



Contents lists available at ScienceDirect

Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy

journal homepage: www.elsevier.com/locate/saa

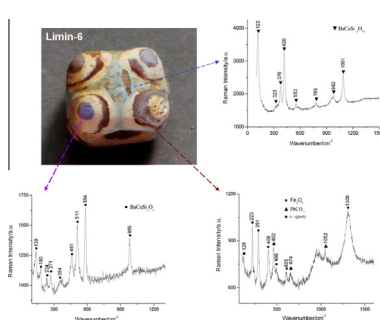
Identification of the man-made barium copper silicate pigments among some ancient Chinese artifacts through spectroscopic analysis

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HIGHLIGHTS

- Raman spectroscopy is used to identify ancient barium copper silicate pigments.
- Some artifacts were analyzed in situ by the portable XRF and Raman spectroscopy.
- The technological development of early native glassmaking in China is discussed.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:

Received 3 September 2014

Received in revised form 10 November 2014

Accepted 20 November 2014

Available online 28 November 2014

Keywords:

Non-invasive analysis

Micro-Raman spectroscopy

Ancient Chinese silicate artifacts

Barium copper silicate pigments

PbO–BaO–SiO₂ glaze

ABSTRACT

This article describes the complementary application of non-invasive micro-Raman spectroscopy and energy dispersive X-ray fluorescence spectrometry to the characterization of some ancient Chinese silicate artifacts. A total of 28 samples dated from fourth century BC to third century AD were analyzed. The results of chemical analysis showed that the vitreous PbO–BaO–SiO₂ material was used to sinter these silicate artifacts. The barium copper silicate pigments including BaCuSi₄O₁₀, BaCuSi₂O₆ and BaCu₂Si₂O₇ were widely identified from colorful areas of the samples by Raman spectroscopy. In addition, other crystalline phases such as Fe₂O₃, BaSi₂O₅, BaSO₄, PbCO₃ and quartz were also identified. The present study provides very valuable information to trace the technical evolution of man-made barium copper silicate pigments and their close relationship with the making of ancient PbO–BaO–SiO₂ glaze and glass.

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Introduction

In 1983, FitzHugh and Zycherman [1] identified a kind of man-made blue pigment with the theoretic formula of BaCuSi₄O₁₀ from some Chinese painted ceramic objects, which were of the collections of different museums abroad China, and were dated to the

Han Dynasties (206 BC–220 AD) or the Warring States Period (475–221 BC). They also found some purple barium copper silicate pigments accompanied with BaCuSi₄O₁₀, and later confirmed that these purple pigments were of the crystalline BaCuSi₂O₆ in 1992 [2]. In 1984, Brill et al. [3] synthesized the purple pigments similar with those mentioned by FitzHugh and Zycherman, and determined that these purple crystals had an empirical formula of BaCuSi₂O₆. Their pioneering research initiated the followed researches related to the ancient man-made barium copper silicate compounds. The scholars began to trace the making technology

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and province of ancient $\text{BaCuSi}_2\text{O}_6$ and $\text{BaCuSi}_4\text{O}_{10}$ crystals through synthetic experiments [4–6] and lead isotope analyses [7]. Meanwhile, more attention was paid on the identification of the barium copper silicate pigments from the artifacts excavated from different places of China [8–13]. Besides $\text{BaCuSi}_4\text{O}_{10}$ and $\text{BaCuSi}_2\text{O}_6$, another barium copper silicate compound, $\text{BaCu}_2\text{Si}_2\text{O}_7$ (Chinese Dark Blue, CDB), was also identified from the pigments used for decoration of the polychrome terracotta figures excavated from the tombs of the Western Han Dynasty (206 BC–8 AD) in Shandong Province, China [11,13,14].

To now, the ancient artifacts, from which the barium copper silicate crystals were found, include beads, tubes, octagonal sticks, Terracotta Army of the First Chinese Emperor, polychrome terracotta figures, ceramic vessels, painted bronze vessels and so on. The beginning time of man-made barium copper silicate crystals identified in compact beads, tubes or sticks so far could be traced back to about eighth to third centuries BC [5,9,12,14]. During the Qin and Han periods (221 BC–220 AD), the $\text{BaCuSi}_2\text{O}_6$ powder was widely used as the pigment to decorate the polychrome pottery figures [10,11,13,15].

It has been proved that the $\text{BaCuSi}_4\text{O}_{10}$ crystal is isostructural to the Egyptian Blue ($\text{CaCuSi}_4\text{O}_{10}$) [16–18]. Both of them have layered structures with $(\text{SiO})_4$ silicate squares forming the structural framework and differs only in the exchanged earth alkali element [5,6]. The natural mineral of $\text{BaCuSi}_4\text{O}_{10}$, effenbergerite, was once found in the Kalahari Manganese Field, South Africa in 1994, but it is so rare in nature and its cultural significance for China was ruled out [19]. Now the scholars usually call the $\text{BaCuSi}_4\text{O}_{10}$ and $\text{BaCuSi}_2\text{O}_6$ compounds as Han Blue or Chinese Blue, and Han Purple or Chinese Purple, respectively [1–15]. Considering the using time of the barium copper silicate compounds, we prefer to use the names of Chinese Blue (CB) and Chinese Purple (CP).

As for the using time, the Egyptian Blue was invented at about 3600 BC and its use was documented since the 4th Dynasty of ancient Egypt (ca. 2575–2467 BC) and lasted from the Middle and New Kingdoms (ca. 1567–1085 BC) to the Greco-Roman period [20,21]. By contrast, the ancient barium copper silicate compounds appeared much later than the Egyptian Blue. Although the present researches have greatly enriched our knowledge, the technical origin and development, raw materials and function of CB and CP in China is still not fully clear. In addition, most of the previous studies were carried on chips or fragments of the artifacts with CB and CP, which were dated to the Han Dynasties and mainly limited to the pigments, octagonal sticks and simple-shaped beads.

In the present study, some beads with eye-shaped decoration of the Warring States Period, which were excavated from different places of China, are analyzed using a micro-Raman spectrometer and a portable X-ray fluorescence spectrometer. Both of the methods have been widely used for the characterization of ancient artifacts, such as glass [22], glaze [23], pigment and others [24,25]. For comparison, other artifacts either excavated or collected were also analyzed. The aim is to shed some new light on the making and use of ancient barium copper silicate compounds and their relationship with the lead-barium silicate (PbO-BaO-SiO_2) glasses in the early period before the Han Dynasties.

Materials and methods

Samples

A total of 28 samples were analyzed by spectroscopic techniques. Among them, 17 samples were unearthed from different places of China by the archaeologists. Samples HNVK-V-82 and HNVK-V-84 were dated to the Han Dynasties. One sample XJ-38A was of was one of the samples which gathered from the

ground of the archaeology site of the Yuan-Ding-Shan cemetery, Li County, Gansu Province. The Yuan-Ding-Shan cemetery was dated to the middle and late Spring and Autumn Period [26]. The other samples excavated from Gansu [27], Hubei [28] and Henan Provinces were all dated to either middle or late of the Warring States Period. The general condition of these samples was listed in Table 1.

Referred to the morphological and chemical characteristics of the samples excavated, the 10 samples listed in Table 2, which are collected by the Shanghai Museum of Glass, are approximately dated from the middle to late Warring State Period. Selected photos of the samples analyzed were shown in Fig. 1.

X-ray fluorescence spectroscopy

In order to have a primary understanding of the chemical properties, major and minor elements of the samples were determined by an OURSTEX 100FA type portable X-ray fluorescence spectrometer (pXRF) before the Raman spectroscopy analysis was performed. A palladium (Pd) excitation tube was employed with voltage of 40 kV for monochromatic and filter modes or 15 kV for direct mode, and with a current of 0.5–1.0 mA. The detector is a silicon drift detector (SDD) with active area of 5 mm² equipped with a polymer window (MOXTEK AP 3.3 film). The X-ray beam spot focused on the sample is about 2.5 mm in diameter. Together with the introduction of a vacuum sample chamber, this pXRF allowed us to quantify the light elements such as Na and Mg. Further details of the pXRF could be found elsewhere [29,30].

A total of nine standard glass samples distributed by Breilander Eichproben und Labomaterial GmbH, Germany, along with other modern optical glass samples, were used to make calibration curves for a number of major, minor and trace elements in PbO-BaO-SiO_2 glass and glassy glaze. The standard glass sample, Corning C, which was not used for the calibration, was measured 12 times to check the precision and accuracy of the method. This equipment shows good stability and the relative standard deviation (RSD) value for most of the major and minor elements detected is less than 6%. The values of relative error for most major elements are less than 7%, but that of BaO reaches 11.23%. Large relatively errors appear for SnO_2 and Sb_2O_3 because of their low concentrations. The values of the low limit of detection (LLD) range from 20 to 1879 $\mu\text{g/g}$. Since its peak overlapping with barium element, the content of TiO_2 was not listed. Relative details can be checked in the supplementary data.

Confocal Raman microspectroscopy

Raman spectra of the samples were obtained non-invasively with a LabRAM XploRa confocal Raman scope spectrometer, which was provided by the Horiba (China) Trading Co., Ltd. This spectrometer is equipped with two air-cooled laser sources (532 nm and 785 nm) and a multichannel air-cooled CCD detector. With the external top USB colour camera and coupling optics, it is convenient to visualize the images of the samples. At the beginning of each experiment, the system is calibrated using the 520.7 cm^{-1} silicon line from a single crystal Si wafer [31].

Usually, the Raman spectrum was obtained with the 532 nm laser beam, a long-working distance objective (50 \times) and a diffraction grating of 1800 gr/mm. The laser power on the focused spot (beam diameter, $\sim 1 \mu\text{m}$) of the artifact changed from about 2–15 mW, as is controlled by LabSpec software through the motorized filter wheel with 5 neutral density filters. The multi windows mode was used for optimized spectral resolution (better than 2 cm^{-1} /pixel) and scanning time. The Spectra-ID software permits the creation of spectra libraries and the search of spectra for identification.

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