Nondestructive identification of ancient Chinese glasses by Raman and proton-induced X-ray emission spectroscopy

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Nondestructive Raman spectroscopy and external-beam proton-induced X-ray emission (PIXE) technique to analyze eight ancient glasses unearthed from the provinces of Henan, Hubei, and Jiangsu, which allowes for a good characterization of the glass matrix and chemical compositions, is carried out. The results indicate that all the eight glass samples could be typically divided into three systems: faience (sample No. SZWG-4), PbO-BaO-SiO_2 (sample Nos. NYWKI-5-1, HNWKII-88, and HNWKII-84), and Na_2O-CaO-SiO_2 (sample Nos. HBWKI-16, HBWKI-17, HBWKI-18, and SZWG-1). Additional relationships between the Raman spectra and parameters, such as residues of raw materials and opacifying agent, are also discussed by respectively comparing them with similar glass samples excavated from other historical sites.

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Glass, as an important artificial material and key evidence for East-West cultural and technical exchange, has played a great role in the course of human civilization[1]. The chemical compositions of ancient glasses are very important for the determination of their types. The analyses currently being used in ancient glasses usually include inductively coupled plasma atomic emission spectrometry (ICP-AES) and scanning electron microscopy (SEM), which are considered as destructive methods. The use of nondestructive techniques, such as Raman spectroscopy and external-beam proton-induced X-ray emission (PIXE), for the characterization of archaeological and historical artifacts has been demonstrated. In the past 20 years, through the close cooperation between archeologists and scientists, some new results about the composition of ancient Chinese glasses have been obtained[2], but very few Raman data have been published. Faience, glass, ceramics, and enamel around the world have been widely studied and compared by Raman spectroscopy in the last decades. In addition, the representative production technologies of the selected artifacts in different areas such as Asian (Vietnamese porcelains and celadon glazes), Islamic, European, and African were also studied in many research[3−13]. Hence, the two techniques should also be applied in the analysis of ancient Chinese glasses with very varied and complex nature.

This study aims to provide some preliminary Raman data on ancient Chinese glasses unearthed in the provinces of Hubei, Henan, and Jiangsu from the late spring and autumn period to the Han dynasty. We confirm the usefulness of these two techniques for a completely nondestructive study of ancient Chinese glasses and clarify the correspondence between the Raman spectra and the results of chemical compositions. Particular attention is also given to the relationship between the Raman spectra and the glass parameters such as residues of raw materials and opacifying agent.

In this letter, eight ancient glasses were provided by Suzhou Administration Committee of Cultural Relics, Nanyang Institute of Cultural Relics and Archaeology, Henan Institute of Cultural Relics and Archaeology, and Hubei Institute of Cultural Relics and Archaeology.

Fig. 1. Photos of the selected ancient Chinese glasses.

Table 1. Introduction of Selected Ancient Chinese Glasses

No.	Shape	Color	Date	Unearthing Site
SZWG-4	Glass Bead	Dark Blue	Late Spring and Autumn Period	Jade Cellar of Wu County, Suzhou, Jiangsu Province
SZWG-1	Glass Bead	Dark Blue		
NYWKI-5-1	Glass-Eye Bead	Black Body with Blue Pupil	The Late West Han Dynasty	M242, Wanjia Garden, Nanyang, Henan Province
HNWKII-88	Animal-Shaped Glass	Blue	The Han Dynasty	Xue Village, Xingyang, Henan Province
HNWKII-84	Cicadas-Shaped Glass	Yellow		
HBWKI-17	Glass Eye Bead	Dark Blue Body, a Light Blue Pupil, and White Circular Pattern	Early Warring States Period	Leigudun, Suizhou, Hubei Province
HBWKI-18	Glass Eye Bead	Light Blue Body, a Dark Blue Pupil, and an Ochre Circular Pattern on the Inlaid White Eyeball		
HBWKI-16	Glass Eye Bead	Light Blue Body and a Dark Blue Pupil on the Inlaid White Eyeball		

Except for SZWG-4, SZWG-1, HNWKII-88, and HNWKII-84, the remaining artifacts have similar shapes, which look like glass eye beads unearthed from the Xu Jialing Tomb in Henan Province[14]. Different typologies and colors are represented together with some glass fragments. A synthetic description of the shape, color, date, and unearthing site of the samples are given in Table 1; photos of all the samples are shown in Fig. 1.

The external-beam PIXE experiments were performed at the NEC 9SDH-2 Pelletron tandem accelerator of Fudan University[14]. The proton beam was extracted through a 7.5-μm-thick Kapton window and traveled 10 mm in air before reaching the glass sample. The beam spot diameter on the sample was 1 mm, and the beam current was 0.01 nA. The original energy of the proton beam was 3.0 MeV. However, the actual energy of the protons reaching the samples was only 2.8 MeV due to the energy loss in the Kapton film and air. An ORTEC Si (Li) detector (165-eV full-width at half-maximum (FWHM) at 5.9 keV), placed at 90° relative to the beam direction, was used. From the measured PIXE spectrum, the atomic composition of the elements with atomic number z larger than 12 in the sample could be obtained by the deconvolution program GUPIX-96. For measuring Na content in the glass, the sample should be cycled by the He gas in order to avoid the atmosphere absorption.

All the samples were examined in a nondestructive fashion using LabRam-1B Raman spectrometer at Fudan University. The scattered light was collected in backscattering geometry by focusing a $\times 100$ objective on the sample. The 632.8-nm line of an He-Ne laser was applied for excitation. The laser power at the focus spot with a beam diameter of about 1 μm on the sample was kept at about 4.3 mW. The spectral resolution was 1 cm^{-1}. The detection system consisted of a multichannel detector. The chemical composition as well as the Raman data are measured at the surface of the samples.

The eight glass samples were first analyzed by the external-beam PIXE technique, and the corresponding results are given in Table 2. As can be seen, the samples could typically be divided into three systems according to the evolution of the glass chemical composition[2]:

(1) System 1: SZWG-4 (K_2O/Na_2O = 2.1) was unearthed from the Yanshan Jade Cellar of Wu County in Jiangsu Province with the CaO content being about 2–4% (by weight). The ratio of K_2O/Na_2O was more than 1 for the weathered surface.

(2) System 2: The lead barium silicate glass samples were discovered from the Wanjia Garden of Nanyang and the Xue Village of Xinyang, which are both in Henan Province. In the chemical composition of these glasses (NYWKI-5-1, HNWKII-88, and HNWKII-84), the BaO content was about 7–12%, PbO about 17–41%, Na_2O plus K_2O < 6%, and others were mostly SiO_2(37–57%).

(3) System 3: The soda lime silicate glass samples include all glass eye beads (HBWKI-16, HBWKI-17, and HBWKI-18) that were unearthed from the Leigudun site in Suizhou, Hubei Province[15]. The chemical composition of these beads shows the ratio $0.1 < K_2O/Na_2O < 0.6$, and the CaO content was about 6%–10%, which is higher than that of system 1. Moreover, considering surface weathering, the actual content of sodium in SZWG-1 (K_2O/Na_2O = 0.9) should be higher than the results. This can be verified by Shi Meiguang's research about beads using the energy-dispersive X-ray analysis (EDX)[16], thus SZWG-1 should belong to soda lime silicate glass.

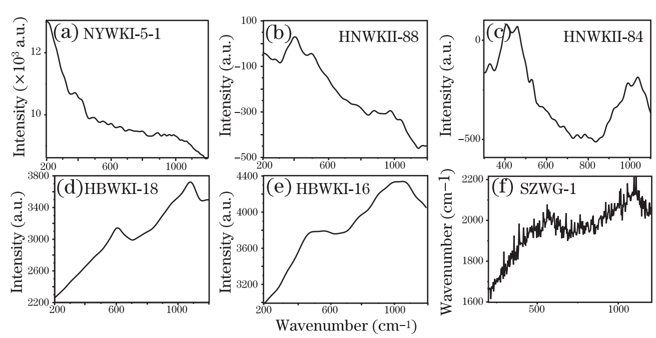

Fig. 2. Raman spectra of the ancient Chinese glasses. (a) NYWKI-5-1, (b) HNWKII-88, (c) HNWKII-84, (d) HBWKI-18, (e) HBWKI-16, and (f) SZWG-1.

Table 2. Chemical Composition of Selected Ancient Chinese Glasses (wt.-%)

No.	Test Point	Na_2O	MgO	Al_2O_3	SiO_2	P_2O_5	K_2O	CaO	TiO_2	Cr_2O_3	MnO	Fe_2O_3	CoO	NiO	CuO	ZnO	BaO	PbO
SZWG-4	Dark Blue	3.11	1.81	2.71	75.85	1.06	6.46	2.27	0.07	0.01	0.00	0.29	0.01	0.02	6.26	0.00	0.00	0.00
NYWKI-5-1	Blue Pupil	4.87	1.34	5.38	57.05	1.27	0.42	1.07	0.00	0.00	0.00	0.38	0.00	0.00	1.49	0.00	7.08	17.73
HNWKII-88	Blue	2.11	1.43	4.43	51.80	1.44	0.09	3.21	0.00	0.07	0.00	0.47	0.00	0.00	0.35	0.00	7.69	24.90
HNWKII-84	Yellow	0.56	0.20	0.78	37.15	4.13	0.14	3.27	0.00	0.04	0.00	0.04	0.00	0.00	0.00	0.04	12.04	40.73
HBWKI-17	Light Blue Pupil	2.50	0.75	3.51	77.03	0.59	1.41	9.52	0.12	0.00	0.02	3.34	0.24	0.00	0.53	0.22	0.00	0.14
HBWKI-18	Light Blue Body	13.43	5.78	5.33	64.28	0.34	2.15	6.45	0.12	0.03	0.00	0.71	0.02	0.00	1.30	0.03	0.00	0.00
HBWKI-16	Light Blue Body	3.29	0.77	3.69	82.88	0.18	0.37	7.13	0.04	0.00	0.00	0.45	0.00	0.00	1.14	0.00	0.00	0.00
SZWG-1	Dark Blue	3.83	2.98	2.53	75.87	0.54	3.58	6.79	0.15	0.05	0.07	0.96	0.00	0.00	2.57	0.10	0.00	0.00

Qualitative and quantitative analyses have been carried out nondestructively on eight ancient Chinese glasses using Raman spectroscopy and external-beam PIXE techniques. Figure 2 lists the representative spectra of six samples, which have test parts that are in the noncrystalline state with two evident envelopes at about 500 and 1000 cm^{-1}. This shows that $I_{500} > I_{1000}$ (I is the intensity of Raman spectroscopy) in the lead barium silicate glass samples (system 2), but reverse phenomena appear in the soda lime silicate glass samples (system 3).

Aside from the typical features of a glassy phase, which will be discussed in the following, most spectra also show the characteristic peaks of one or more crystalline phases, which serve as residues of raw materials or opacifiers within the glass matrix. A synthesis of the identified phases can be found in the following discussion.

All comparisons were made according to the evolution of the chemical composition of ancient Chinese glasses, and the analysis of the Raman spectra was preceded within three systems.

A clear differentiation between the lead barium silicate glass and the soda lime silicate glass is possible because the connectivity of [SiO_4] polymeric units can be studied through the relative intensities of Si-O stretching and bending modes at about 1000 and 500 cm^{-1}, respectively[3,5,8,9,11]. Although the six samples all belong to glass state, the Raman signatures of systems 2 and 3 are quite different in Fig. 2. With the SiO_2 content decreased from system 3 (64%–82%) to system 2 (37%–57%), more and more fluxes, such as alkali and alkali-earth metal ions, enter the silicate network and break the connection between the silicate and bridge oxygen in silicate tetrahedrons. Thus, the number of non-bridge oxygen (NBO) increases. The interaction between the NBO and these modifiers can not only form a series of new ligands in glass matrix, but also reduce the strength of the Si-O_b-Si stretching modes[17]. We can then compare the relative content of SiO_2 in the ancient glasses through their Raman spectra. In addition, the envelope at around 500 cm^{-1} in the Raman spectra of lead barium silicate glasses always shows a declining baseline, which may be relevant to the vibration of Pb-O in the low frequency of about 140 cm^{-1}.

Aside from the typical feature of glassy phase, additional crystalline phases have been detected within the glass matrix of SZWG-4, which may be attributed to the residues of raw materials used during the glass manufacturing process. Figure 3 shows a strong peak at 465 cm^{-1}, indicating that there should be some larger particles of quartz that were not completely fused in the sample. Another kind of crystal that yields three peaks at 553, 776, and 1093 cm^{-1} was the malachite ($Cu_2(OH)_2CO_3$), which is always a paragenetic mineral in the oxidation zone of copper deposits. For the carbonate group, Raman bands were observed at 1090 (ν_1) and 769 cm^{-1} (ν_2). The band for Cu-O stretching mode was found at 553 cm^{-1} [18,19]. The abovementioned results of Raman spectroscopy showed that the crystals in SZWG-4 are residues of raw materials like quartz particles. We also found some beads that are made of malachite and bronze artifacts in the same tomb. The malachite was easily decomposed at about 473 K, thus the alteration product of some copper minerals may be deposited on the surface of the sample; this probable caused the vibration peaks of the malachite observed in SZWG-4. It can be inferred that people had learned how to use these kinds of minerals as raw materials for glass making in the Late Spring and Autumn period. These Raman data are consistent with the chemical compositions from the external-beam PIXE (SiO_2 of 75.85% and CuO of 6.26%); hence, SZWG-4 should belong to a faience with glass phase in it and malachite deposit on the surface.

Raman spectroscopy has been a powerful method of identifying tiny crystalline phases. For the glass samples, the calcium antimonite has been characterized not only in the inlaid white of HBWKI-16, but also in the white circle of HBWKI-17. Generally speaking, the calcium antimonite is a typical opacifying agent for all the opaque white glass samples, such as the HBWKI-16 and HBWKI-17 samples. However, it is also used as opacifiers for other colors and as colorants to produce mixed colors[20].

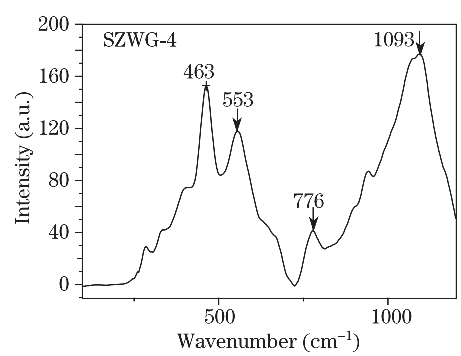

Fig. 3. Raman spectrum of SZWG-4. +: quartz, ↓: malachite.

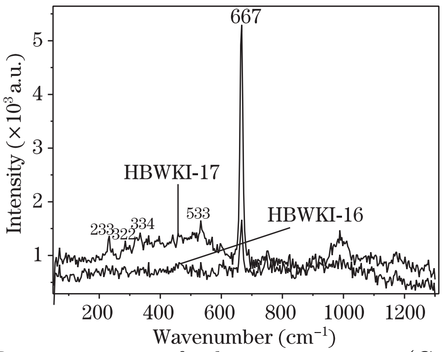

Fig. 4. Raman spectra of calcium antimonite ($CaSb_2O_6$).

As presented in Fig. 4, $CaSb_2O_6$ is characterized by Raman bands with a strong peak at 667 cm^{-1}, sometimes together with several less intense bands (at about 233, 322, 334, and 533 cm^{-1}), which was in good agreement with the published values[3,4]. According to the standard Raman spectra, we can easily discern that the crystalline inclusion is just $CaSb_2O_6$, rather than $Ca_2Sb_2O_7$. A specific group of opacifiers cannot be obtained only in the chemical composition by the PIXE. Therefore, Raman spectra can provide a lot of useful information about this problem.

A new analysis of the three glass eye beads unearthed from the Tomb of the Leigudun site[21] has been reported. Among the three glass eye beads, Lgd-1 and Lgd-2 are very similar in appearance to HBWKI-16. As an opacifying agent, Sb_2O_5 (1.12%–5.47%) was found in different colors, including the white part of the beads belonging to soda lime silicate glass, by means of X-ray fluorescence (XRF). Meanwhile, Sb_2O_5 ($\leq$ 1.6%) also appeared in some single-colored glass beads excavated from Xinjiang Province from the West Zhou dynasty to the West Han dynasty[2]; however, the existing states of antimony in these samples must be further analyzed. Our analytical results demonstrate that the white parts of these glass eye beads (HBWKI-16 and HBWKI-17) should be both effectively opacified by means of antimony, i.e., $CaSb_2O_6$.

In conclusion, the use of Raman spectroscopy combined with PIXE data for the analyses of eight glass samples that were unearthed in the provinces of Henan, Hubei, and Jiangsu from the Late Spring and Autumn period to the Han dynasty shows its unique advantages. These powerful nondestructive techniques can classify ancient Chinese glasses into three different systems: faience, soda lime silicate glasses, and lead barium silicate glasses. Monitoring stretching and bending envelopes from their Raman spectra appear to be a simple and convenient way of determining the relative content of SiO_2 in the ancient glasses. This study also demonstrates some information about the residues of raw materials such as quartz during the glass manufacturing process. The alteration product of some copper minerals like malachite is also discussed by Raman scattering. Furthermore, the unique Raman spectra of the opacifying agent in some white parts of the two glass eye beads (HBWKI-16 and HBWKI-17) lead to the identification of calcium antimonite ($CaSb_2O_6$). Because of the complexity and diversity of ancient Chinese glass, further research should be done in the future.

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