

The Evolution of Al₂O₃ Content in Ancient Chinese Glasses

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Abstract. Based on the evidence from museums, collectors, the dug out of the grave, the evolution of Al₂O₃ content in Chinese glasses from Western Zhou to Qing dynasty was documented in this paper in detail. It was found that Al₂O₃ contents in ancient Chinese glasses were relatively higher than those of outside of China in the world. This is the character of the ancient Chinese glasses which is caused by not only the high Al contents in the raw materials but also by the Chinese people's preference of the milky glasses similar to jade

Keywords: Ancient Chinese glasses, evolution, and Al₂O₃ content

1 Introduction

According to archeologists and experts, ancient Chinese glasses started from Western Zhou in 11th century B.C. The main contents were potassium silicate (K₂O-SiO₂) and alkali calcium silicate (K₂O-CaO-SiO₂). Content of lead barium silicate (PbO-BaO-SiO₂) in glasses appeared in Warring States. High lead content silicate was also found in the period of Eastern Han. Potassium lead silicate (K₂O-PbO-SiO₂) was found in glasses in the early Tang dynasty. Potassium calcium silicate glasses were developed in Song and Yuan dynasties [1,2]. The glass workshops were most located closely to bronze and ceramic factories in order to get materials, minerals including Al₂O₃ contained sandy rocks, sand stone, quartz sand, silicate rocks, heavily Al₂O₃ contained limestone, feldspar, clay, slag and leftover ores. This is one of the reasons why various Al₂O₃ content is in the ancient Chinese glasses, especially in Boshan's glasses at the end of the Yuan dynasty and the beginning of Min dynasty. The Al₂O₃ concentration in Boshan's glasses could be higher than 6%. The Al₂O₃ content in ancient Chinese glasses were reported in literature; however, the influence of Al₂O₃ concentration in ancient Chinese glasses was not discussed in previous publications [1-3]. Based upon the evidence of glasses in the Chinese history, the evolution of Al₂O₃ contents in ancient Chinese glasses is presented and the variation of it with time is analyzed and discussed in this paper.

2 Western Chou Period (1046 BC-770 BC)

This is the beginning period of the ancient Chinese glasses, which consisted of mainly quartz. It was manufactured by mixing quartz, ash of grass and wood, and water, and then heating up to 700-800°C. Most parts in the glasses were un-melt quartz particles, only small parts were glass. These parts were not real glass but precursors of glasses corresponding to Faience [3] in foreign countries. The quartz materials contained Al_2O_3 impurity, sometimes clay was added as well in order to form the shape of the product. Therefore, there was certain amount of Al_2O_3 in the glass. The typical glass contents were 89-94% SiO_2 , 0.3-3.5% Al_2O_3 , 0.3-3.5 R_2O [1]. Most of R_2O are K_2O ; however, Na_2O appeared in only a few glasses. Some glass samples contained CaO [4]. It is called potassium silicate system glass in literature, in fact, it should be potassium alumina silicate glasses.

3 Eastern Chou and Warring States Period (770 BC -221 BC)

About 3000 years ago, Shang to Chou dynasty, ceramic pottery was transformed into the Proto-initial porcelain. The primitive porcelain appeared by using CaO as melting assistant agent in primitive porcelain. Once CaO became one of the glass materials, the limestone mines were massively dug. Some of CaO was used in glass at the same time KNO_3 began to be used as a melting assistant in glasses. Therefore, the content of K_2O in this period is higher than Eastern Chou period [5]. The compositions of glass in this period were 68.9-83.7% SiO_2 , 3-6.5% Al_2O_3 , 0.75-4.3% MgO , 6-8% CaO , 2.2-10.9 K_2O , and 1.9-7.9% Na_2O [3,4,6]. Few glass samples even contained more than 10% Al_2O_3 , e.g., the white parts of its eyes in the “dragonfly’s eyes” glass in Warring States period had 14.3% Al_2O_3 . At the end of Warring States period, Al_2O_3 in glasses was 11.74% [4]. This unique composition in glass systems, $\text{K}_2\text{O}(\text{Na}_2\text{O})\text{-CaO}(\text{MgO})\text{-Al}_2\text{O}_3\text{-SiO}_2$, differed from Egypt glasses. The bronz products were very popular during Shang Chou dynasties. The wastes in the bronz shops were used to make glasses. Galena mine mainly PbS was also used as a melting assistant agent, however, BaSO_4 commonly co-existed with Galena mine. The waste materials also contains Al_2O_3 , such that a new glass system, $\text{PbO-BaO-Al}_2\text{O}_3\text{-SiO}_2$, was formed. Glass samples with 3-5% Al_2O_3 were found with PbO higher than 24% but lower than 30%.

4 Qin (221 BC~206 BC), Western Han (206 BC~25 AD), Eastern Han (25 AD~220 AD), There Kingdom, and Southern and Northern Dynasties Period

There was no new specific glass system from 221-206 BC during the brief time of the Qin dynasty. In Western and Eastern Han (206 BC~ 220 AD), PbO-BaO-SiO_2 glass system is dominant. Low PbO (less than 10%) contained glass were few. Most were medium PbO (less than 30% but higher than 24%) and high PbO (higher than 30%) glasses. The content of Al_2O_3 in glasses is very low, between 1 to 3%. Few samples had below 1% Al_2O_3 content. Few glasses had 6-7% Al_2O_3 in them. For example, the simulated jade glass plates on the gold and jade clothes sewn with gold wires in Western Han period dug out from grave in Yangju contained 59.5% SiO_2 , 2.34% Al_2O_3 , 32.27% PbO , 19.09% BaO , 0.16% Fe_2O_3 , 0.3% CaO , 0.13% K_2O , and 0.29% P_2O_5 .

Metallurgy Alchemys well developed in Eastern Han dynasty, metallic Pb was extracted from lead mines which provided the material for high PbO content glasses. In literature, quartz and Pb were used to make glasses which indicated high PbO content glasses without BaO in them. The glass system was mainly $\text{PbO-Al}_2\text{O}_3\text{-SiO}_2$. For example, the yellow beads in Eastern Han contained 17.16% SiO_2 , 6.53% Al_2O_3 , 0.87% Fe_2O_3 , 69.3% PbO ,

0.07% BaO, 1.13% CaO, 0.84% K₂O, 0.65% Na₂O, 0.35% CuO, 0.08% TiO₂, and 2.95% P₂O₅ [3].

Before the Han dynasty, the manufacturing methods of glasses mostly used were core-formed, kiln-casting, and press to the shape; hence it was not required for a strict viscosity-temperature relationship. Even high content Al₂O₃ glasses, i.e., high hardening velocity of Al₂O₃, were also pressed to form various shapes. In the time period of Three Kingdom, Southern and Northern Dynasties, frequent interactions between Chinese and foreign cultures were intensified such that the glass blowing technique was introduced from Rome. In Northern Wei dynasty period, ca. 500 AD, glass blowing was taught by Persian technicians. Finally glasses can be made without mode by glass blowing, and glass containers with empty interior could be made in China. Furthermore, the size, volume, and productivity of glass hardware were increased tremendously. This is the turning point of the Chinese glasses in history. In order to fabricate the glass products by blowing, the viscosity of the glass preform needed to be low enough so that high viscosity lead barium silicate glasses were replaced by low viscosity PbO content lead silicate glasses.

5 Sui Dynasty (581-618 AD), Tang Dynasty (618-907 AD), Five Dynasty (907 – 960 AD) and Song Dynasty (960-1279 AD) Period

Sui dynasty did not last long but the entire country of China was governed by it which ended the splitting of China by Southern and Northern Dynasties. Glass industry in China entered a recovery period. Technicians were hired from western Asia, Great Yuch Chin, to manufacture glasses. They used high lead silicate compositions to blow glass bottles, cups, cases, colorful beads, and other decorative items. After Tang replaced Sui dynasty, political, economic, and culture environments flourished which provided a favored environment for the development of industries including glass manufacturing. Further interaction with West Asia resulted in new glasses such as Sszanian glass, Islam's glass products, and Na₂O-CaO-SiO₂ glasses.

Metallurgy Alchemy after Tang dynasty, from roasted lead method to niter technique or niter-sulfur method used mixed metallic lead and KNO₃ (Niter) or lead, sulphur, and KNO₃ to obtain PbO containing lots of K₂SO₄. Therefore glasses based on PbO, containing K₂O, to form K₂O-PbO-SiO₂ composition system in which there were 35-68% SiO₂, 1.5-2.5% Al₂O₃, 35-65% PbO and 8% K₂O [3, 4]. Those glasses had low viscosity, slow hardening speed, and longer stability period working range. They were suitable for glass devices made by both molding and blowing techniques. They could also be used to make glass products by pouring, mold pressing, and rolling press methods.

Tang dynasty adapted the sodium calcium silicate composition system in which there were 44-47% SiO₂, 1.3-2.8 Al₂O₃, 5.3-6.8% CaO, 0-6.4% MgO, 10-18% Na₂O, and 0-6.4% K₂O [3,4]. The contents of soda lime less than lead glass in China were caused by the lack of the Na₂CO₃·NaHCO₂·2H₂O resources in the mines. Only green, blue glass pieces found in Xin Jiang Kuqa were soda lime silicate glasses, the compositions were 64-67.18% SiO₂, 1.48-2.21% Al₂O₃, 0.43-0.97% Fe₂O₃, 0.04-0.08% PbO, 0.01-0.05% BaO, 5.94-8.37% CaO, 3.56-4.81% MgO, 1.62-3.79% K₂O, 15.77-16.19% Na₂O, 0.01-0.28% CuO, 0.03-0.08% MnO, 0.91% Cl, and 0.08% Ti₂O₂. The green glass discovered in Hubei Li-shou tomb was also soda lime silicate glass in which there were 61.58% SiO₂, 1.66% Al₂O₃, 0.69% Fe₂O₃, 6.27% CaO, 6.43% MgO, 17.86% Na₂O, and 3.53% K₂O [3,4]. A significant progress of porcelain was made in Song dynasty but no improvement in glass was achieved. Most glass systems were similar to those found in Tang dynasty; the PbO content was high. The compositions were 27.88-36.93% SiO₂, 0.32-2.62% Al₂O₃, 0.10-4.39% Fe₂O₃, 40.15-66.86% PbO, 0.17-3.52% CaO, 0.04-0.31% MgO, 8.45-14.78% K₂O, 0.08-0.13% Na₂O, and 0.18-1.44% CuO [3,4]. During Liao (907 AD-1125 AD) and Jin (1125 AD- 1234 AD)

dynasties, lots of western glasses were imported. Glasses in these periods were found in Northeastern China and Inner Mongolia, they all had Sassanian style, Byzantian style and Islam style. This indicated that the new forms and shapes of the glasses were quite different from those in Sui and Tang dynasties. Significant glass products were made by heat press without the mode, but the main compositions were still high lead content glass system.

6 Yuan (1206-1368 AD), Ming (1368-1644 AD), and Qing (1616-1911 AD) Dynasties Period

Special glass manufacturing agents were established in Yuan dynasty, therefore the production was more developed than in Song, Liao, and Jin dynasties. Main manufacturer was located Sangdong Boshan, using local feldspar, fluorite as 30% main glass materials contained 10 – 13% Al_2O_3 in limestone feldspar. The glass were potassium calcium aluminum silicate ($\text{K}_2\text{O-CaO-Al}_2\text{O}_3\text{-SiO}_2$). The blue glasses dug out in pot furnace contained 58.48% SiO_2 , 6.58% Al_2O_3 , 0.30% Fe_2O_3 , 9.8% CaO , 0.06% MgO , 4.42% Na_2O , 16.07% K_2O , 0.23% TiO_2 , 0.81 CuO , and 4.99% F [4]. The glasses had high alumina content, fluorine was introduced by using gross stone fluorite to enhance the melting and milky opal.

Most were high Al content glasses at the end of Yuan dynasty and the beginning of Min dynasty. Glass chess stones, hairpin, beads, round plate with a hole at the center were found in Boshan glasses in Min dynasty. Most dug out glasses had high Al_2O_3 content from 8.5 to 9.88% [4]. High concentration of Al_2O_3 was caused by the use of local feldspar and the fluorite. High content Al_2O_3 in fluorite was used for milky opal in decorative glasses.

High Al content materials were still used in Boshan at the beginning of Qin dynasty until Empire Kangxi ordered to established imperial glass factories in 1696. French Kilian Stumpt participated the initial plans and he hired French technicians. The glass factory was finished in 1700. Finally northern and southern Chinese glass masters combined the Chinese traditional and foreign techniques to make glasses. Again, high Al content was found in decorative glasses due to feldspar used as raw materials and the addition of Al_2O_3 . The character of high Al content glasses was high viscosity, non-uniformly melting, easily forming stripes. In order to improve the qualities of glasses and adopt the characteristic of foreign techniques, the content of Al_2O_3 was reduced in Chinese glasses. For example, only 0.08% Al_2O_3 in non-color glass bowl in Empire Palace Museum was found. There was 0.15 to 1.97 % Al_2O_3 found in other transparent glasses which were very close to the content of Al_2O_3 in modern domestic and foreign glasses. In addition to the composition of $\text{K}_2\text{O-CaO-Al}_2\text{O}_3\text{-SiO}_2$ in the imperial glass factory, 4 to 5 % PbO was added to glass composition to improve color and melting point, and prolong the qualities of the glass melts. Sometime B_2O_3 was also added in the potassium calcium silicate glass composition to reduce the thermal expansion coefficient and improve the thermal stability.

Years between 1736 (the first year of Qianlong empire) and 1765 (the 30th year of Qianlong empire) were the best period of Chinese glasses. Yearly production of treasurers, decoration, and etiquette was more than 10,000 pieces [7]. Melt glasses had a very high quality, more than 30 beautiful colors, more overlaid colors, unique Chinese characters, which formed worldwide famous Qianlong glass.

The pure soda was imported in China at the end of Qiang dynasty which expanded the application of sodium calcium silicate glasses. The green plate glasses stored in Empire Palace Museum contained 69.8% SiO_2 , 1.22 % Al_2O_3 , 0.29% Fe_2O_3 , 14.1% CaO , 0.09% MgO , 0.25% PbO , 0.28% K_2O , and 11.98% Na_2O [4] which was very close to the glass composition used in Europe by Lubber method.

Glasses, except those produced by the imperial glass factory in Qing dynasty, were also produced in factories in Beijing, Guangzhou, Boshan, Suzhou and Shanxi. However, the kinds, qualities, and quantities could not be compared to those produced in imperial glass factory. At the end of Qing dynasty the manufacture of Chinese glasses were significantly decayed.

TABLE THE Al_2O_3 CONTENT IN ANCIENT CHINESE GLASSES IN DIFFERENT TIME PERIODS

Time of Periods	Al_2O_3 content
Western Chou Period (1046 BC -770 BC)	0.3-3.5%
Eastern Chou and Warring States Period (770 BC -221 BC)	3.0-6.5%
Qin (221 BC~206 BC), Western Han (206 BC ~25 AD), Eastern Han (25 AD~220 AD), Three Kingdom, and Southern and Northern Dynasties Period	below 1.0 to 6.53%
Sui Dynasty (581-618 AD), Tang Dynasty (618-907 AD), Five Dynasty (907-960 AD), and Song Dynasty (960-1279 AD) Period	0.32-2.62%
Yuan Dynasty (1206-1368 AD),	6.58%
Ming Dynasty (1368-1644 AD),	8.5-9.88%
Qing (1616-1911 AD) Dynasty	0.08-1.97%

7 Conclusion

By analyzing the compositions in ancient Chinese glasses, the content of Al_2O_3 fluctuated but it was still quite high. Therefore, Al_2O_3 content is a very important indicator in the development history of the ancient Chinese glasses. The reasons for its high content were introduced high content quartz and mineral wastes. Some places, such as Boshan, the local feldspar was used in main glass composition. The other main reason for the high content of Al_2O_3 was the glasses were used to simulate jade which was a Chinese favorite jewelry. For example, simulated center-holes round jade, simulated semi-annular jade pendant, simulated jade pendant for decoration and burial pieces, these pieces were partial transparent or wholly opaque, hence highly Al_2O_3 content and high viscosity were required. Even the stripes introduced by Al_2O_3 were not a concern. When fluorite used as opacifier, the Al_2O_3 concentration must be high.

Chinese empires especially empires in Qing dynasty loved the milky glasses so most of items produced by the imperial glass factory were milky white and colorful milky. Exhibited items such as daily used items, worshiped items, snuff bottles in Empire Palace Museum were mostly milky pieces, only few were transparent glasses. Adding a fixed amount of Al_2O_3 could reduce the crystallization and small cracks around the crystalline particles.

Except the decorative items used in western ancient glasses, living items such as wine glasses, water glasses, lamp covers, mirror *etc.* were also produced. The whiteness and transparency became very important quality indicator of the glasses. Venice people in the 15th century used relatively pure quartz sand, recrystallized pure alkali to make sodium calcium silicate glasses similar to crystal which was called *Cristallo*. There was only 0.86 to 1.31% Al_2O_3 in it but at the same time in China the sodium calcium silicate glasses contained 6-7% Al_2O_3 in Min dynasty.

English Ravenscroft in 1670 developed $\text{K}_2\text{O-PbO-SiO}_2$ glass, which had high refractive index and high transmission. It was more like simulated crystal than *Cristallo*. It was called lead crystal glass [8]. Even though the PbO content was about 30%, similar to the content in high lead Chinese ancient glasses, the Al_2O_3 content was below 1%. Of course Fe_2O_3 , TiO_2 , CuO and other impurities were low, forming a new lead crystal glass but its contents were widely used in the world.

In summary, high Al_2O_3 content was a unique character in ancient Chinese glasses at the end of the Qing dynasty [9]. The reduction of Al_2O_3 content in transparent and flat glasses finally happened at the end of the Qing dynasty. The Al_2O_3 content in the sodium calcium silicate glasses was similar to that in the international glass composition. The Al_2O_3 contents in Ancient Chinese Glasses in different time periods were listed in the Table for the future reference.

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