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# Opaque ancient $K_2O$ – $PbO$ – $SiO_2$ glass of the Southern Song Dynasty with fluorite dendrites and its fabrication

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## Abstract

Here we first report a piece of  $K_2O$ – $PbO$ – $SiO_2$  ancient glass opacified by fluorite dendrites with archaeological background. This piece of glass was excavated from Nanhai I shipwreck, a merchant ship once heading for Southeast Asia, but sinking near Yangjiang, Guangdong province. Analysis of scanning electron microscopy with energy dispersive spectroscopy, X-ray diffraction and Raman spectroscopy were used to identify the glass matrix and the fluorite dendritic crystals within it. The elemental feature is consistent with the prevailing  $K_2O$ – $PbO$ – $SiO_2$  glass system during Tang and Song Dynasties. However, the presence of fluorite dendrites with almost no Na, Al and P elements strongly suggests an astonishing conclusion that the fluorite has already been used as an opacifying agent around 800 years ago. Moreover, through replication of glass samples with similar compositions to the ancient one, it is suggested that fluorite dendrites with a similar size can be obtained when fired at around 1000–1050 °C and cooled within the furnace. On the basis of different crystal growth outcomes of two cooling strategies and the presence of the large undisturbed dendrite, it is inferred that the original glass vessel was probably made though die-casting instead of blowing technique.

**Keywords:** Ancient opaque glass,  $K_2O$ – $PbO$ – $SiO_2$  system, Fluorite, Dendrite, Nanhai I shipwreck

## Introduction

Through the decades, the overall outline of the ancient Chinese glass technology has been drawn clearly. Although it is not as early for the ancient Chinese to fabricate glass as the ancient Mesopotamian, the development of ancient Chinese glass is rather complicated and commonly considered independent because of the distinctive chemical compositions, especially the  $BaO$ – $PbO$ – $SiO_2$  glass system [1]. Unlike the  $NaO$ – $CaO$ – $SiO_2$  glass systems prevailing in the ancient middle-west Asia and the Mediterranean region, the Chinese glass history can be divided into the following 5 stages described by Gan [2]:  $K_2O$ – $CaO$ – $SiO_2$  system (800–400 B.C.), where  $K_2O/Na_2O > 1$ ;  $BaO$ – $PbO$ – $SiO_2$  and  $K_2O$ – $SiO_2$  systems (400 B.C.–200 A.D.);  $PbO$ – $SiO_2$  system (200–700 A.D.);  $K_2O$ – $PbO$ – $SiO_2$  system (600–1200 A.D.); and

$K_2O$ – $CaO$ – $SiO_2$  system (1200–1900 A.D.). But the possible technological communication and trades between the west and the far east are also affirmative since soda-lime-silicate glass beads were also found in the marquis tombs date to 500–400 B.C. in Hubei and Henan, central China [2] and at 18 sites from 200 B.C. to 1300 A.D. in the Taklamakan Desert in Xinjiang, the center of the Silk Routes [3]. Apart from the glass communication through the Silk Road starting from the Warring States period or even earlier, another route was the Maritime Silk Road. Although it is famous for the Chinese porcelain exportation and spice importation, the discovery of potash-lead-silicate glass vessel fragments and beads from Singapore (14th A.D.) [4] provides us new evidences of the glass trade from China to the South Asia. Also, there are various archaeological evidences for ancient glass importation from the Southeast Asia [5]. One of the most important archaeological findings these years in China regarding to the Maritime Silk Road is the fully loaded merchant ship Nanhai I date to the late Southern Song Dynasty

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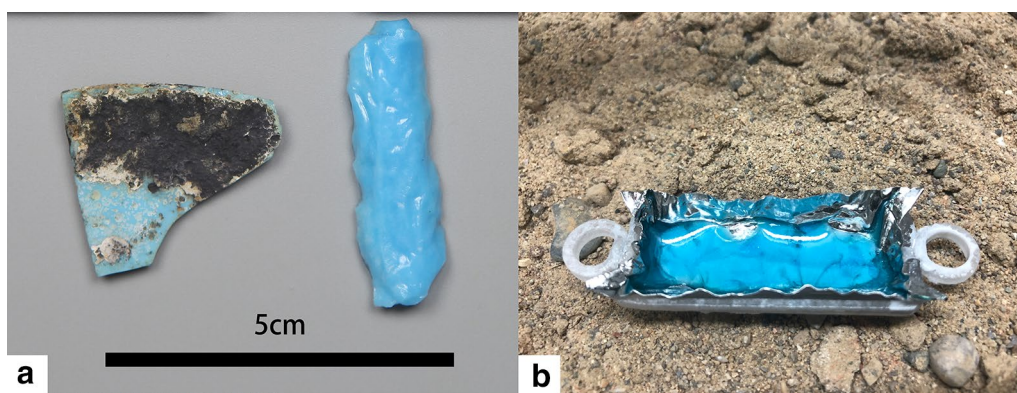
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(1127–1279 A.D.), which once headed for the South Asia but sank not far away off the shore near Yangjiang city, Guangdong province, China. The shipwreck was salvaged in whole in 2007 and is still under scientific excavation. This ship is believed to be constructed in Fujian, China and head to the Java Sea with fully loaded cargos. The recovered artifacts include porcelain, gold and silver wares, bronzes, iron objects, coins, tin wares, lacquered wares, timbers, cinnabar, large amounts of bivalves and some plant seeds [6]. Additionally, apart from these major cargos, a very limited amount of glass vessel fragments and beads were filtered out of the sludge. After a preliminary analysis, these glass vessels and beads can be categorized as two distinctive glass systems, i.e.,  $K_2O-PbO-SiO_2$  belonging to typical Chinese glass during the Southern Song Dynasty and  $Na_2O-CaO-SiO_2$  belonging to the west. And more interestingly, the  $K_2O-PbO-SiO_2$  glass contains unique dendritic fluorite ( $CaF_2$ ) crystals in its glass matrix resulting in the opacity. The opacifiers of glass appeared early in China (c. 1000–600 B.C.) of probable Western origin have been identified as lead antimonate ( $Pb_2Sb_2O_7$ ) and calcium antimonate ( $Ca_2Sb_2O_7$ ) [7]. In early Chinese high-potassium glass, tin oxide was the main opacifier [7–9]. In some case, the presence of fluorite is considered as a technology of modern times [10]. In the early research in 1963 [11], fluorite was detected in the opaque greenish jade-like glass Buddha head date to the Tang Dynasty. This glass head had been cast in mold because of the molding line along the forehead, nose and mouth. So far, it is the only literature reporting the fluorite opacifying glass before the Song Dynasty. The glass found in Singapore date to 14th century has the same  $K_2O-PbO-SiO_2$  chemical feature with fluorite crystals, which was also considered by the author as being produced in China [4]. Also in the 14th century, the glass production had turned to  $K_2O-CaO-SiO_2$

glass system in Boshan, Shandong province, China. The excavation there has provided us with blue opaque glass opacified by fluorite like [12]. Additionally, fluorite was detected in  $K_2O-PbO-SiO_2$  enamel of cloisonné wares in 15th–19th centuries by Raman spectroscopy [13] and the crystalline form was found to be cubic in the 16th–17th-century cloisonné samples [14]. Nevertheless, there is no report on the fluorite opacifier in the glass of Song Dynasty and the dendrite different from the previously reported cubic fluorite. Here in this paper, the blue opaque  $K_2O-PbO-SiO_2$  glass from Nanhai I shipwreck is analyzed in detail, in hope of providing basic information of this kind of glass and answering its possible fabrication technique.

### Materials and methods

So far, a very limited number of blue glass vessel fragments (coated by black and white corrosion layers) was discovered from sediments within the layer ① of cabin C11c of the Nanhai I shipwreck. For its rarity, only one piece (in Fig. 1a, left piece) was allowed to be fully examined. Scanning electron microscopes (SEM, Hitachi TM3030 and Phenom XL) with energy dispersive spectrometer, X-ray diffraction (XRD, Bruker D8 Discover with GADDS detector) and Raman spectroscopy (BWTEK i-Raman PLUS) were used to identify the chemical compositions and crystalline phase in the glass sample and its replicas. Prior to the SEM/EDS analysis, the glass cross-section was prepared and polished to prevent from possible interference of surface corrosion. The SEM/EDS analysis was carried out in low vacuum mode with acceleration voltage of 15 kV. The XRD analysis and Raman spectroscopy were carried out on clean spots on the sample surface and polished cross-section. The XRD analysis covered the range of  $2\theta$  from  $5^\circ$  to  $105^\circ$  and used the GADDS area detector and  $Cu\ K\alpha$  1 radiation source



**Fig. 1** a The appearance of the glass fragment from Nanhai I (left one) and its chemical replica (right one); b the platinum crucible with glass inside and the quartz glass boat

with a scanning time of 4 min in total. The light source of the Raman spectroscopy was 532 nm and the testing time varied from 10 to 120 s depending on the Raman intensity and quality of the spectrum of each sample.

To further understand its fabrication, a series of glass pieces with different firing conditions were manufactured based on the composition measured by EDS and using an electric tube furnace under oxidizing atmosphere. Specifically,  $K_2CO_3$  (AR, from Tianjin Zhiyuan Chemical Reagent Co. Ltd.),  $SiO_2$  (silica gel, from Beijing Ocean Chemical Engineering Co. Ltd.),  $Pb_3O_4$  (AR, from Sinopharm Chemical Reagent Co. Ltd.),  $CaF_2$  (AR, from Beijing Liyi Fine Chemicals Co. Ltd.) and  $CuO$  (AR, from Sinopharm Chemical Reagent Co. Ltd.) were mixed and transferred to a quartz boat with platinum lining (shown in Fig. 1b) to prevent reaction between the quartz boat and the glass product during firing. The weights of the raw materials are approximately 0.30 g  $K_2CO_3$ , 0.89 g  $SiO_2$ , 0.76 g  $Pb_3O_4$ , 0.14 g  $CaF_2$  and 0.01 g  $CuO$  with some variation in every operation. Prior to the mixture of the raw materials,  $K_2CO_3$  and  $SiO_2$  were heated at 400 °C to eliminate absorbed and crystal water. The temperature during firing was monitored by gallium thermometer which was placed symmetrically to the quartz boat. Through the observation during firing, the remaining air bubbles didn't escape from the glass melts until the temperature reached around 950 °C as the viscosity decreased. Thus, to achieve similar bubble-free glass as the ancient one, the firing temperatures were set at 950 °C, 1000 °C and 1050 °C, respectively. During firing, the tube firing chamber was directly open to the air to maintain an oxidizing atmosphere. It took several minutes to heat the furnace to the set temperature before the raw material powder melted within another several minutes and was kept for 1 h. Two different cooling strategies were adopted, i.e. direct air cooling (Replica 4) and cooling within the furnace (Replica 1–3).

## Results and discussion

### Features of the blue vessel fragment

The blue vessel fragment excavated from Nanhai I shipwreck chemically belongs to the  $K_2O$ – $PbO$ – $SiO_2$  glass

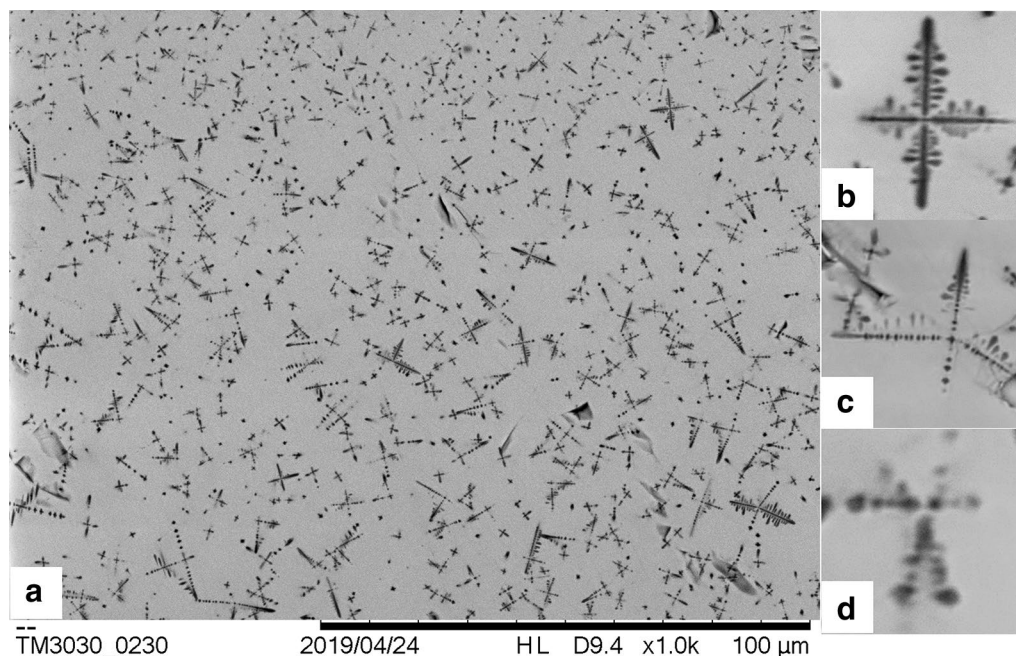
system containing 10.24 wt%  $K_2O$ , 37.07 wt%  $PbO$ , and 44.66 wt%  $SiO_2$  with the presence of fluorine (1.61 wt%) (Table 1). The most significant feature of the glass piece is the opacity caused by micro-dendrites in its glass matrix, shown in Fig. 2. From different two-dimensional figures (Figs. 2b–d, 3a), it can be concluded that these crystals belong to isometric system. In the two-dimensional image observed under SEM, most of the typical dendrites are around 10  $\mu m$  in size. Smaller ones are 1–2  $\mu m$  in size, which are also probably part of larger crystals that are nearby or not in the same plane. The EDS elemental results in Fig. 3 shows the main elements of the dendrite are Ca and F with the quantitative ratio of nearly 1:2, suggesting the dendrite to be fluorite. Additionally, the absorption at 319  $cm^{-1}$  in the Raman spectrum of the ancient glass (in Fig. 4) is the characteristic absorption of fluorite [14, 15] and the signals in the XRD pattern (in Fig. 5) are also consistent with multiple planes of fluorite [16]. The dendritic form can only be formed from liquid glass phase instead from the unmelted raw materials. In addition, the large undisturbed dendrite in Fig. 3a indicates a relative stable crystalline condition without external forces. There are three possible fluorine sources from natural minerals available in ancient times, i.e. cryolite ( $Na_3AlF_6$ ), fluorite, and fluorapatite ( $Ca_5F(PO_4)_3$ ). By chemical analysis (shown in Table 1), very limited amounts of  $Na_2O$  and  $Al_2O_3$  were detected and no  $P_2O_5$  presented in the glass, suggesting the source of fluorine can only be fluorite. Thus, to replicate this kind of glass, the main raw materials are probably fluorite, potash ( $K_2CO_3$ ), silica sand (quartz) and lead oxide (e.g.  $Pb_3O_4$ ) with a tiny amount of copper oxide (or other copper containing minerals) as the coloring agent.

### Replication of the glass

According to the chemical composition of the ancient glass sample, similar formulas were used in replicas shown in Table 1. One of the most important factors of manufacturing the glass is the firing temperature. As was observed during the firing process, at about 700 °C the powder showed an evident decrease in volume and started melting. At 900 °C, the melting process was

**Table 1** Chemical compositions of the ancient glass and its replicas (wt%)

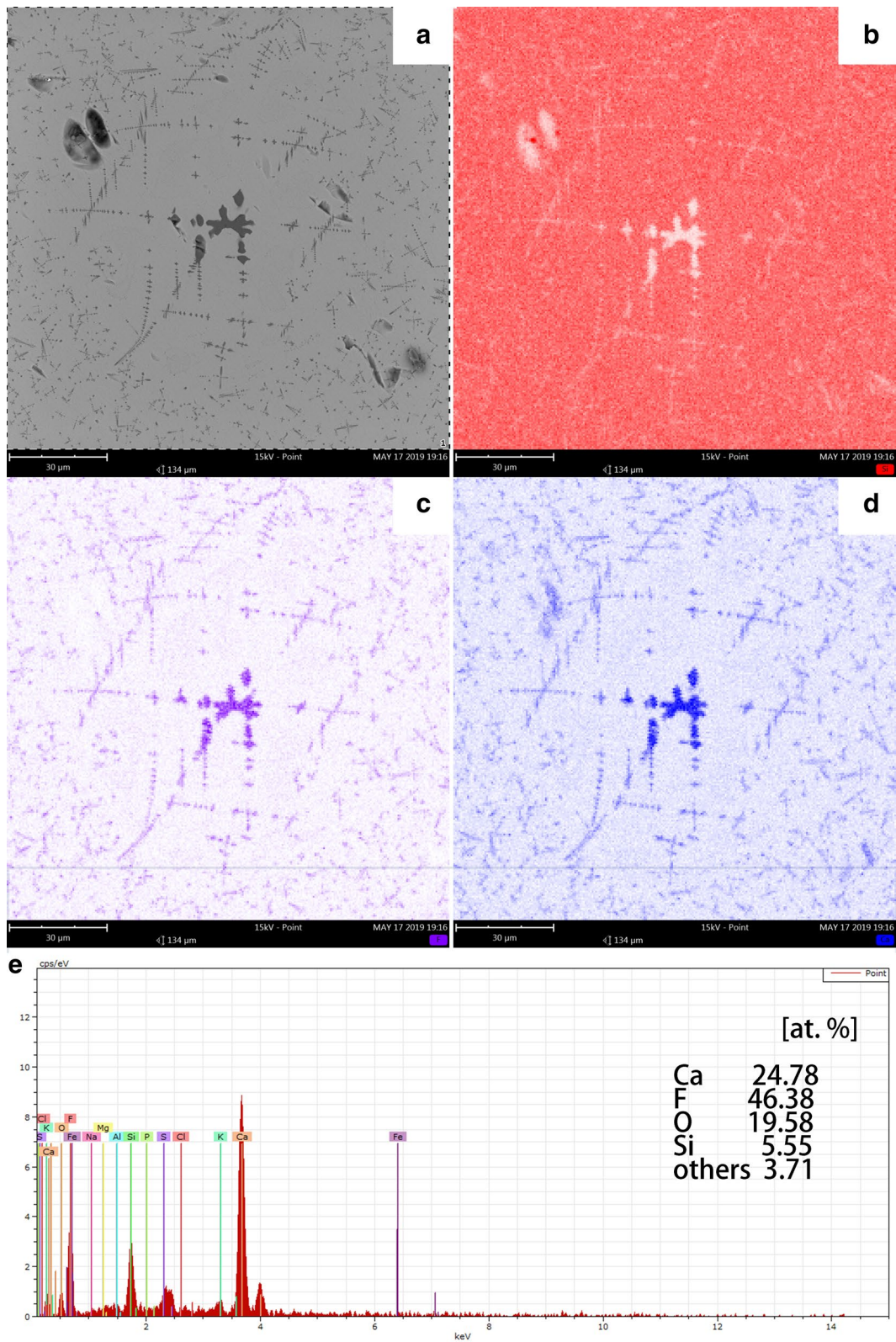
Sample	Temp. (°C)	Cooling	PbO	$SiO_2$	$K_2O$	CaO	CuO	$Al_2O_3$	$Na_2O$	$Fe_2O_3$	MgO	$P_2O_5$	F
Ancient glass	Unknown	Unknown	37.07	44.66	10.24	4.84	0.53	0.44	0.26	0.18	0.18	ND	1.61
Replica 1	950	In furnace	36.41	44.69	11.53	5.59	0.62	ND	ND	ND	ND	ND	1.16
Replica 2	1000	In furnace	35.70	44.29	11.26	6.46	0.67	ND	ND	0.13	ND	ND	1.48
Replica 3	1050	In furnace	35.14	44.92	11.06	6.32	0.85	0.10	0.33	ND	ND	ND	1.28
Replica 4	1000	In air	36.64	44.24	11.37	5.79	0.47	ND	0.17	ND	ND	ND	1.31



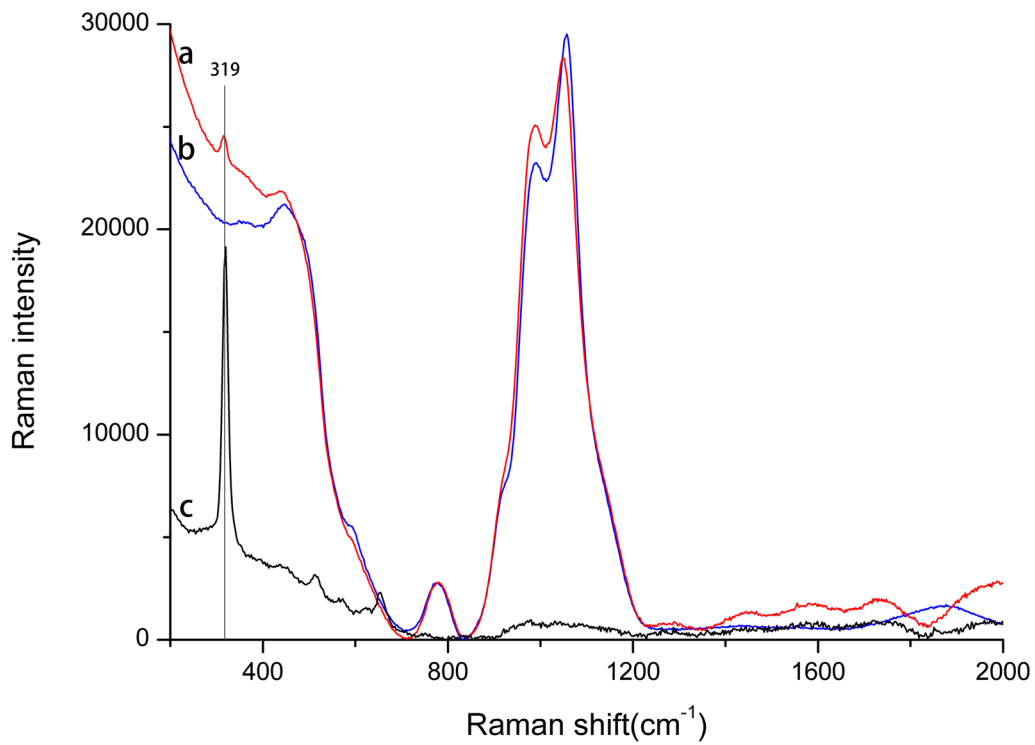
**Fig. 2** Microstructure of the ancient blue glass cross-section (**a**); and enlarged different two-dimensional figures (**b–d**) showing the isometric dendritic form

seemingly completed but apparent air bubbles and pits remained. As the temperature increased to 950 °C, the melts seemed to look perfect. However, the observation under the SEM (Fig. 6) shows there were some large unmelted fluorite particles in the samples fired at 950 °C as well as 1000 °C. The uniformity can be achieved when the firing temperature was raised to 1050 °C. In addition, at a relatively slow cooling rate, i.e., cooling within the furnace (the cooling rate from 1000 to 700 °C is shown in Fig. 7), the different firing temperatures resulted in different dendrite sizes. Shown in Fig. 8, the size of most dendrites in the sample fired at 950 °C is approximately 5 μm or below, evidently smaller than those in the ancient one. Those in the samples fired at 1000 °C and 1050 °C are around 10 μm, similar to those in the ancient one. As the initial cooling temperature rising, the size of the crystals became larger (Fig. 8, from a to c), which indicates the crystallization temperature range is from a temperature higher than 1000 °C to one lower than 950 °C. Another important factor is the cooling speed, which greatly influence the crystallization by the duration of a certain temperature range. When the melting glass was directly cooled in the air, the fluorite crystals became extremely small, around 300 nm in size (Fig. 8d). However, since the sizes of both primary and secondary branches of large

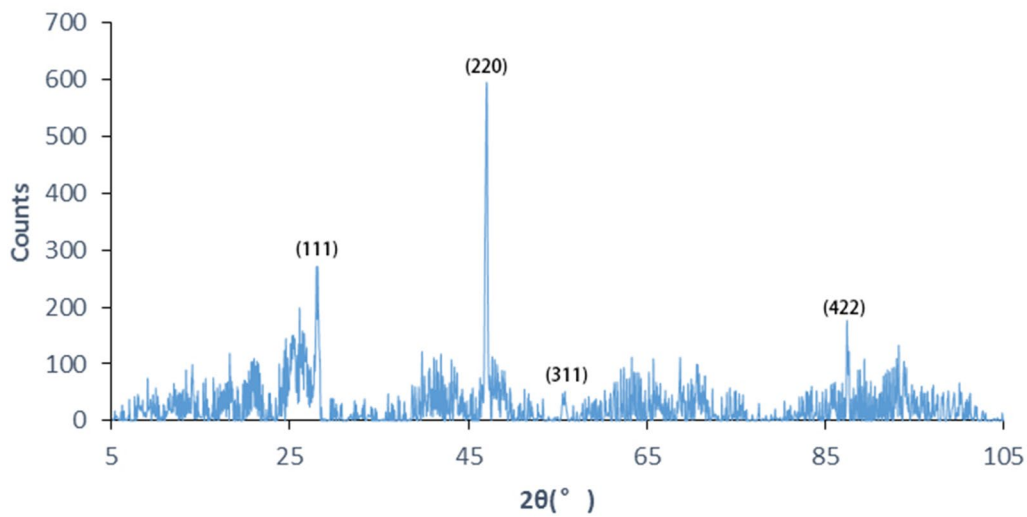
dendrites in Fig. 8a–c and nano-size crystals in Fig. 8d are comparable to the wavelength of visible light, the opacity of these glass products resulted from Mie scattering are almost identical. Thus, the size of the crystals is not necessarily important when it comes to the opaque appearance, which otherwise might be an indication of shaping process. It is well-known that the die-casting technology was widely used in ancient Chinese bronze production. The same technology was also commonly used in glass making [1]. One possible hypothesis is that the glass uncovered from Nanhai I shipwreck was made by die-casting, as the cooling rate in the mold might be comparable to that in the furnace in our experiments. In the other glass blowing technology situation, when the glass melts were taken from the crucible, ready for blowing, it must have experienced an air cooling process, probably resulting in nano-size crystals similar to those observed in the experimental air cooling sample (Fig. 8d). Additionally, the shaping process by blowing can probably cause distortion or even fractures of large dendritic crystals. But as shown in Fig. 3a, the largest crystal observed (about 100 μm) showed no evident distortion. Therefore, it is proposed that the well-grown fluorite dendrites in the blue glass fragment is probably an evidence supporting the die-casting hypothesis.



**Fig. 3** Elements mapping of the largest crystals observed: **a** BSE image, **b** Si element distribution representing glass matrix, **c** F element distribution, **d** Ca element distribution; and **e** the composition of the central region of the dendrite in **a**



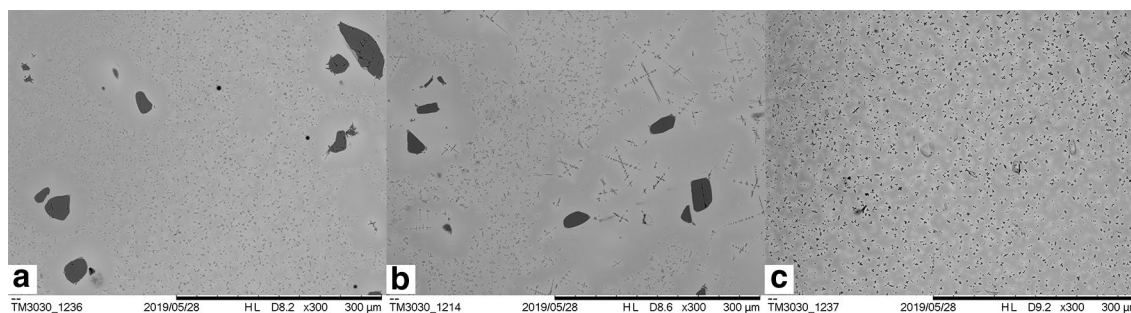
**Fig. 4** Raman spectra of (a) the ancient glass sample, showing the absorption of fluorite at 319 cm<sup>-1</sup>; (b) replicate glass sample with no fluorite addition, showing the glass background; and (c) fluorite powder



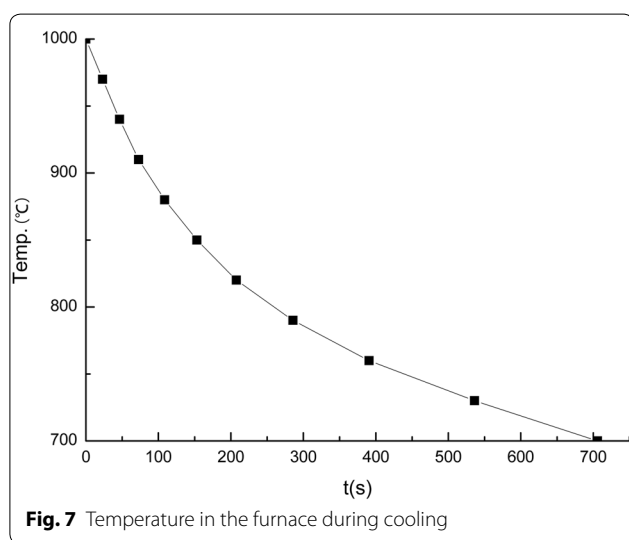
**Fig. 5** XRD spectrum of the ancient glass sample

One more phenomenon observed during the firing process is that the quartz glass boat and tube chamber reacted with some volatiles from the glass (shown in Fig. 9a), although direct contact was avoided by using

platinum lining. Consequently, an evident new layer on the amorphous silica surface with additional Pb and K elements that were absent originally can be seen. The loss of volatiles containing Pb and K can result in



**Fig. 6** Microstructures of the replica samples in large scale, from a to c referring to Replica 1–3, showing the unmelted fluorite particles (large dark ones in a and b) and none in c



**Fig. 7** Temperature in the furnace during cooling

compositional changes in the glass and thus possibly influence the opacity, e.g., a thin transparent layer free of fluorite crystals in the sample, e.g. Replica 2 (Fig. 9c), and almost completely transparent glass if the glass was in thin plate shape and the firing time is more than two hours as we observed. However, a faster cooling rate of the near-surface layer or thin plate glass is certainly another influential factor to the transparency apart from the compositional changes. Even if the volatile effect can truly result in a transparent layer, it is limited and may

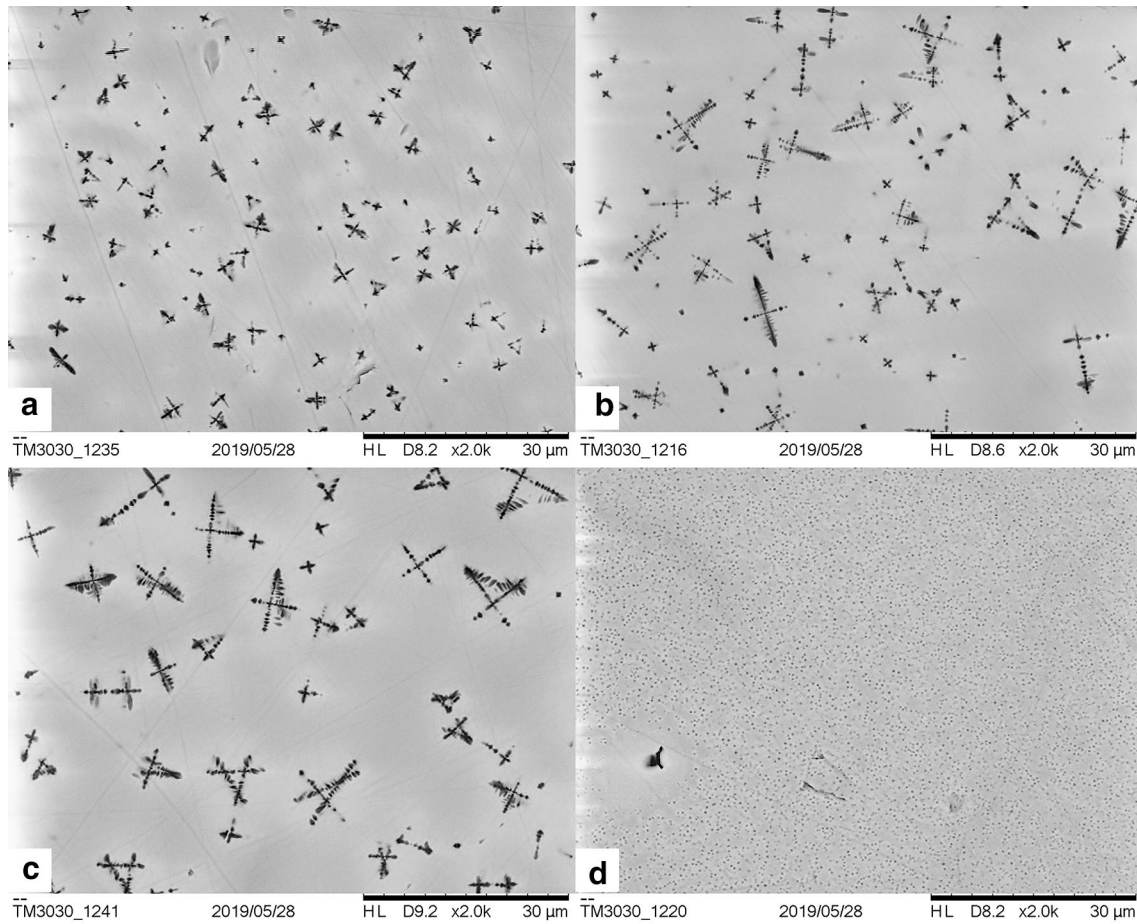
possibly not influence a large-scale glass production of this kind.

### Conclusion

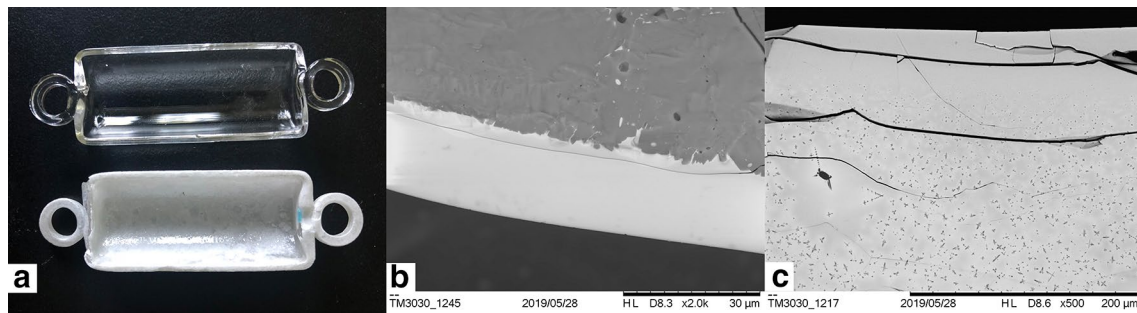
The glass piece described in this paper has provided a strong evidence for this fluorite opacifying technique used in the Southern Song Dynasty (12th–13th centuries). Now therefore, we are becoming clearer about the fluorite usage as an opacifying agent in glass manufacture from Tang Dynasty to Ming Dynasty or even Qing Dynasty if considering enamel as glass. Our finding has undoubtedly supplemented the missing link in the Southern Song Dynasty and provided an insight of the continuous development and inheritance of this fluorite opacification technique in ancient Chinese glass making. Additionally, here we first report fluorite dendrite in the ancient Chinese glass.

Apart from the demonstration of fluorite in the glass, possible firing temperature (1000–1050 °C) and proper cooling rate are also provided via the replication of the glass samples with similar chemical compositions. A further indication according to the cooling rate and undistorted large dendrite is that this piece of glass was more likely to be made by die-casting than by blowing.

The replication combined with observation of crystalline phases in this study has demonstrate itself a useful method for discussing and interpreting the possible technique of ancient glass making.



**Fig. 8** Microstructures of the replica samples: **a–c** referring to Replica 1, 2 & 3 cooled within the furnace show an increase in dendrite size as the firing temperature rising from 950°C to 1050°C; **d** referring to Replica 4 cooled in the air shows the much smaller nano-size crystals



**Fig. 9** **a** The appearances of the quartz glass boats before and after firing process; **b** the microstructure of the amorphous silica surface layer, showing a new reaction layer formed on the amorphous silica with volatile  $K_2O$  and  $PbO$ ; and **c** the transparent layer free of fluorite dendrites near the surface of the Replica 2



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### Authors' contributions

All the experiments were designed and carried out by YZ, YJ and KW. The data were analyzed by YZ and YJ. The sample was excavated under the help of JS and YC. The manuscript was written by YZ and YJ, and revised by KW and DH. All authors read and approved the final manuscript

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### Availability of data and materials

The datasets analyzed during the current study are available from the corresponding author on reasonable request.

### Competing interests

The author declare that they have no competing interests.

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