Characterization on mosaic glass found at Phu Khao Thong, southern area of Thailand

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Abstract. Glasses in forms of ornament and decorative objects have been found in Thailand for several hundred years. The mosaic glass used in this work was only one piece that excavated at Phu Khao thong archaeological site in Ranong Province, southern area of Thailand. Micro-beam X-ray fluorescence spectroscopy (µ-XRF) based on synchrotron radiation was firstly carried out to analyze its elemental composition and distribution. Scanning electron microscope coupled with energy dispersive X-ray fluorescence spectroscopy (SEM-EDS) and (PIXE) were also used to characterize the composition. The main composition of this mosaic glass sample found in Thailand was a lead-based silicate glass. The colorations were affected from transition metals, especially iron, copper and manganese. It was shown that although it looked the same, but the main composition was different to that of Persia and South Asia, especially the lead content. However, it demonstrated the long distance trade or exchange network of the ancient time.

1. Introduction

It was known that the mosaic glass which fabricated from variously colored glass cans or rods and wedges fused together was a very special kind of multifariously colored artistic glass and used for the creation of exceptional vessels as well as decoration plates for furniture and various architectonical elements. Archaeological resources suggested that it was firstly produced in a continuation of Iron Age (700-100 BC). Previous studies on Roman mosaic glass using SEM-EDS, PIXE, LA-ICP-MS, electron microprobe and Raman microspectroscope showed that it was mainly as soda-rich, sodium-calcium-silicate glass which used quartz sand, limestone and natron as raw materials. It was also found that the color of glass was caused by the addition of certain minor- or trace elements as colorants, and microcrystals as opacifiers [1-5].
Phu Khao Thong is one of the significant ports of ancient communities between 1st and 4th century A.D. (Indo-Roman Trade) where located on the Peninsular Thailand that connected with other ports in South-East Asia, India and Middle East. Many archaeological objects were excavated at this site such as roulette wares, head of ring, carnelian intaglio (Roman), seal in the form of the Srivatsa (India), fragments of glass and pottery (Persia), and beads; glass, stone and gold (Vietnam, India and Persia). Some were tested by scientific analysis such as XRF and XRD, and concluded that they were the trading and cultural exchange goods [6-10].

This work was firstly concerning the composition of the glass artifact (Figure 2) excavated at Phu Khao Thong archaeological site by using µ-XRF, SEM-EDS and PIXE.

2. Experimental
The sample is a fragment which excavated in the 60-70 cm.d.t., on 2005 A.D. at Phu Khao Thong archaeological site. Its size is approximately 0.7x1.0x0.3 cm. It is composed of reddish-, yellowish and greenish opaque glasses. It is more intensively corroded on the surface due to storage in soil.

No destructive sample preparations such as cutting and finishing were allowed on this sample. It was only cleaned with distilled water and then dried by hot air oven method for 24 h to make it the same moisture. Three X-ray spectra were collected for SEM-EDS and PIXE measurements at different positions on the surface of each color.

Prior to the analysis of the samples, their chemical composition measured using PIXE and EDS were compared. The standards used were optical glasses with known chemical compositions. It was found that the relative errors of the measured values for PIXE and EDS were less than 10 %. Results from PIXE, therefore, could be compared to those from EDS [11]. SEM-EDS has lower sensitivity for heavy elements. Therefore, PIXE was only used to determine concentrations of sodium, aluminum, magnesium and silicon. Silicon was treated as an internal standard with known concentration previously determined by PIXE. Previous works which used this were published [12-16].

Its structure and composition were analyzed using a Hitachi SU1500 SEM with a Horiba Emax energy dispersive X-ray fluorescence spectrometer (EDXRF) at Coax Group Corporation Co., Ltd. in Bangkok (Thailand). The system was operated at a high voltage of 15 kV, an elapsed lifetime of 50 sec and a magnification of X1,000 and X2,000.

PIXE that was used to analyze this sample based on a 2-MeV proton beam produced by a 1.7 MV tandem Tandetron accelerator at the Plasma and Beam Physics Research Facility of Chiang Mai University (Thailand). The proton beam was collimated with a diameter of 1 mm, and the beam current on the sample was 10 nA. The detector used was of Si(Li) type. A 74-µm mylar foil with 0.38% relative hole area was placed in front of the detector as an absorber to reduce the count rate caused by impurities of low atomic number elements. Quantitative analysis of PIXE spectra of the chemical composition (\(Z \geq 13\)) in the sample was performed and represented as oxides using GUPIXWIN code [17-18]. The quantitative calibration included the normalization at (100%-x) of the oxide sum, while the value of x is a sum of Na₂O and MgO determined by EDS. The elemental compositions were conventionally determined in weight percent.

Micro-beam energy dispersive X-ray fluorescence spectroscopy (µ-XRF) using synchrotron radiation at the beamline 6 (BL6b) of the Synchrotron Light Research Institute (Thailand) was used to detect the presence of metals and their contribution in the sample. The BL6b utilizes continuous synchrotron radiation which is a white beam from the bending magnet with energy range above 2 keV. In this beamline, beryllium window with the thickness of 100 µm is used to filter out low energy. At the sample holder, 2 motorised stages with the precision of 1.5 µm have been used to control a sample. The detector used at the end-station is Si(PIN) detector from AMPTEK, USA with an active area is 13 mm² and energy resolution of 160eV at the Mn K\(\alpha\) emission line [19]. The schematic of beamline and setup for µ-XRF at BL6b was shown in Figure 1.
3. Results and discussion

Chemical composition data obtained by EDS and PIXE was given in Table 1. It was lead-silicate glass. SiO$_2$ and PbO showed relatively high concentration, while Na$_2$O concentrated less than 1.0 wt%. MgO, Al$_2$O$_3$, K$_2$O and CaO were presence with concentration approximately 1, 4, 2 and 5 wt%, respectively. The high lead concentration suggested that it was used as the flux [11, 20-22]. It was well known that lead-containing glass has been used for decoration for several hundreds of year [23]. Furthermore, the contents of K$_2$O and MgO confirming that the alkali used was indeed soda. Concentrations of Al$_2$O$_3$ and CaO seem to point the use of quartz sands as the silica resource [3, 24-26]. Moreover, the PIXE analysis showed the presence of trace elements of Cr and As which was confirmed by using $\mu$-XRF, as shown in Figure 2. Minor components determined were transition metals such as MnO, Fe$_2$O$_3$, and CuO corresponding to impurities from raw materials used or intentionally added as colorants [27]. It was revealed that a mixture of copper and red was red and green coloration in glass matrix more than 1400 years BC [20]. The high ratio of MnO:Fe$_2$O$_3$ (approximately 1) in green- and yellow- colored glass matrices indicated manganese was intentionally added as a decolorant [24]. The presence of trace elements such as Ti, Cr and As may be also impurity in raw materials, the more details will be studied.

It was known that all of ancient glasses were slightly yellowish or greenish colors which affected from iron contamination in sands used as silica resource. Opacity in glass was generally due to the presence of a dispersion of crystals in a translucent glass matrix [25]. The enriched lead oxide was not only play of a network-forming oxide that made the lower melting temperature [28], but also used as the main opacifiers from the beginnings of the glass production in the Near East and Egypt around 1500 B.C. through to the Roman period [3, 23, 25-26,29-33].

From above results, it was found that the opaque red, yellow and green colored glasses were generated from the presented of manganese, iron and copper with influence by lead and arsenic.

Table 1. Chemical composition of the mosaic glass sample from Phu Khao Thong using EDS and PIXE

| Area  | Na$_2$O | MgO | Al$_2$O$_3$ | SiO$_2$ | K$_2$O | CaO | TiO | MnO | Fe$_2$O$_3$ | CuO | PbO |
|-------|---------|-----|-------------|---------|-------|-----|-----|-----|------------|-----|-----|
| Red   | 0.75    | 1.02| 3.03        | 74.50   | 2.03  | 6.90| 0.17| 0.24| 2.32       | 2.80| 6.79|
| Yellow| 0.46    | 0.96| 2.45        | 71.56   | 2.63  | 5.29| 0.14| 0.69| 0.70       | 0.18| 13.72|
| Green | 1.09    | 1.33| 2.68        | 74.19   | 2.98  | 6.62| 0.19| 0.74| 0.84       | 3.45| 5.45|
Figure 2. Detectable elements (a) and elemental distribution (b) of mosaic glass sample from Phu Khao Thong using μ-XRF at BL6b.
Figure 3. SEM micrographs of mosaic glass sample from Phu Khao Thong

It was also shown that the surface of the sampled part of the glass was more corroded, as shown in Figure 3. Due to environmental and soil chemical effects during its burial period, part of Na had been dissolved. In contrary, the concentration of Al was relatively high because it was insoluble [3].

4. Conclusion
This glass fragment was composed of a lead-silicate glass, which was poor in Na$_2$O, K$_2$O and MgO, but contained appreciable amounts of CaO and Al$_2$O$_3$. The oxides of Si, Al, Ca, K and Na defined as the basic composition of the glass recipe, other components were added as colorants or as an additional flux material. The colors of the glass sample were in many cases caused by the addition of certain minor- or trace elements, which in their ionic form were integrated into the network structure of the glass matrix. An additional introduction of microcrystals as opacifiers and colorants led to form of opaque glass and to a mixture of the coloring effects.

This mosaic glass which found in Thailand presented a particular composition differs from the Roman glass in its Na, Al, K and Ca contents. This type of glass is widely distributed in Persia and South Asia which is a mineral soda-alumina glass [34]. Advanced researches will be worked.

This study has confirmed the advantages of using µ-XRF, SEM-EDS and PIXE in archaeological applications. The results from EDS and PIXE corresponded with these from µ-XRF. The combined information of the composition and topological data is necessary for understanding the origins of the mosaic glass. The results have also yielded important information about the ancient overseas trading.

Acknowledgements
This work was partly funded by the Faculty of Science at Kasetsart University. Authors were kindly thanks Captain Boonyarit Chansuwan from the 15th Regional Office of Fine Arts at Phuket Province for supporting the glass sample. The Synchrotron Light Research Institute (Public Organization) at Nakhon Ratchasima, Coax Group Corporation Co., Ltd.(Bangkok) and the Plasma and Beam Physics Research Facility at Chiang Mai University (Chiang Mai) were also thanked for providing µ-XRF, SEM-EDS and PIXE, respectively.

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