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Original article

X-ray and optical spectroscopic study of the coloration of red glass used in 19th century decorative mosaics at the Temple of the Emerald Buddha

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ABSTRACT

The Temple of the Emerald Buddha in Bangkok, Thailand is noted for its glass mosaic decorations on exterior walls and statuary. The original mosaic artwork dates to the early 19th century and is composed of variously-colored, mirrored glass pieces. In this work, we examine the chemical composition and optical properties of the red glass manufactured at that time. Through the use of X-ray and optical spectroscopies, we demonstrate evidence that the 19th century craftsmen produced "ruby-gold" glass, wherein the red coloration is caused by the dispersal of nanoscale metallic gold particles throughout the glass matrix.
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1. Introduction

Built in 1782, the Temple of the Emerald Buddha is the largest Buddhist temple in Bangkok, Thailand. During the reign of King Rama III (1824 to 1851), the temple was restored as additional halls, pagodas and towers were constructed. The temple renovation included the use of mosaics composed of thin, mirrored glass in place of the more traditional gold-on-red lacquer art to decorate external walls and pillars of the Ordination Hall enshrining the Emerald Buddha [1,2]. These decorative glasses, commonly called Kriab mirrors, are leaded glass containing from 10% to 50% lead by weight (see Table 1 and reference [3]. They were fabricated in glasshouses sponsored [4] by Thai royalty. They are thin (300 μm to 1000 μm), translucent, and variously-colored. Glass of all colors was coated with a reflective metal paste on their back surface and affixed to exterior surfaces of the Ordination Hall using natural latex.

The royal Glass Department Production was terminated during the reign of King Rama V (1868 to 1910). Thus, the Kriab glass has not been produced in Thailand in over 100 years. Scant records of the glass-making techniques remain. Eight manuscripts National Library of Thailand [5] titled in Thai as "Textbook of glass melting" belonged to Prince Pramoch, the Head of Glass Production Department of King Rama IV, and were later donated to the National Library of Thailand in 1915. The language in these records is archaic and difficult for the modern reader. Some information on glass fabrication can be interpreted from these sources [6], such as a list of raw materials which includes, tin, saltpeter, gold, lead, red soil, bronze, white stone powder and coloring glazes. No details of the manufacturing process remain which are known to us.

Over decades and with exposure to 20th century air pollution, the adhesion of the glass pieces to the walls degraded. By the time of the latest restoration of the Temple, beginning in 1982, the integrity of the mosaics was compromised by the loss of significant numbers of glass pieces. Without ready means of reproducing glass in the original style, commercially-sourced glass mirrors were imported and used in restorations beginning in 1982. The modern and original glasses have several aesthetic differences, as shown in Fig. 1. The modern glass is thicker, differently colored, and more reflective than the original glasses. The conservators of the Temple are interested in future restoration to more closely resemble the original visual appearance. Scientists at the Synchrotron Light Research Institute, Thailand's national synchrotron user facility, were asked to investigate [3] the composition of original Kriab mirror pieces from the Ordination Hall.

In this paper, we examine original specimens of red-colored glass from the Temple. The physical mechanism by which small, spherical, metal inclusions drive the coloration of glass has been understood for over a century [7,8] with dispersed gold resulting in a red coloration. Some extant historical glasses are colored red by

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Table 1
Major elements determined by EDX-WDX SEM [mass fractions, expressed as percentages, as oxides]. Uncertainties are discussed in the text.

	KMHR1	KMSR2	KMHCL2
SiO^2	37.99 (9)	37.59 (77)	68.42 (42)
TiO^2	<0.15	<0.15	<0.15
Al^2O^3	1.41 (9)	1.20 (13)	1.71 (8)
Fe^2O^3	0.37 (5)	0.31 (4)	1.37 (7)
MnO	<0.15	<0.15	1.01 (5)
MgO	0.53 (12)	0.56 (11)	0.65 (15)
PbO	46.33 (103)	51.77 (124)	1.27 (3)
CaO	0.94 (4)	0.90 (8)	8.45 (7)
Na^2O	3.86 (5)	3.86 (14)	12.96 (28)
K^2O	0.78 (1)	0.81 (3)	1.09 (2)
Sum	92.20 (103)	97.01 (131)	96.92 (31)

the presence of dispersed, nanoscale gold and called "ruby-gold" glass. The most famous example is the Lycurgus Cup, a Roman artifact dating from the fourth century C.E. [9] which is a brilliant red when seen under transmitted light. Lost in Europe during the middle ages, this coloration technique remained used throughout the Arab world during that period [10]. It was rediscovered and widely used in Europe beginning in the seventeenth century [10,11]. Small gold particles can be dispersed in glass by adding either hydrous chloroauric acid ($HAuCl_4 \times H_2O$) or potassium aurocyanide ($KAu(CN)^2$) to the molten glass followed by a reducing agent such as SnO_2, along with control of redox conditions as the glass is annealed [12]. The reducing agent serves as an electron source, reducing the gold to its zero-valent state. As the glass cools and anneals, spherical inclusions with diameters in the range of 20 nm to 100 nm are dispersed throughout the glass. This mechanism has been inferred [13] as the source of the red coloration of similar period glasses from Thailand on the basis of the presence of gold in proton-induced x-ray emission (PIXE) spectra, but has not been demonstrated quantitatively.

Haslbeck et al. [12] explain how a reducing agent such as SnO_2 added to a glass melt along with a gold salt can act as an electron source, reducing the gold to the metallic nanoparticles responsible for red coloration. To test the conjecture that mid-nineteenth century Thai craftsmen may have used a similar technique to make red glass, we have performed a chemical analysis using wavelength and energy dispersive X-ray spectroscopy (WDX/EDX) and laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS) to determine concentrations of major, minor, and trace elements in the glasses. We then applied X-ray and optical spectroscopy methods to characterize the gold content of our red glass samples.

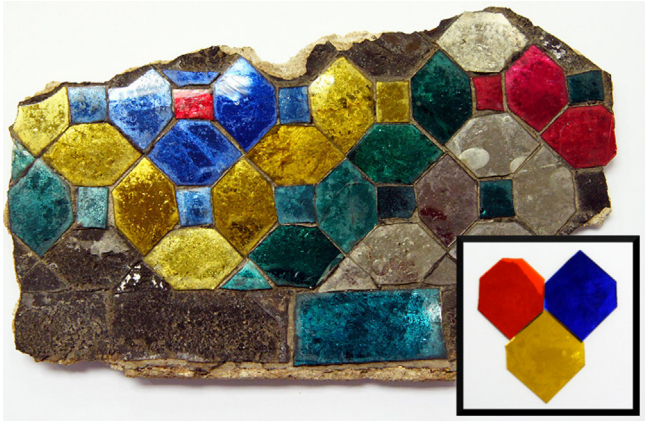

Fig. 1. Original Kriab glass mosaic on a piece of concrete wall on display in the Museum of the Temple of the Emerald Buddha. (Inset) Examples of modern, commercial glass used in 20th century restorations.

In this paper, we demonstrate that gold is present in these red glass specimens in a metallic form and in a size and concentration known to produce red coloration. We discuss other possible coloration mechanisms, but conclude that gold is the principle coloring agent of these glasses.

2. Experimental methods

The glass samples studied here were obtained from the Thailand Bureau of the Royal Household [4] and come from different locations around the Temple. Sample KMHR1 was a hexagonal piece originally from one of eight inner pillars of the Ordination Hall and part of a pattern like the one shown on the left of Fig. 1. It was removed from the pillar at the time of a restoration effort in 1982. The piece measured by X-ray and optical spectroscopy is one of three pieces cut from the hexagon and used for different analyses. It is about 5 mm by 12 mm and 600 μm thick. Sample KMSR2 was removed a mosaic pattern like the one shown in Fig. 1 decorating a damaged piece of a concrete wall and housed in the Museum of the Temple of the Emerald Buddha. It is approximately square, about 8 mm on a side, and 960 μm thick. Both samples were cleaned with ethanol prior to X-ray and optical measurements. The samples are shown in the inset to Fig. 3.

Both pieces have weathered surfaces on the sides shown in Fig. 3 and both pieces are partially covered on the reverse side by the oxidized remains of the tin-lead alloy used to make the reflective Kriab mirrors. Both pieces have sharp edges indicative of having been formed into mosaic pieces by scoring and breaking, rather than by cutting while in a hot, softened state. Finally, both pieces are uniformly colored throughout their bulk.

X-ray Absorption Spectroscopy (XAS) data at the gold L_{III} edge (11919 eV) were measured at beamline X23A2 at the National Synchrotron Light Source at Brookhaven National Laboratory in New York, USA. This is an unfocused bend magnet beamline using a Si(311) monochromator of a fixed-exit, Golovchenko-Cowan [14] design. Harmonic rejection is made by a single bounce, flat, Rh-coated mirror. An argon-filled ionization chamber was used as described below to measure the intensity of the incident beam, which was about 10^9 photons per second in a spot of 1.5 mm in the horizontal and 0.5 mm in the vertical. At this low flux density, radiation induced changes in speciation are rarely observed, even in hydrated samples. No such changes were observed in the data presented here or in any other XAS measurements made on the Kriab glasses. A four-element, Si-drift, energy-discriminating detector was used to measure the X-ray fluorescence intensities. All fluorescence XAS spectra were corrected for dead-time using the algorithm of Woicik et al. [22].

Because the glass pieces have very low concentrations of gold, the XAS data were measured in the fluorescence geometry. The glass pieces are, however, too thick to allow transmission of the beam at the energy of the Au L_{III} edge for the purpose of measuring a reference for energy calibration. Given the large number of scans measured on each sample and the relatively poor angular repeatability of the monochromator, measurement of an energy calibration reference is essential. To do this, we replaced the standard ionization chamber used to measure the incident intensity, I_0, with the argon-filled, four-channel, ionization chamber described by Ravel et al. [15]. This is shown schematically in Fig. 2. Using the same slit assembly described in that paper to define the multiple incident beams, the two central channels were blocked at the slit assembly using lead tape. This left the inboard and outboard beams, which are separated by 14 mm, for use in the experiment. The sample was placed in the path of the outboard beam, which was used to measure the fluorescence. The inboard beam passed beside the glass sample unimpeded, then struck a gold foil through