Calcium ions have less radius of 0.1nm and electric field strength but higher atomic weight contrast to silica tetrahedron, so it contributed to densify the samples despite of being the external body of the network[12]. Moreover, the increasing amount of CaO in the glass samples helped the Na$_3$Ca$_6$(PO$_4$)$_5$ crystal and Zn$_2$P$_2$O$_7$ crystal crystallization, and the transformation from the glass phase to a crystalline phase benefited really to the density of the glass interior.

3.5. Discussion

To be a network modifier, Calcium ions did not participate in the formation of glass structure, but existed in the network gap in the form of ions[13]. With the characteristic of the less radius and lower field intensity, Ca$^{2+}$ made it easy to separate from the glass network and boost more phosphorus rich phase separated from each other and form dispersed phase. Therefore, as the amount of CaO increased, it would destroy the network structure of the glass, and more small groups like Si-O and P-O were produced. The P$^{5+}$ field intensity ($Z/r^2=3462.6nm^{-2}$) was strong enough to attract network modifier, and the new phase enriched phosphate separated from the silica tetrahedron network was formed. In the second phase the concentration of the ions is enough to crystallize and produce the Na$_3$Ca$_6$(PO$_4$)$_5$ crystal. Because Ca$^{2+}$ did not participate in the formation of network structure and existed in the form of network external body and gap, Ca$^{2+}$ would occupy the original position of Zn$^{2+}$ with the increase of CaO content. Therefore, The migrated zinc ions would bind to the previous separated P-O ion groups to form a new substance Zn$_2$P$_2$O$_7$ crystals. which explained why Na$_3$Ca$_6$(PO$_4$)$_5$ and Zn$_2$P$_2$O$_7$ crystal peak intensity enhance with the increase of the content of CaO.

4. Conclusions

Opaque glass with different concentrations of CaO were prepared by one-step methods, and the impact of the CaO content on the phase separation, microstructure, and properties was systematically studied. with the increase of CaO content, the transmittance and density of glass increased, but the Coefficient of thermal expansion and the whiteness were decreased. when the amount of CaO was 12wt.%, the glass was changed into semi opaque. with the increasing of the content of CaO, the crystal peak intensity of Na$_3$Ca$_6$(PO$_4$)$_5$ and Zn$_2$P$_2$O$_7$ gradually increase. To be a network modifier, Calcium ions in Na$_2$O-CaO-SiO$_2$-P$_2$O$_5$ system would destroy the glass network and promote the separation of the second phase and the crystallization.
5. Acknowledgment
This work was supported by the National Science Foundation of China (NSFC, No. 51873032) and the Chinese Ministry of Science and Technology. (Grant No.2013G11009).

6. References
[1] Deng L, Zhang X, Zhang M, Jia X. Effect of CaF₂ on viscosity, structure and properties of CaO-Al₂O₃-MgO-SiO₂ slag glass ceramics. 2018 J. Non-Cryst. Solids. 500 310-316.
[2] Shi J, He F, Ye CQ, et al. Preparation and characterization of CaO-Al₂O₃-SiO₂ glass ceramics from molybdenum tailings. 2017 Mater. Chem. Phys. 197 57-64.
[3] Dai B, Zhu HK, Zhou HQ, et al. Sintering, crystallization and dielectric properties of CaO-B₂O₃-SiO₂ system glass ceramics. 2012 J. Cent South Uni. Tech. 19 2101-2106.
[4] Ku HW, Lim TY, Kim JH. Effects of forming and cooling temperature on the opaque properties of translucent opal glass for the glass diffuser of LED lighting. 2013 J Korea Cryst Grow Crys Tech. 23 246-254.
[5] Ku HW, Lim TY, Hwang J. Development and characterization of translucent opal glass for diffuser of LED lighting. 2012 Korean J. Mater. Res. 22 650-657.
[6] Majhi M, PyareR, Singh SP. Studies on preparation and characterizations of CaO-Na₂O-SiO₂-P₂O₅ bioglass ceramics substituted with Al₂O₃, TiO₂ and ZrO₂. 2012 J. Biomater. Tissue Eng. 2 154-169.
[7] Veit U, Rüssel C. Density and Young’s modulus of ternary glasses close to the eutectic composition in the CaO-Al₂O₃–SiO₂-system. 2016 Ceram. Int. 42 5810-5822.
[8] Takahashi S, Neuville DR, Takebe H. Thermal properties, density and structure of percaleic and peraluminus CaO-Al₂O₃-SiO₂ glasses. 2015 J. Non-Cryst. Solids. 411 5-12.
[9] Doveidar H. Density of CaO-Al₂O₃-SiO₂ glasses with(CaO/Al₂O₃)≥1; the hidden factors. 2017 J. Non-Cryst. Solids. 471 344-348.
[10] Kucharczyk S, Sitarz M, Zajac M, Deja J. The effect of CaO/SiO₂ molar ratio of CaO-Al₂O₃-SiO₂ glasses on their structure and reactivity in alkali activated system. 2018 Spectro. Acta Part A. 194 163-171.
[11] Cheng JS, Xiao ZF, Yang K, et al. Viscosity, fragility and structure of Na₂O-CaO-Al₂O₃-SiO₂ glasses of increasing Al/Si ratio.2013. Ceram. Int. 39 4055-4062.
[12] Deng LB. Zhang XF, Li BW, et al. Influence of CaF₂ on the crystallization and corrosion resistance of CaO-Al₂O₃-MgO-SiO₂ slag glass ceramics. 2016 Mater. Rev. 30 128-133.
[13] Wei PF, Zhou HQ, Zhu HK, et al. Microstructure and microwave dielectric properties of CaO–B₂O₃–SiO₂ glass ceramics with various B₂O₃ contents. 2011 J. Cent South Uni. Tech. 18 1359-1364.