Received: 1 September 2014

Revised: 30 December 2014

(wileyonlinelibrary.com) DOI 10.1002/xrs.2586

Accepted: 31 December 2014 Publish

SPECTROMETRY

Published online in Wiley Online Library

Y_RAV

Understanding the blue color in antique mosaic mirrored glass from the Temple of the Emerald Buddha, Thailand[†]

Wantana Klysubun,^a* Christoph A. Hauzenberger,^b Bruce Ravel,^c Prapong Klysubun,^a Yuying Huang,^d Weeraya Wongtepa^a and Panidtha Sombunchoo^a

Two samples of the blue glass produced in the middle 19th century from the Temple of the Emerald Buddha in Bangkok, Thailand, were studied in order to understand the origin of its blue color. The oxide components and trace elements are quantitatively determined by scanning electron microscopy coupled with energy-dispersive and wavelength-dispersive spectrometry and laser ablation inductively coupled plasma mass spectroscopy techniques. The results identify the glass type as soda-lime-silica glass with high lead content. The 3d transition elements detected include iron, manganese, cobalt, and copper. Combined analyses of X-ray absorption near edge structures and optical absorbance lead to a conclusion that the antique glass is primarily colored in blue by the divalent cobalt with additional yellow coloration as a result of the trivalent iron. The tetrahedral coordination geometry of these two species was deduced from the XANES pre-edge intensity and the optical absorption bands of their d-d transitions. The redox ratios of Fe²⁺/Fe³⁺, Mn²⁺/Mn³⁺, and Cu¹⁺/Cu²⁺ in the original blue glass and the reference glasses were determined by the *K*-edge XANES analysis. The blue color of the antique glass can be reproduced in a laboratory glass on the basis of composition and melting conditions. Copyright © 2015 John Wiley & Sons, Ltd.

Introduction

The art of mosaic glass mirror decoration is one of the ten major categories of traditional Thai crafts.^[1–3] In the original style, a geometric mosaic pattern is created. Small pieces of simple polygonal shapes are cut from mirror tiles and adhered to cover a surface using a black varnish made from native lacquer trees. This thin, translucent, colored, glass mirror, used in intricate patterns, is known in Thai as Kriab mirror. The optically brilliant mirroring is because of a lead-alloy coating on the back side of the glass.^[4] Total thickness of the mirror is typically less than 1 mm. Kriab mirror mosaics are commonly used in Buddhist and royal architectures, particularly in historical temples, palaces, and on antique royal utensils and paraphernalia. A few examples are shown in Fig. 1.

In this paper, we examine samples of blue Kriab mirror from the Temple of the Emerald Buddha in Bangkok, which is Thailand's most important and sacred temple. The temple is the site at which the Thai royal family performs religious ceremonies on major Buddhist holidays. It is also where major monarchical ceremonies, for example, the coronation of the king, is held. The glass samples were originally located in the Royal Pantheon, forming a part of the mosaic (shown in Fig. 1) decorating the base of commemorative statues of King Rama I, II, and III. The Royal Pantheon was built in 1856 during the reign of King Rama IV (1851–1868).^[5] The most significant evidence supporting the supposition that the Kriab mirror was made by Thai craftsmen of the Royal Glass Making Department in 19th century is a collection of eight archaic, handwritten logbooks dated to 1860–1861,^[6] in which legible information on raw materials and melting procedures are insufficient to reproduce the glass by modern glass makers. Knowledge of Kriab mirror production began to disappear when the Royal Glass Making

from the loss of significant numbers of mirror pieces as a result of degradation of the natural adhesive. Because the process to reproduce the original glass mirror was not preserved, commercial glass mirror was imported and used as substitute in the latest restoration beginning in 1982. Compared with the original Kriab mirror, the modern glass mirror is thicker, differently colored, and more reflective than the original glass mirror. Thailand's Bureau of the Royal Household aims to improve future restoration by using mosaic mirrors that more closely resemble the original materials. The objectives of this study are to understand the origin of the blue color in the antique glass and to identify the composition of the glass. This information will be used in the future

Department was terminated in late 19th century.^[3] Over the follow-

ing century, most of the mosaics in the temple complex suffered

- * Correspondence to: Wantana Klysubun, Synchrotron Light Research Institute, 111 University Ave., Muang, Nakhon Ratchasima 30000, Thailand. E-mail: wantana@slri.or.th
- [†] Presented at the European X-Ray Spectrometry Conference, Bologna, Italy, 15–20 June 2014.
- a Synchrotron Light Research Institute, 111 University Ave., Muang, Nakhon Ratchasima 30000, Thailand
- b Karl-Franzens-Universtät Graz, Graz 8010, Austria
- c National Institute of Standards and Technology, Gaithersburg, MD 20899, USA
- d Shanghai Synchrotron Radiation Facility, Shanghai Institute of Applied Physics, Chinese Academy of Sciences, 239 Zhangheng Road, Pudong, Shanghai 201204, China



Figure 1. Antique mirror mosaics in the Temple of the Emerald Buddha on the base of the Kings' statues at the Royal Pantheon (left), on a pillar at the Royal Chapel (middle), and modern mirror mosaics on a pillar at the Royal Chapel after the restoration (right).

renovations to produce glass more faithful to the original. We employed multiple analytical techniques to investigate the original blue glasses. Major and minor elements in the glass were quantified by scanning electron microscopy (SEM) coupled with energy-dispersive and wavelength-dispersive spectrometry (EDX and WDX) while trace elements, requiring lower detection limits, were quantified by laser ablation inductively coupled plasma mass spectroscopy (LA-ICP-MS). In addition, the metallic layer coated on the back side of the antique glass was probed to search for lead and other constituents.

Ligand field theory predicts the color induced by a transition metal ion coordinated with oxygen neighbors, explaining the most common coloring mechanisms in silicate glasses.^[7–9] The splitting of degenerate energy levels of d electrons in a transition metal ion is caused by the electric field of the oxygen ligands. The difference of electronic energy between a ground state d level and excited state d levels depends on the coordination geometry and the oxidation number of the metal ion. The electronic d-d transitions occur under relaxed selection rules resulting in selective absorption of specific wavelengths in the visible region. This gives rise to the appearance of colors in glasses. Optical spectroscopy is used to identify coloring ions in glasses by studying absorption bands of the electronic d-d transitions.^[10,11] For examples, Co²⁺ ions in a tetrahedral coordination, Fe²⁺ ions in an octahedral coordination, and Cu²⁺ ions in an octahedral coordination all impart blue colors of different hues and intensities. Mn³⁺ ions in an octahedral coordination account for the purple color. Tetrahedral Fe³⁺ ions generate green-yellow color whereas tetrahedral Mn²⁺ ions generate pale yellow-orange color. The d-d transition does not occur for the empty d shells of Ti4+ ions and the filled d shells of Cu¹⁺ ions; therefore, these ions do not colorize glasses. It should be noted that the shade of a particular color gets darker with higher concentration of the coloring ions and increased thickness of the glass.

We used optical spectroscopy to understand the color contributions from several transition metals found in the antique glass. Interpretation of optical data is complicate because of combined optical absorption from several ionic species. Thus, the elemental selectivity of X-ray near edge absorption spectroscopy (XANES)^[12,13] was used to distinguish the speciation of transition metal ions in mixed valent states. Electronic transitions from a core level (for example, 1s or 2p) to valent states result in characteristic absorption number of the probed ions. Coordination geometry can also be deduced from XANES spectra.^[14,15] Finally, we synthesized series of glasses on the basis of the chemical composition of the original blue glasses. The remade glasses were used as references for a comparative study on coloration.



Figure 2. Photographs of the antique blue glasses (B1 and B2) and reference glasses (R1–R6 and S1–S3) used in this study.

Materials and methods

Antique samples

Two samples of the antique blue glass mirror from the Royal Pantheon, shown in Fig. 2, were studied. Sample B1 was originally cut in a diamond shape, and sample B2 was originally cut in a triangular shape. Because there is insufficient quantity of the reflective materials on the samples B1 and B2 to be analyzed by our instruments, the metallic coating from green and yellow glass mirrors that were collected from the same mosaic were studied instead.

Compositional analysis

Small pieces of the antique glass samples were cut and mounted in resin (Technovit 5071) for compositional analysis. The resinembedded sample was polished and cleaned in an ultrasonic bath of deionized water. Reflective materials were removed from the yellow glass and the green glass mirrors, cut perpendicular to the coating layer, and used for compositional analysis.

Concentrations of major elements expressed as simple oxides, including SiO₂, TiO₂, Al₂O₃, FeO, MnO, MgO, CaO, PbO, Na₂O, and K₂O, were determined by a JEOL 6310 SEM equipped with an Oxford EDX and a Microspec WDX spectrometer at the Institute of Earth Sciences, University of Graz, Austria. Samples were coated with carbon, and a conductive film was used to make electrical contact with an aluminum sample holder. Analytical conditions were set to 15 kV accelerating high voltage and a sample current of 6 nA. A defocused beam (about $6 \times 10 \,\mu\text{m}$ spot size) was used to minimize the loss of volatile elements such as sodium. Lead and sodium were analyzed by the WDX spectrometer, which has a typical detection limit of 0.05 wt%. All other major elements were analyzed by the EDX spectrometer with a detection limit of 0.1 to 0.15 wt%. Natural mineral standards and the BCR-2G glass from the USGS^[16] were used for standardization: Si (Swarovski lead glass), Ti, Ca (titanite), Al, K (adularia), Fe (BCR-2G), Mn (rhodonite), Mg (BCR-2G), Na (jadeite), and Pb (Swarovski lead glass). The BCR-2G reference material was analyzed for quality control at the beginning, in the middle, and at the end of the measurements of the glass samples. Major elements could be reproduced within certified values. The results of EDX-WDX SEM analysis are shown in Table 1. The totals of the oxide components do not sum to 100 wt%. The low totals are likely related either to H₂O content in the glass, elements not analyzed (e.g. halogenides and sulfur), or to a loss of Na during analyses despite the low current and defocused beam that were used. The uncertainties of the oxide concentrations were determined from the standard deviation of 3 to 8 measurements at different spots on the sample.

Concentrations of trace elements in the glasses were analyzed with a LA-ICP-MS system (laser ablation unit: ESI NWR 193; ICP-MS: Agilent 7500) at the Central Lab for Water, Minerals and Rocks, NAWI Graz, Karl-Franzens-University Graz, and Graz University of

Table 1. Means and standard deviations of elemental concentrations
determined by SEM EDX/WDX, expressed as wt% oxides

	B1	B2	R1	R2	R3		
SiO ₂	52.1 ± 0.9	53.7 ± 0.2	57.8 ± 2.3	63.2 ± 3.0	62.5 ± 0.7		
AI_2O_3	1.6 ± 0.1	1.4 ± 0.1	5.5 ± 4.7	2.3 ± 0.8	1.9 ± 0.2		
TiO ₂	<0.1	<0.1	<0.1	<0.1	<0.1		
FeO	0.7 ± 0.1	1.3 ± 0.1	0.8 ± 0.2	<0.1	0.9 ± 0.0		
MnO	0.1 ± 0.0	0.1 ± 0.1	0.2 ± 0.1	<0.1	0.2 ± 0.1		
MgO	0.3 ± 0.4	0.3 ± 0.1	0.3 ± 0.1	0.4 ± 0.0	0.5 ± 0.0		
PbO	27.6 ± 1.2	25.9 ± 1.2	23.4 ± 2.5	24.2 ± 1.9	22.5 ± 0.4		
CaO	5.6 ± 0.2	5.7 ± 0.1	5.2 ± 0.5	4.4 ± 0.2	5.1 ± 0.1		
Na ₂ O	6.6 ± 0.1	6.7 ± 0.1	4.8 ± 0.3	4.5 ± 0.2	4.5 ± 0.1		
K ₂ O	1.4 ± 0.1	1.2 ± 0.1	1.2 ± 0.3	1.3 ± 0.1	1.3 ± 0.0		
P_2O_5	ND	ND	0.3 ± 0.1	0.3 ± 0.1	0.3 ± 0.1		
Sum	96.0	96.3	99.5	100.6	99.7		
ND, not detected.							

Technology, Austria. The material was ablated with a 193 nm laser pulsed at 9 Hz. The laser beam spot size was 75 μ m, and the energy density was 6.5 J/cm². Helium was used as the carrier gas at 0.8 l/min flow, and data were acquired in time-resolved mode. For each analysis, a gas blank was obtained for background correction. The laser was active for 60 s followed by 50 s washout time. To get rid of possible surface contamination, the first few seconds from the laser ablation signal, when the topmost surface is ablated, is excluded from quantification. The standard glass NIST610^[17] was routinely analyzed for standardization and drift correction while standards NIST612,^[17] NIST614, and BCR-2^[18] were analyzed as unknowns to monitor the accuracy of the measurements. All standards could be reproduced to within ±10% of the certified

Table 2. Means and standard deviations of elemental concentrations determined by LA-ICP-MS, expressed as mg/kg oxides							
	B1	B2	R1	R2	R3		
TiO ₂	562 ± 17	538 ± 5	116±6	119±6	115 ± 4		
V_2O_5	18 ± 1	22 ± 0	2 ± 0	2 ± 0	2 ± 0		
Cr_2O_3	40 ± 1	43 ± 0	3 ± 0	2 ± 0	2 ± 0		
MnO	1303 ± 25	1147 ± 13	2872 ± 59	16 ± 0	2320 ± 73		
CoO	1472 ± 33	1186 ± 28	1524 ± 86	1 ± 0	1476 ± 70		
NiO	39 ± 1	36 ± 0	:0 3±0 1:		2 ± 0		
CuO	709 ± 13	739 ± 6	1310 ± 42	11 ± 1	1234 ± 36		
ZnO	512 ± 9	365 ± 7	779 ± 6	705 ± 42	366 ± 10		
As_2O_3	646 ± 16	535 ± 20	722 ± 13	879 ± 77	4 ± 0		
Rb ₂ O	41 ± 1	33 ± 1	12 ± 0	9±1	10 ± 0		
SrO	118 ± 4	100 ± 1	32 ± 2	26 ± 3	24 ± 1		
ZrO ₂	40 ± 2	51 ± 2	80 ± 1	53 ± 3	83 ± 5		
Ag ₂ O	9 ± 0	11 ± 0	ND	ND	ND		
CdO	12 ± 0	24 ± 0	ND	ND	ND		
SnO ₂	834 ± 17	1328 ± 44	1041 ± 7	1103 ± 56	3 ± 0		
Sb_2O_3	231 ± 3	317 ± 2	475 ± 7	387 ± 15	1 ± 0		
BaO	790 ± 38	812 ± 16	1172 ± 75	1268 ± 149	17 ± 0		
CeO ₂	10 ± 0	12 ± 0	5 ± 0	3 ± 0	3 ± 0		
Bi ₂ O ₃	9 ± 0	11 ± 0	ND	ND	ND		
UO ₂	14 ± 0	12 ± 0	ND	ND	ND		
ND, not detected.							

values. Silicon was used as an internal standard. The results of LA-ICP-MS analysis are shown in Table 2. The uncertainties of the oxide concentrations were determined from the standard deviation of 3 to 8 measurements at different spots on the sample.

Glass synthesis

Reference glasses were prepared from 60 g batches using the recipes shown in Table 3, in which common oxides, sodium carbonate as a source of Na₂O, potassium carbonate as a source of K₂O, and silica were used as reagents. The quantity of silica was adjusted to yield a total mass fraction of 100%. All batches were melted in ceramic crucibles at 1450 °C for 3 h. The ramping rate from room temperature was 10 °C/min. To quench, molten glass was poured on a steel plate and pressed to form a thin slab (about 1.5–2.5 mm thick). These glass slabs were annealed afterward at 500 °C for 5 h to reduce crack and shatter.

The remade glasses shown in Fig. 2 are divided into two series, named R and S. In the R series, their major oxide components were prepared with mass fractions comparable to those of the original blue glasses. To study coloring effects of cobalt, copper, iron, and manganese in the antique glasses, individual colorants (CoO, CuO, Fe₂O₃, or MnO) and combinations were selectively added to the glass batches. The S series glasses were synthesized to study the influence of lead on color given by copper oxide. Glasses R1–R3 were analyzed by SEM-EDX/WDX and LA-ICP-MS to examine possible loss of the constituents and contamination from our glass making process. These results are shown in Tables 1 and 2. In general, the analyzed composition agrees with the batch composition, except for alumina, which is 0.4-4.0 wt% higher than the guantity used in the glass batch; magnesium (0.3–0.5 wt% MgO) and phosphorous (0.3 wt% P_2O_5), neither of which were deliberately added; and lead, which loses 0.8-2.5 wt% PbO. In addition, contamination at the level of 0.04-0.05 wt% CuO and 0.01-0.02 wt% ZnO was observed.

X-ray absorption near edge spectroscopy

For the antique glass samples and the reference glasses in the series R, XANES spectra at the *K*-edges of Co, Fe, Mn, and Cu were measured in fluorescence mode at beamline BL8,^[19] Synchrotron Light Research Institute, Thailand. The synchrotron beam was monochromatized using a double crystal monochromator (DCM) equipped with Ge(220) crystals. The beam size at the sample was 10 mm (width) × 1 mm (height). Incident beam intensity and fluorescence signals were recorded by an ionization chamber (filled with mixed N₂ and He gases) and a 13-element germanium detector, respectively. Standard metal foils were used for photon energy calibration with uncertainty of 0.2 eV. Common oxides were also measured as references.

Cu K-edge XANES spectra of the reference glasses in the series B were measured at the National Institute of Standards and Technology beamline X23A2 located at National Synchrotron Light Source, USA. The synchrotron beam was monochromatized using a Si(311) Golovchenko–Cowan DCM.^[20] A flat, Rh-coated mirror was used for harmonic rejection. The incident beam and fluorescence signals were recorded using an N₂-filled ionization chamber and a four-element silicon drift detector, respectively.

All of the XANES spectra were averaged from 3 to 11 scans. The averaged spectra were baseline subtracted and normalized using the software Athena.^[21]

Table 3. Batch compositions of the reference glasses, expressed as wt% oxides									
	R1	R2	R3	R4	R5	R6	S1	S2	S3
	Blue	Clear	Blue	Clear	Light yellow	Violet-blue	Green-blue	Green	Light blue
SiO ₂	58.20	59.70	58.60	59.60	58.50	59.50	59.10	39.10	76.70
Na ₂ O	6.60	6.60	6.60	6.60	6.60	6.60	6.60	6.60	14.00
CaO	5.50	5.50	5.50	5.50	5.50	5.50	5.50	5.50	5.50
K ₂ O	1.30	1.30	1.30	1.30	1.30	1.30	1.30	1.30	1.30
AI_2O_3	1.50	1.50	1.50	1.50	1.50	1.50	1.50	1.50	1.50
PbO	25.00	25.00	25.00	25.00	25.00	25.00	25.00	45.00	0
MnO	0.24	0	0.24	0	0.24	0	0	0	0
Fe_2O_3	1.00	0	1.00	0	1.00	0	0	0	0
CoO	0.18	0	0.18	0	0	0.18	0	0	0
CuO	0.08	0	0.08	0.08	0	0	1.00	1.00	1.00
ZnO	0.06	0.06	0	0.06	0.06	0.06	0	0	0
As_2O_3	0.08	0.08	0	0.08	0.08	0.08	0	0	0
SnO ₂	0.10	0.10	0	0.10	0.10	0.10	0	0	0
Sb_2O_3	0.04	0.04	0	0.04	0.04	0.04	0	0	0
BaO	0.11	0.11	0	0.11	0.11	0.11	0	0	0

Optical spectroscopy

All glass samples were prepared as thin slabs by polishing to the desired thicknesses. The reference glasses in series S are 1 mm thick. For comparing absolute absorbance, the antique glass B1 and the reference glasses in series R are all 0.4 mm thick. Optical absorption spectra were recorded on a UV-Visible spectrometer (Agilent Cary 300) in transmission mode from 190 to 900 nm. The absorbance A is defined as log (1/T), where T is the ratio of the transmitted intensity to the incident intensity.^[22] Because the incident beam size ($8 \times 1 \text{ mm}$) is larger than all sample sizes, a mask with a 5 mm diameter circular opening was placed in the center of the beam in front of the sample. For all of the measurements, a blank mask was used to record the incident beam intensity whereas a stopper was used to record the background signal subtracting from both the incident and the transmitted intensity.

Results and discussion

Antique blue glasses

As shown in Table 1, the antique glass B1 is identified as lead glass with 52.1% SiO₂, 27.6% PbO, 6.6% Na₂O, and 5.6% CaO (all percentages reported here are wt% if not noted otherwise). The glass B2 has similar composition as B1. Lead has been used as substitute for Na₂O and CaO in otherwise soda lime glasses, which is typically characterized by 74% SiO₂, 13% Na₂O, and 11% CaO.^[23] The earliest examples for lead-silicate glasses, dating to between the second and the eighth century are found in Southeast Asia, particularly in China, Japan, and Korea.^[24] Lead silicate glasses have been luxury products in the West since the early 17th century after the patent on 'crystal glasses' by George Ravenscroft in England.^[25] Crystal-like appearance arises from the increase of refractive index from 1.51 in ordinary glasses to 1.54 with 8% PbO.^[26] Lead in the Thai blue glasses of the 19th century was likely used for the same reason. Heavy elements, such as barium and zinc,^[27] can also increase the refractive index of silicate glass, but they are present in the glasses B1 and B2 at trace levels, less than 0.1 wt% oxides. Lead crystal glasses were one of major products from local glassmakers for the temple as they produced not only the blue glasses but also yellow and red glasses, which have 16 and 45 wt% PbO, respectively.^[4,15] Aluminum oxide in the blue glasses is comparable to the typical 1.7% in modern soda lime glasses.^[23] The presence of alumina benefits the antique glasses to be more durable during indoor weathering of over a century; visual inspection shows no crizzling or opacification and only a small degree of corrosion.

All of the 3d transition elements, except scandium, were detected in our blue glasses. Therefore, any of these transition elements may contribute to the blue color of the Thai glasses. Iron is found at the highest concentration, 0.7% FeO in B1 and 1.3% in B2. Earlier experiments found that the addition of iron oxide in a soda lime glass could result in blue and green colors through the control of reduction–oxidation equilibrium of Fe²⁺ and Fe³⁺ by control of composition and melting conditions.^[10,11] Manganese was detected at 0.13% in B1 and 0.12% in B2. Manganese oxide is commonly used to make purple glasses.^[8,11] On the other hand, it has been used since the second century to make colorless glasses by removing the pale greenish color from low levels of iron impurities.^[28] A redox reaction between iron and manganese in the Thai blue glasses is expected to contribute a light yellow color, as shown in the reference glass R5.

Cobalt was detected at 0.15% CoO in B1 and 0.12% in B2. The presence of cobalt in our antique glasses was predicted because this element has been widely used to produce the famous deep 'cobalt blue' color in glasses since the Bronze Age.^[24] However, the blue color in the antique glasses is noticeably different from the blue imparted by cobalt in the reference glass R6, which appears a bit more violet. Copper was detected at 0.07% CuO in B1 and B2. Copper oxide was identified as blue and turquoise colorants in Bronze Age glasses.^[24] On the other hand, the famous 'copper ruby' red color can be achieved via a different mechanism, that is, the formation of copper in the antique glasses is low, we assert that it does not contribute significantly to their coloration. The reference glass R4, doped with 0.08% CuO, is nearly colorless.

Titanium is found in the ancient glasses at 0.06% TiO₂. If it is present as Ti^{3+} , it may impart violet–purple color.^[9] However, its coloring effect, like that of copper, is barely observable because of the very low concentration. Chromium, nickel, and vanadium are present at very trace levels, less than 0.05% in oxides; thus, these elements are also not expected to affect the blue color in the antique glasses.

The heavy elements mostly found in B1 and B2 are tin (0.08–0.13% SnO₂), arsenic (0.05–0.07% As₂O₃), and antimony (0.02–0.03% Sb₂O₃). All of them are reducing agents in glasses that can chemically react with coloring metal ions.^[30,31] Antimony is the most efficient to remove colors from Cu²⁺ and Mn³⁺ contaminants by reducing them to colorless or weak coloring chemical states, i.e. Cu¹⁺ and Mn^{2+.[31]} The reducing effects of tin, arsenic, and antimony will be further discussed in the next section.

The EDX/WDX analysis shows that metallic compounds used as reflective coating are 94.8% Pb-3.0% Sn-2.2% Sb in one sample and 48.8% Pb-50.3% Sn-0.9% Sb in the other sample.

XANES interpretation

For a given X-ray absorbing element, absorption fine features near the threshold or the edge observed in a XANES spectrum are sensitive to its valence state (oxidation number), type of neighboring atoms, and local coordination geometry. XANES has been effectively used not only to identify chemical species but also to quantitatively analyze valence and local geometry. We applied XANES to gain information on the valence and ligand geometry of transition metal ions in our glasses. The fact that XANES probes every single metal ion makes it a suitable complementary technique for studying colorless or weak coloring ions, which are undetectable by optical spectroscopy. XANES analysis in this section was performed on the basis of edge-energy position, which increases proportionally with the oxidation number.^[12,13] The edge position of a XANES spectrum is defined as the maximum peak position of its first derivative spectrum. XANES data of the antique glass B1 and B2 are identical within the statistical errors; thus, the following discussion applies to both of them.

Co K-edge XANES spectra of the antique glass B1 and reference glass R6 are shown in Fig. 3. They have similar absorption features. The reference glasses R1 and R3 were also measured but not shown in Fig. 3, as they are nearly identical to the B1 and R6 spectra. The edge position appears at 7716.7 ± 0.3 eV, which is 0.1 eV lower than that of divalent cobalt in CoO. Thus, cobalt ions in these glasses are divalent. The pre-edge peak (7708.7 ± 0.2 eV) is much higher in the glasses than in CoO. The Co²⁺ ions in CoO are octahedrally bonded with oxygen ions whereas in Co₃O₄, one third of cobalt is divalent ions in octahedral symmetry and two third is trivalent ions in

tetrahedral symmetry. For a 3d transition element, the pre-edge peak arises from the 1s to 3d transitions that are forbidden in octahedral symmetry by the dipole selection rule; however, it can occur at very low probability as a result of its quadrupole character. None-theless, the dipole selection rule is relaxed in tetrahedral symmetry as a result of significant hybridization of the 3d and 4p levels, giving rise to an enhanced pre-edge peak.^[32] Thus, the pronounced pre-edge peak seen in the B1 and R6 spectra suggests that the Co²⁺ ions in the lead glasses are in a tetrahedral geometry. The similarity between Co *K*-edge XANES spectra of the R6 glass, in which only cobalt was added, and those of B1, R1, and R3 glasses, which have the other colorants (Fe, Mn, and Cu) and reducing agents (Sn, As, and Sb) indicates that the divalent cobalt ions in the lead glasses are stable and thus are not involved in redox reactions with those other coloring and reducing elements.

Fe K-edge XANES spectra of the ancient glass B1 and reference glass R5 are shown in Fig. 4. The edge position $(7123.4 \pm 0.3 \text{ eV})$ observed in the B1 spectrum is the same as in the Fe₂O₃ spectrum, indicating that Fe ions in the glass B1 is trivalent. Compared with the B1 spectrum, the R5 spectrum is similar, but its edge is 0.9 ± 0.3 eV lower than the Fe_2O_3 edge and $2.7 \pm 0.4 \text{ eV}$ higher than the FeO edge, suggesting that a mixture of Fe²⁺ and Fe³⁺ ions is present in the glass R5. Using a linear relationship between the edge position and oxidation number observed in the standard iron oxides, the Fe^{2+}/Fe^{3+} ratio in the glass R5 is 0.25 ± 0.08 . The prominent pre-edge peak, at about 7114.6 ± 0.2 eV, is attributed to the enhanced 1s to 3d transitions of the Fe³⁺ ions in a tetrahedral geometry. Coordination numbers of between 2.7 and 4.1 were reported for lead glasses containing 15 wt% PbO.^[4,33] Although the reducing agents (Sn, As, and Sb oxides) were added in R1, but not in R3, the same Fe²⁺/Fe³⁺ ratio is observed. Therefore, the reduction of iron in the reference glasses likely results from the firing atmosphere in the closed electrical furnace where oxidation condition is not be fully attained. In contrast, the oxidation of iron in the antique glass implies that the firing was performed in an excess of oxygen.

Mn K-edge XANES spectra of the antique glass B1 and reference glass R5 are shown in Fig. 5. These two spectra and those of the reference glasses R1 and R3 are identical. The edge position is $2.0 \pm 0.3 \text{ eV}$ above the MnO edge and $5.7 \pm 0.4 \text{ eV}$ below the Mn₂O₃ edge, suggesting the Mn²⁺/Mn³⁺ ratio of 0.74 ± 0.06 . Tetrahedral coordination of Mn²⁺ is confirmed by the



Figure 3. Co K-edge XANES spectra of the antique glass B1, reference glass R6, and cobalt standards (Co metal, CoO, and Co_3O_4).



Figure 4. Fe K-edge XANES spectra of the antique glass B1, reference glass R5, and iron standards (Fe metal, FeO, and Fe_2O_3).



Figure 5. Mn K-edge XANES spectra of the antique glass B1, reference glass R5, and manganese standards (Mn mesh, MnO, and Mn_2O_3).

pronounced pre-edge peak seen in the glass data. Coordination numbers of 3.2 and 3.6 were previously reported for the soda lime and lead glasses.^[4] The analyzed redox ratios of manganese and iron in the glasses lead to a conclusion that Fe³⁺ imparts light yellow color, exhibited by the reference glass R5, to the cobalt blue color in the Thai glasses.

Cu *K*-edge XANES spectra of the antique glass B1 and reference glass R3 are shown in Fig. 6. They show distinct absorption edge peaks at about 8983.4 eV, which are 1.4 eV higher than that of the Cu₂O standard, and their amplitudes are much larger. The edge peak of Cu₂O arises from the 1s to 4p transitions,^[34] which is a characteristic of the monovalent copper ions in the cuprite structure and often used as indicative of the colorless Cu¹⁺ ions in glasses.^[14,15,35,36] The observed peak shift and intensification suggests that the local atomic environment of Cu¹⁺ in the glass is different from that of Cu₂O in which a copper ion bonded with a linear pair of oxygen ions. The difference of the absorption features is also expected between the Cu²⁺ in glass and in CuO where the former is expected to be in octahedral symmetry by the ligand field coloration, but the latter is in square planar geometry. This



Figure 6. Cu *K*-edge XANES spectra of the antique glass B1, reference glass R3, and copper standards (Cu metal, Cu₂O, and CuO). The fit curve is discussed in the text.

ambiguity precludes the quantification of ionic species on the basis of edge position of standard copper (I) and (II) oxides. Using an alternative deduction, the B1 spectrum is fit to a linear combination of R3 and CuO; the best fit R3: CuO ratio is 0.70 ± 0.01 corresponding to the fit curve shown in Fig. 6. Therefore, we conclude that the redox ratio of Cu¹⁺/Cu²⁺ in the antique glass is lower than in the reference glass and that the monovalent copper is dominant. Because the reference glass R4, representing the color contribution of copper (0.08 wt% CuO) in the antique glasses, is nearly colorless, the blue color as a result of Cu²⁺ ions in the antique glasses would be negligible at this very low concentration.

To clearly observe the coloration of the Cu^{2+} species, we increase the batch concentration to 1.0 wt% CuO in the glasses S1, S2, and S3. As a result, turquoise color is created in the glass S1 containing 25 wt% PbO. When increasing the lead content to 45 wt% PbO, the intense green color develops in the glass S2. Interestingly, without lead, the soda lime glass S3 is light blue. Therefore, lead significantly controls the coloration of oxidized copper ions. More reference glasses were synthesized to study influence of lead on cobalt, iron, and manganese colorants, but their d-d transition colors are not significantly altered. Figure 7 shows Cu *K*-edge XANES spectra of the glasses S1, S2, and S3. Increasing the lead concentration, the Cu¹⁺ peak is suppressed and remains as a mere step, as seen in the glass S3. This result indicates that lead promotes Cu²⁺ speciation in the glass.

Optical absorbance

Absorbance spectra of the antique glass B1 and the reference glasses R2–R6 are shown in Fig. 8. In the glasses (B1, R3, and R6) containing Co^{2+} ions, strong absorption peaks are observed at about 648, 595, and 530 nm as a result of the d-d transition of Co^{2+} in tetrahedral geometry. The triple peaks are assigned to the A₂ to T₁ transition that splits because of the spin-orbital momentum coupling.^[10] The glasses B1, R3, and R5 show very weak absorption, which appears as a small shoulder at about 380 nm. This peak corresponds to one of the triple A₂ to T₁ transitions of Fe³⁺ in tetrahedral geometry.^[10,37] The other two weaker transitions (435 and 555 nm) cannot be observed in our studied glasses. These weak transitions were previously observed in 85SiO₂–15Na₂O (in mol%)



Figure 7. Cu K-edge XANES spectra of the reference glasses S1–S3 and copper standards (Cu₂O and CuO).



Figure 8. Optical absorbance spectra of the antique glass B1 and reference glasses R2–R6.

glass doped with 5000 ppm Fe^[37] and 74SiO₂-16Na₂O-10CaO (in mol%) doped with 2.5 wt% Fe₂O₃.^[10] The presence of iron in the Thai blue glass B1 and the reference glass R3, albeit at low concentration (0.7–0.9 wt% FeO), contributes optical absorption in the violet region. This contribution is consistent with the absorbance of the glass R5 and thus corresponds to the light yellow color. The molar extinction coefficient of Mn²⁺ in tetrahedral symmetry is about one order of magnitude lower than that of Fe³⁺; therefore, the Mn²⁺ d-d transitions at 420 nm^[10] are hardly seen in the R5 optical spectrum. In addition, the absorbance spectra of the glasses R2 and R4 suggest that trace copper and other constituents in the glass absorb almost equally at all wavelengths. Thus, their optical contributions simply reduce overall transparency of the glasses.

A broad absorption band as a result of copper ions is clearly seen in the glasses S1–S3 doped with 1.0 wt% CuO as shown in Fig. 9. The absorption band maxima are at 765 nm for the turquoise glass S1 with 25 wt% PbO and the light blue glass S3 without PbO. In a light blue soda lime glass doped with 0.3 wt% CuO, similar absorption band is observed at 800 nm and assigned to the singlet E_g-T_g



Figure 9. Optical absorbance spectra of the reference glasses S1, S2, and S3.

transition of Cu^{2+} in distorted octahedral symmetry.^[10,38] When the lead content is increased to 45 wt% PbO as in the glass S2, the absorption band is shifted to lower wavelength (720 nm). The green color develops as the near-UV absorption extends from 300 to 400 nm. This is unusual for the Cu^{2+} d-d transition; further investigation is needed to understand this phenomenon.

Conclusion

Two samples of the original blue glass produced in the middle 19th century, which has been inlaid as decorative mosaics at the Temple of the Emerald Buddha in Bangkok, Thailand, were quantitatively analyzed and identified as a type of lead glass with a composition of 53SiO₂-27PbO-6.7Na₂O-5.7CaO in wt%. The 3d transition elements detected by the SEM-EDX/WDX and LA-ICP-MS instruments include iron (0.7–1.3 wt% FeO), manganese (0.1 wt% MnO), cobalt (0.12–0.15 %wt), and copper (0.07 wt% CuO). Coloration by the d-d transitions of these elements in soda lime glass have been extensively studied by optical spectroscopy and X-ray absorption fine structure spectroscopy but not for lead glasses.

The XANES results reveal a single oxidation state of Co²⁺ in the original glass that produces the primary blue color. This blue color is modeled by the reference glass R6 doped with cobalt oxide as shown in Fig. 2. The tetrahedral geometry of the divalent cobalt is identified by the enhanced pre-edge peak in the XANES data and by the strong triple A_2 to T_1 transitions seen in the optical absorption data. A single oxidation state of Fe³⁺ and mixed oxidation states of Mn²⁺ and Mn³⁺ at the Mn²⁺/Mn³⁺ratio of 0.74 are identified in the original glass. The Fe³⁺ ions impart light yellow color as shown in the reference glass R5. This secondary yellow color, albeit at low intensity, significantly contributes to the final blue color of the original glass distinguished from the blue color commonly seen in the cobalt-doped modern glasses. The A₂ to T₁ transition of Fe³⁺ was observed in the near UV region at 380 nm. The very low concentrations of Cu²⁺ and Mn³⁺ in the antique glass preclude observation of their d-d transitions through optical spectroscopy. Although the concentration of Mn²⁺ is not low, the Mn²⁺ d-d transition is not observed in the optical data as a result of its relatively small extinction coefficient. In contrast, the XANES technique demonstrates its exceptional sensitivity by its ability to detect, at 0.07 wt% CuO, a mixed valent states of colorless Cu^{1+} and Cu^{2+} ions; the monovalent copper is dominant in the antique glass. We also investigated the effect of lead content to the blue color of Cu²⁺ ions in silicate glass and found that the initial blue color can be changed to turguoise and green with the increase of lead content to 25 and 45 wt% PbO, respectively. The increase of lead results in a blue shift of the $Cu^{2+} A_2 - T_1$ absorption band and the increase of absorption in near UV region (300-400 nm).

As final remarks, the recipe of glass R3 and melting conditions for an electrical furnace were successfully developed; the blue color of the remade glass and the original glass is nearly identical. We have demonstrated the chemical and structural similarities. From this work, we have formulated the recipe for glass sample R3 as a candidate for future restorations at the Temple.

Acknowledgements

With assistance from Prof. Jong-orn Berananda, samples of Kriab mirror from the Temple of the Emerald Buddha were provided by Thailand's Bureau of the Royal Household under the permission of Her Royal Highness Maha Chakri Sirindhorn. This work was funded by Synchrotron Light Research Institute and the Twentieth Session of China-Thailand Joint Committee on Science and Technology Cooperation (20-628J). Lihua Wang at Shanghai Synchrotron Radiation Facility, Onsulang Sophiphun at Suranaree University of Technology, and Supanun Lapboonrueng at Synchrotron Light Research Institute are thanked for their experimental assistance. Use of the National Synchrotron Light Source, Brookhaven National Laboratory, was supported by the US Department of Energy, Office of Science, Office of Basic Energy Sciences, under Contract No. DE-AC02-98CH10886. The silica reagent used in this study was provided free of charge by Natural Sand Glass Co., LTD (Rayong, Thailand).

References

- B. Srikanok, P. Kongpokanun, *Chang Sip Mu*, Amarin Printing and Publishing, Bangkok, **2006**.
- [2] W. Udomkulyaruk, S. Dhumrikul, S. Hothong, Moradok Chang Sin Thai, Starprint, Bangkok, 1999.
- [3] S. Boonrod, Buddhasin Rattanakosin, Wattana, Bangkok, 1983.
- [4] W. Klysubun, B. Ravel, P. Klysubun, P. Sombunchoo, W. Deenan. Appl. Phys. A 2013, 111, 775.
- [5] S. Diskul, *History of the Temple of the Emerald Buddha*, the Bureau of the Royal Household, Bangkok, **1992**.
- [6] Pramoch, Tumra Hung Kra Jok, Ancient Manuscript Division, National Library of Thailand, 1860.
- [7] A. Paul, Chemistry of Glass, Chapman and Hall, London, 1982.
- [8] K. Nassau, *The Physics and Chemistry of Color*, Wiley, New York, **2001**.
- [9] A. K. Varshneya, Fundamentals of Inorganic Glasses, Academic Press, California, 1994.
- [10] D. Möncke, M. Papageorgiou, A. Winterstein-Beckmann, N. Zacharias. J. Archaeol. Sci. 2014, 46, 23.
- [11] P. F. Schofield, G. Cressey, P. Wren Howard, C. M. B. Henderson. Glass Technol. 1995, 36, 89.
- [12] G. Bunker, Introduction to XAFS: A Practical Guide to X-Ray Absorption Fine Structure Spectroscopy, Cambridge University Press, Cambridge, 2010.
- [13] S. Calvin, XAFS for Everyone, CRC Press, Florida, 2013.

- [14] W. Klysubun, Y. Thongkam, S. Pongkrapan, K. Won-in, J. T-Thienprasert, P. Dararutana. Anal. Bioanal. Chem. 2011, 399, 3033.
- [15] B. Ravel, G. L. Carr, C. A. Hauzenberger, W. Klysubun, J. Cultural Heritage 2014, 10.1016/j.culher.2014.06.001
- [16] R. Wolf, S. Wilson, U.S. Geological Survey Fact Sheet 2007-3056, USGS Reference Materials Program, USGS, 2007.
- [17] N. J. Pearce, W. T. Perkins, J. A. Westgate, M. P. Gorton, S. E. Jackson, C. R. Neal, S. P. Chenery. *Geostand. Newsl.* **1997**, *21*, 115.
- [18] K. P. Jochum, M. Willbold, I. Raczek, B. Stoll, K. Herwig. Geostand. Geoanal. Res. 2005, 29, 285.
- [19] W. Klysubun, P. Sombunchoo, W. Deenan, C. Kongmark, J. Synchrotron. *Radiat.* 2012, 19, 930.
- [20] J. A. Golovchenko, R. A. Levesque, P. L. Cowan. Rev. Sci. Instrum. 1981, 52, 509.
- [21] B. Ravel, M. Newville, J. Synchrotron. Radiat. 2005, 12, 537.
- [22] M. Thomas, Ultraviolet and Visible Spectroscopy, John Wiley & Sons, New York, 1996.
- [23] J. E. Shelby, *Introduction to Glass Science and Technology*, The Royal Society of Chemistry, Cambridge, **2005**.
- [24] J. Henderson, *Ancient Glasses*, Cambridge University Press, Cambridge, **2013**.
- [25] K. Hellemans, A. Vincke, S. Cagno, D. Herremans, W. De Clercq, K. J. Janssens. J. Archaeol. Sci. 2014, 47, 121.
- [26] R. H. Doremus, Glass Science, John Wiley & Son, New York, 1994.
- [27] H. Scholze, Springer-Verlag, Glass, New York, 1991.
- [28] J. Henderson, Scientific Analysis in Archaeology and Its Interpretation, Oxbow Books, Oxford, 1989.
- [29] P. Colomban, J. Nano. Res. 2009, 8, 109.
- [30] Z. D. Xiang, M. Cable. Phys. Chem. Glasses 1997, 38, 167.
- [31] C. Stålhandske. Glasteknik Tidskrift 2000, 55, 65.
- [32] L. Galoisy, G. Calas, M. A. Arrio. Chem. Geol. 2001, 174, 307.
- [33] F. Pinakidou, M. Katsikini, P. Kavouras, F. Momninou, T. Karakostas, E. C. Paloura, J. Non-Crystalline. *Solids* 2008, 354, 105.
- [34] C. Maurizio, F. d'Acapito, M. Benfatto, S. Mobilio, E. Cattaruzza, F. Gonella, *Eur. Phys. J. B*, **2000**, *14*, 211.
- [35] I. Nakai, C. Numako, H. Hosono, K. Yamasaki. J. Am. Ceramic Soc. 1999, 82, 689.
- [36] A. Silvestri, S. Tonietto, F. D'Acapito, G. Molin, J. Cultural. Heritage 2012, 13, 137.
- [37] D. Ehrt, M. Leister, A. Matthai. Phys. Chem. Glasses 2001, 42, 231.
- [38] S. P. Singh, A. Kumar. J. Mat. Sci. **1995**, 30, 2999.