Elemental distribution of the greenish-Thai decorative glass

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Abstract. Glasses have been used in ornaments and decorations in Thailand for several hundred years, especially various colors of decorative glass which called Ancient Thai Glass (ATG) that made by Thais were found as architecture components of historical materials. Nowadays, the ATG has been almost broken and no products. Restoration with glass for conservation can be found with the modern imported glass (MIG) which bought from the market that brought from the foreign countries. However, it was shown that the colors of ATG were unchanged for hundreds of years, while as those of MIG were mostly changed within ten years. In this work, scanning electron microscope coupled with energy dispersive X-ray fluorescence spectrometer (SEM-EDX) was used to characterize the structure and composition of the greenish-ATG compared with those of MIG. It was found that the glass substrate of the ATG was lead-based glass, while as that of the MIG was soda-based one. It was revealed that the green coloration came from the Cu, Fe and Cr ions that doped into the glass matrix that confirmed with either the EDX or line scan. The results from this work are used as information that understanding the characteristics and how their production. X-ray fluorescence spectroscopy can be applied successfully in the historical glass study. It can be concluded that this technique can be applied successfully in the field of archaeology.

1. Introduction

Glasses have been used in ornaments and decorations in Thailand for several hundred years as seen by archaeological evidences, such as, decorative glass and glass beads discovered in regions throughout the country. Decorative glasses called Ancient Thai Glass (ATG) can generally be found as architectural components in places, such as, ancient palaces and Buddhist temples which have been center points among Thai commoners for centuries. Various colors of glass ranging from transparent to blue, green, red, and amber have been found. Under the tropical sun, it gives out an artistic harmony of flamboyance and serenity [1-4]. Figure 1 show an artifact decorated with 0.5-2.0 mm sheets of glasses coated with a thick reflecting metal film similar to an ancient glass mirror. As the glasses have kept deteriorating over time, restorations must be performed routinely to preserve these cultural crafts for later generations to appreciate. The most recent restoration work was done about 150 years ago.
However, presently there are no glass makers producing this type of glasses. At that time, they used conventional method which the melting was processed by adding small amount of colorant into the glass mixture. It was known that they were more shade of color from slightly to dark green. They may be produced at different factories and the use of chemically raw materials. However, it was possible that they were made in the same one, slight compositional differences between glass samples may be a result of variables in the glass production or the use of chemically similar raw materials with different batches [5-6]. Only modern, imported, difficult-to-cut glasses, called modern imported glass (MIG) with greater thickness and shorter lifetime are available in the market.

The previous studied using scanning electron microscopy and Raman spectroscopy confirmed that the ATG was lead-based glass and MIG was soda-based glass. It was also because of the presence of lead in the composition that made G-ATG samples color unchanged [4-7].

X-ray spectroscopy that is one of non-destructive techniques is widely used to study in archaeological science. Scanning electron microscope coupled with energy dispersive X-ray fluorescence spectrometer (SEM-EDX) is well-known as an appropriate technique for investigation of archaeological or historical objects. Scanning electron microscope (SEM) was used to analyze a line scan on cross-sections of samples. The elemental composition of the sample was characterized using energy dispersive X-ray fluorescence spectrometer (EDX) [8-10].

![Image](image.png)

**Figure 1.** The greenish-Thai decorative glass samples.

2. Experimental study

In this work, two greenish-Thai decorative glass samples namely G-ATG and G-MIG were used to analyze. They were collected to study because the green colored glass must be used for conservation and restoration the ancient cultural artifacts. The shade of color demanded was slightly green that could not buy in the market. Its property was less studied while other types of coloring glass were already studied [4-7 and 11-13].

The ATG sample was collected from the Bureau of the Royal Household at the Grand Palace (Bangkok), while the MIG one was bought from the market. They were coated with a thin layer of graphite to prevent charging of the sample surface prior to the scanning electron microscope observations.

The cross-sections were investigated using a Jeol JSM-6335F field emission scanning electron microscope (FESEM), operated at 15 kV. The compositional elements of these samples were analyzed using the Oxford Instrument INCAx-sight energy dispersive X-ray fluorescence spectrometer (EDX), operated with Si(Li) detector. Line scans were carried out with 20 runs each sample and at a live time of 100s for each run.

3. Results and discussion

Figure 2 showed the EDX line scan and concentration profiles in the samples. The scan over a line resulted information about the element relative distribution on the selected line. It was found that the
The glass substrate of the G-ATG sample was lead-based glass, while as that of the G-MIG one was soda-based glass. The line scan showed the compositions of the metal backing of G-ATG was contained with majority of Pb and minority of Al, Fe, Cu, Cr and Mn, while as that of G-MIG was Mg, Ti, Fe, Cr, Al and Cu. It was also showed that the green color was affected from Cu, Fe and Cr. The line scan indicated the same metallic ions. However, the previous and advanced studied found that the colors of the ATG was colorant melted together with glass, but those of the MIG was coloring mixture coated.

**Figure 2.** The line scans of the greenish-Thai decorative glass samples.
4. Conclusion

Scanning electron microscopy and X-ray fluorescence spectroscopy that are non-destructive methods were suitable to investigate the surface coating of Thai decorative glasses. Obtained images showed the morphological structure, while EDX analysis allowed details on compositions of both the glass substrate and the metal backing. It was revealed that the green coloration came from the Cu, Fe and Cr ions that doped into the glass matrix. It was confirmed either the EDX or line scan. It can be concluded that these equipment can be applied successfully in the field of archaeology.

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