

Introduction

Colored transparent and opaque glass was produced since the second millennium B.C in the Eastern Mediterranean, although the first vitreous colored materials date back to the 5th millennium B.C. Colored transparent glass was obtained by the addition of metal transition elements such as Co^{2+} , Cu^{2+} and Fe^{2+} to obtain blue, turquoise and green tinges, Fe^{3+} and Mn^{2+} to produce yellow-brown and Mn^{3+} to obtain purple. The color obtained depends not only on the oxidation state of the metal but also on its coordination in the glassy matrix and on the nature of the glassy matrix (alkali or lead glasses). Opaque glasses and glazes were also produced by the addition/crystallization of mixed metal oxides with a high light scattering capability. Lead-antimony and lead-tin oxides are found in yellow glass and calcium-antimony oxide and tin oxide in white glass. Silver and gold colloidal metal particles were also used in Roman times to obtain dichroic glass. Both transparent and opaque red glasses and enamels were also obtained by the precipitation of copper and cuprite nano- and micro-crystallites.

Decorated glazed ceramics started being produced in early Islamic times circa 7th century AD. In order to enhance the decorations tin glazes were introduced in the 8th century AD and with them new pigments and techniques. A range of shades and surface effects (brilliance and opacity) are obtained depending on the method of application (underneath or above the glaze), the use of a single or several firings, the preprocessing of the materials (raw pigments, pre-fired pigments, fritted glassy mixtures or powdered glass) and the firing conditions (temperature and atmosphere of the kiln). In order to study those differences in the methods of production between different workshops, polished cross sections of the glazes are usually analysed by means of Optical Microscopy and Scanning Electron Microscopy.

In particular, SEM is a basic tool for the determination of the morphology, size and distribution of the crystallites combined with an EDX or WDX detector for ascertaining their chemical composition. However, the identification of the crystallites may be handicapped by their small size (below the micrometer) and/or low element contrast. Moreover, chemical analysis of the microcrystallites is also limited by the analyses as the penetration of the electron beam determines the minimum size of the probed volume and also by the detection limit (about 0.1 % or 0.01% using the EDX or WDX detector respectively). The use of μ -XRD has proved to be a powerful tool in the study of glaze technology[1] and also of glaze decorations[2,3]. In particular, in the study of brown and black decorations, magnetoplumbite - $\text{PbFe}_{12}\text{O}_{19}$ -[2], and various manganese based compounds [3], are identified and their presence correlated to differences in the technology of production.

Other techniques have been also used for the analyses of glazes and glaze pigments such as Raman microspectroscopy, with particular emphasis to the non-destructiveness of the techniques and its application to the surface of the ceramic glaze decorations [4].

In this paper, we present how the combination of μ -XRD, SEM and Optical Microscopy of a selection of glaze decorations including manganese brown, antimonate yellow, red copper luster and cobalt blue helps in the identification of pigment compounds and distribution across the glass/glazes decorations. We obtain direct information on the technology of production.

Materials and methods

In order to illustrate how the analyses of the microcrystallites give information about different technological processes, six samples are presented. Three manganese brown decorations corresponding to different geographic origin and periods: *ml62*, 11th century brown and green decorated tin glaze from Mallorca (Spain), *ms04*, 13th century brown and green decorated tin glaze (Catalonia, Spain) and, the brown decoration from a *scn11*, polychrome 17th century late Renaissance Italian [5]. Two red copper lusters corresponding to 9th century Abbasid polychrome luster production (Iraq), *p717*, and a 16-17th century Safavid luster production (Iran), *p702*. A cobalt blue tin glaze sample, *sbg20*, from Catalonia is also studied.

SEM-EDX and micro X-ray diffraction performed at the European Synchrotron Radiation Facility (ESRF) have been performed on polished thin cross sections (about 50 μm thick) of the glazes [1]. Small fragments (a few millimeters) of the samples were embedded in an epoxy-resin from which cross sections of the glazes were cut. The surfaces were polished to allow Optical Microscopy and SEM analysis. Micro-XRD analyses were performed from the same glaze preparations.

Scanning electron microscopy (SEM) is the basic and most used tool for the determination of the morphology, size and distribution of the crystallites, combined with EDX detector for ascertaining their chemical composition. A Zeiss DSM 960A SEM with Link Isis L200B EDX Detector was used (20 kV, 1.5 nA). However, the identification of the crystallites may be handicapped by the small size (on the micrometer size) and low element contrast. In this case, identification and structural information of the crystallites may be obtained by means of X-ray diffraction, but the small size and low volume fraction of the crystallites make their detection difficult in conventional diffractometers. The advantage of using synchrotron light is the high brilliance and probe size spot of some tens of micrometers, and tunable X-rays energy for the measurements. Using a thin cut of the polished cross sections, it is also possible to study the nature and spatial distribution of the crystalline compounds. SR- μ -XRD was performed on beamline BM16 at the ESRF (Grenoble, France) in transmission geometry, using 0.78 \AA wavelength (16KeV), and, taking advantage of the layered structured, a 100 μm x 30 μm spot size and recorded using a CCD detector.

The combination of SEM-EDX and micro X-ray diffraction has proved to be very powerful tool for the investigation.

Results

Manganese brown decorations in tin glaze ceramics 11th-17th century AD

Manganese decorations in tin glazes have always been assumed to happen as manganese ions dissolved in the glaze. If fired oxidizing conditions it occurs as Mn^{3+} producing a purple color whereas fired in a reducing atmosphere occurs as Mn^{2+} producing a weak yellow-brown color. However, the original oxide grains added in the paint react during firing with the molten/soft glaze and there is no reason why Mn bearing compounds should not be produced. In a previous study concerning glaze technology we identified by means of Synchrotron Radiation μ -XRD the presence of braunite, $\text{Mn}^{2+}\text{Mn}^{3+}_6(\text{O}_8)\text{SiO}_4$, in the manganese richest areas of the brown decorations, although

it was not possible to identify whether the crystals were formed in the glaze during the firing or not [1]. Braunite has also been recently identified in 17th century Portuguese tiles [6]. Following this study further, a selection of manganese decorations on tin glazed ceramics from the 10th to the 17th centuries is in process of study with the aim of identifying the presence of those and other manganese compounds[3]. The identification of the compounds formed is expected to give direct information on the nature, processing and firing of the raw pigments and may be used as a technology tracer, characteristic of each period or workshop.

To check the presence of braunite in other 17th century brown decorations, a polychrome late renaissance Italian majolica [5], has been analyzed. **Figure 1** shows the area analyzed a brown line separating blue and yellow decorations. The color decorations are applied on the top of the glaze. The glazes are characterized by the presence of large amount of inclusions of quartz/feldspars -sanidine (K,Na)AlSi₃O₈, JPDF 01-83-1657- and cassiterite -SnO₂, JPDF 01-077-0452- crystallites over which the decorations were applied which can be seen in the SEM backscattering image of the polished cross section of the brown decoration. The SEM image shows the presence of particles of lead antimonate (white crystallites) as well as some manganese rich crystallites (darker crystallites with blurry edges). Micro-XRD determines the presence of at least two types of lead-antimonate (Pb₂Sb₂O₇) crystallites with a pyrochlore crystal structure -Fd3m, a=10.44 Å and a=10.40 Å respectively- and braunite Mn²⁺Mn³⁺₆(O₈)SiO₄ -JPDF 01-071-1791-. The two distinct lead antimonates identified may be related to the presence of Fe or Sn substituting Sb in various amounts in the pyrochlore structure [7,8]. The yellow pigment is synthesized previous to its application on the ceramic glaze firing the lead and antimony oxides at temperatures of about 1000°C. The addition of a flux such as NaCl (often through plant ashes) is also described to facilitate the reactivity of the oxides. Moreover, the addition of tin and iron in the synthesis of the lead antimonate yellows was also common practice since Roman times.[9] Finally, some reactivity of the lead antimonate particles with the surrounding glass is also expected to happen which could result in the incorporation of iron or tin in the pyrochlore structure. Braunite is determined in the brown decoration and it is the same compound determined in Portuguese and Catalan contemporary brown decorations.

However, this is not the case in earlier manganese brown decorations on tin glaze ceramics such as in the 10th to 12th century Islamic brown and green caliph and almohade tin glaze ceramics. **Figure 2** shows the micro-XRD data obtained from a cross section of an 11th century ceramic from Mallorca. The brown pigment has also been applied on the surface of the glaze. The separation between the brown and the white glaze below is clearly seen in the optical images. In this case a mixture of hausmannite -Mn²⁺Mn³⁺₂O₄ JPDF 01-080-0382-, braunite - Mn²⁺Mn³⁺₆SiO₁₂ JPDF 01-071-1791- and kentrolite - Pb²⁺₂Mn³⁺₂Si₂O₉ JPDF 00-020-0587- is identified. The reduction of Mn⁴⁺ first to Mn³⁺ and then to Mn²⁺ and the reaction with a silica rich matrix are responsible for the formation of the hausmannite and braunite further reacting with the lead from the glaze may lead the formation of kentrolite. Although this last transformation happens at relatively low temperatures, 650°C [10] and remains stable at least up to 840°C, the transformation to hausmannite requires higher temperatures about 1000°C [11]. This suggests a two-step process, first a high temperature firing of the pigment previous to its application which leads the formation of hausmannite and braunite, then the prefired pigment is applied on the raw white glaze precursor and the

whole fired again at a lower temperature. Archaeological evidences have shown the use of fritted materials for the production of glazes in this period [12].

Later in the 13th to 15th century in Catalonia the brown decorations were applied directly on the ceramic surface and also beneath the white glaze. **Figure 3** shows the SEM backscattering image of a polished cross section of a brown decoration applied above the glaze and the corresponding micro-XRD data. In this case the presence of dark crystallites is clearly seen: they are identified as bustamite, a manganese bearing pyroxene $-(Ca,Mn)Si_2O_6$ JPDF 01-083-1931-. In order to determine the firing conditions, the MnO-SiO₂ phase diagrams should be considered [13] where Mn-pyroxenes appear at firing temperatures of about 950°C. Therefore, in this case the original manganese pigment has been dissolved in the melt and the manganese pyroxenes recrystallize from it. In the interface between the ceramic and the glaze the formation of sanidine type feldspars and pyroxenes are also seen. The feldspars formed at the interface are known to incorporate lead and in this case they also incorporate manganese from the pigment and iron.

Therefore, the manganese containing brown decorations shown, demonstrated how the presence of different crystallites in the brown decorations may be related to the method of application (prefritted or raw initial pigment mixture) and firing temperature.

Islamic copper luster decorations

Lusters are known to be nanostructured layers formed by small particles of metallic copper and/or silver and, in some, cases cuprite. Consequence of the reduced luster layer thickness (below the micrometer) the determination of compounds forming them is heavily limited. Although grazing angle XRD is normally used, it is also possible to determine them from a cross section of the glaze surface using μ -XRD. **Figure 4** shows XRD patterns corresponding to two copper lusters; a red copper luster from the polychrome 9th century Abbasid production (Iraq), labeled *p717*, and dark brown copper luster from 17th century Safavid production (Iran), labeled *p702*. The red copper Abbasid luster is formed only by metallic copper nanoparticles –JPDF 01-85-1326-., while the brown copper Safavid luster is also formed by metallic copper nanoparticles but it also contains cuprite nanoparticles –JPDF 01-78-2076-. It is possible to estimate the size of the diffracting nanoparticles from the peak width which is of about 50 nm for *p717* but only 20 nm for *p702*. Other diffracting peaks are related to the presence of quartz –JPDF 00-33-1161- and also pyroxenes -JPDF 01-71-1494- in the glaze.

Cobalt blue decorations in Catalan tin glaze Renaissance ceramics

The last example corresponds to the analysis of a 16th century cobalt blue decoration from Catalunya. Cobalt was used since ancient times to produce blue tinged glazes. Cobalt is mainly dissolved in the glaze providing the blue color. The source of cobalt is known to have varied from cobalt containing salts to cobalt bearing sulfide ores since ancient times and, as a result, a large range of compounds was used. During the 16th century in Italy [5,14,15, 16] a peculiar arsenium rich cobalt pigment called *zaffre*, which was obtained by trade through Venice was used. *Zaffre* is an impure cobalt oxide prepared by roasting cobalt minerals such as cobaltite (CoAsS) and erythrite (Co₃(AsO₄)₂·8H₂O), which was invented in the Erzgebirge region of Saxony in about 1520 AD by Peter Weidenhammer [5,13]. The use of this pigment is demonstrated in

the Italian productions by the high amount of arsenic present in the glazes leading the formation of calcium-lead arsenate crystallites [5,14,15, 16]. Calcium lead arsenates of compositions close to $(\text{Ca,Pb})_3(\text{AsO}_2)_2$ have been determined in Derutta and Gubbio, as well as, in some Della Robbia productions [15]. However, the exact nature of these crystallites has not yet been identified. Arsenium bearing cobalt blues have also been identified in Spain after the 16th century [17,18]. A cobalt blue decoration found in Sant Bartomeu del Grau Catalonia and dating 16th century AD, shows also a high amount of arsenic associated to the cobalt blue and the presence of large hexagonal crystallites of lead rich arsenates concentrated near the glaze-ceramic interface as shown in **Figure 5**. The optical image clearly shows the application of the cobalt pigment underneath the glaze, where the lead rich arsenates are found. SEM-EDS obtained from several of those crystallites shows a variable composition around 0.7% Na₂O, 0.7% K₂O, 1.6% MgO, 2.6% CaO, 29.3% As₂O₃, 65.1% PbO. The crystallites determined are in all the cases calcium far poorer than the ones determined in the Italian productions. μ -XRD shows the presence of a predominant hexagonal phase which corresponds relatively well with a lead rich arsenate -JPDF file 00-031-1083 of NaKPb₈(AsO₄)₆ with crystalline structure P63/m, a=b= 10.08Å, c=7.362Å- but as by SEM-EDS Ca is also detected lattice parameters has been adjusted and fitted to a=b=10.115 Å, c=7.277Å (larger a and b and smaller c).

Conclusions

A combination of Optical Microscopy, SEM-EDS and μ -XRD has been used to study a selection of color decorations on tin glaze ceramics. The identification of kentrolite, braunite, haussmanite and bustamite as Mn pigments in different kind of ceramics demonstrated how the presence of different crystallites in the brown decorations may be related to the method of application (prefritted or raw initial pigment mixture) and firing temperature. The nature and size of the nanoparticles in luster decorations although forming a submicron layer were determined. Finally, the lead calcium arsenates appearing in some cobalt decorations correspond to a main hexagonal phase with crystalline structure P63/m, a=b=10.115 Å, c=7.277Å.

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Figure captions

Figure 1. Left: Optical and SEM-BSE image corresponding to the brown decoration corresponding to the polychrome late Renaissance Italian tin glaze ceramic (*sn11*). Right: μ -XRD data corresponding to, from top to bottom, the brown pigment, the yellow pigment and to the glaze.

Figure 2. Left: Optical image of a the samples and a cross section of the brown decoration corresponding to an 11th century Almohade tin glaze ceramic from Mallorca (*ml62*). Right: μ -XRD data corresponding to, from top to bottom, the brown and white glazes.

Figure 3. Left: Optical and SEM-BSE image corresponding to the brown decoration corresponding to a brown and green 13th century Catalan tin glaze ceramic (*ms04*). Right: μ -XRD data corresponding to the crystallites of present.

Figure 4. Top left: Optical and SEM-BSE image corresponding to the red lustre from a polychrome 9th century Abbasid lustre ceramic from Iraq (*p717*). Bottom left: 17th century Safavid red lustre ceramic from Iran (*p702*). Right: μ -XRD data corresponding, from top to bottom to the lustre decorations from samples *p717* and *p702*.

Figure 5. left: Optical microscope and SEM-BSE images. Right: μ -XRD data corresponding to sample *sbg20*.

Figure 1

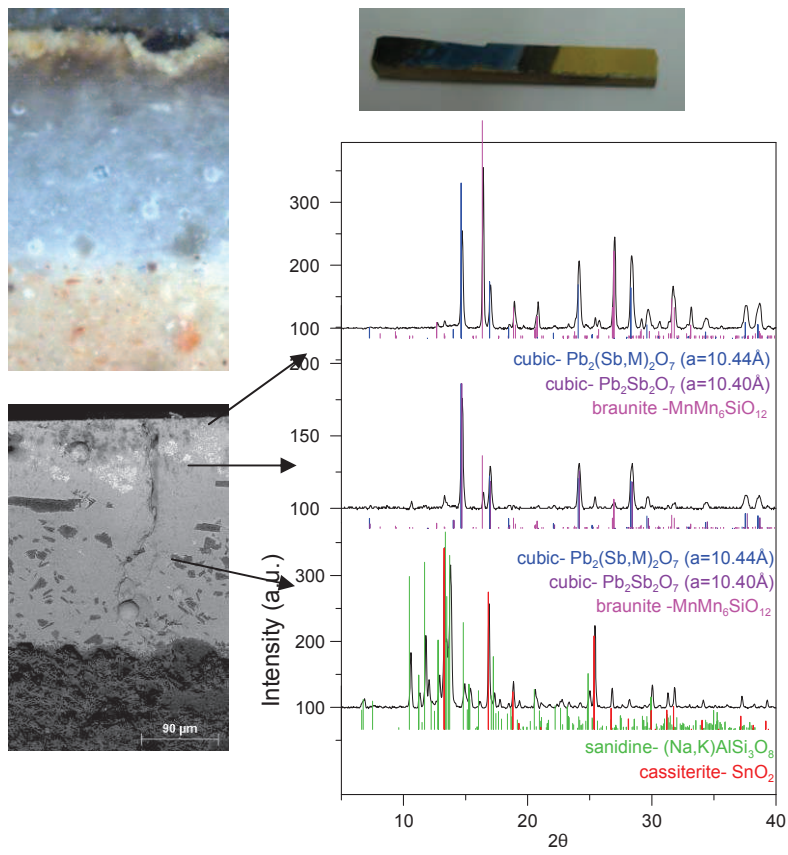


Figure 2

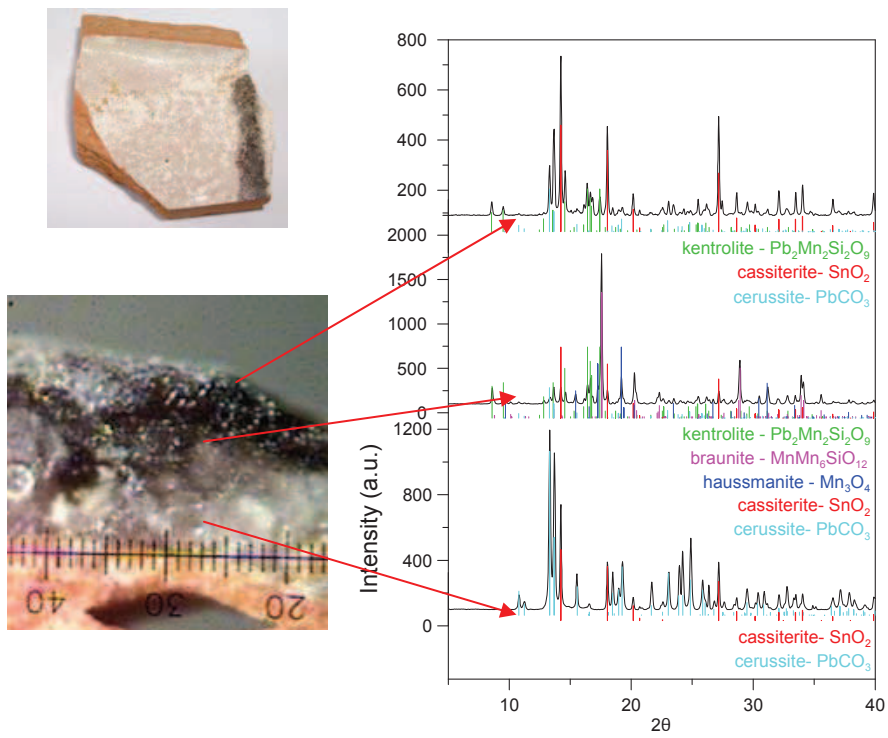


Figure 3.

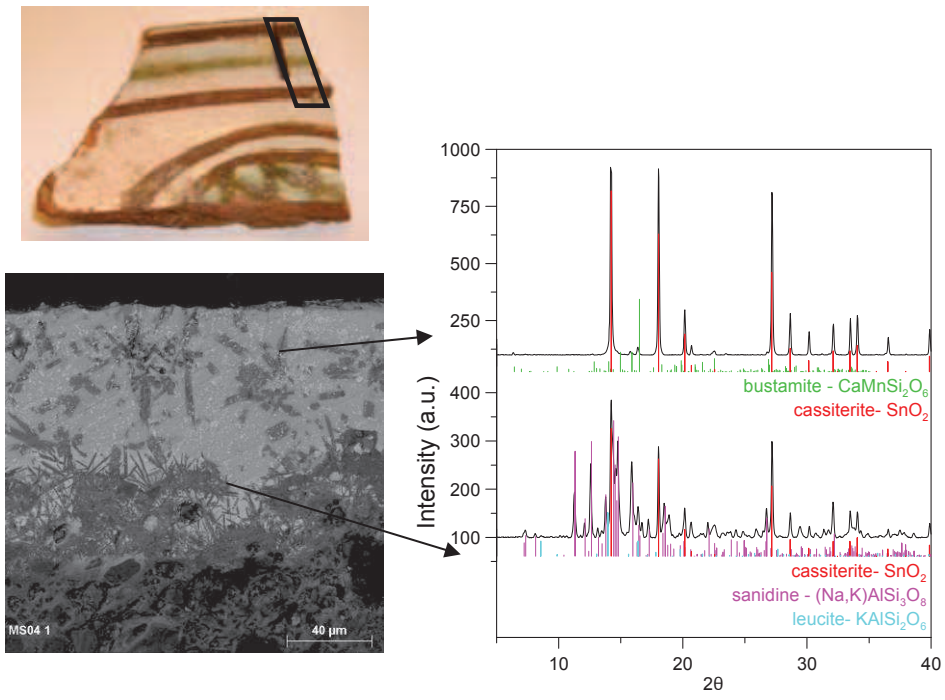


Figure 4

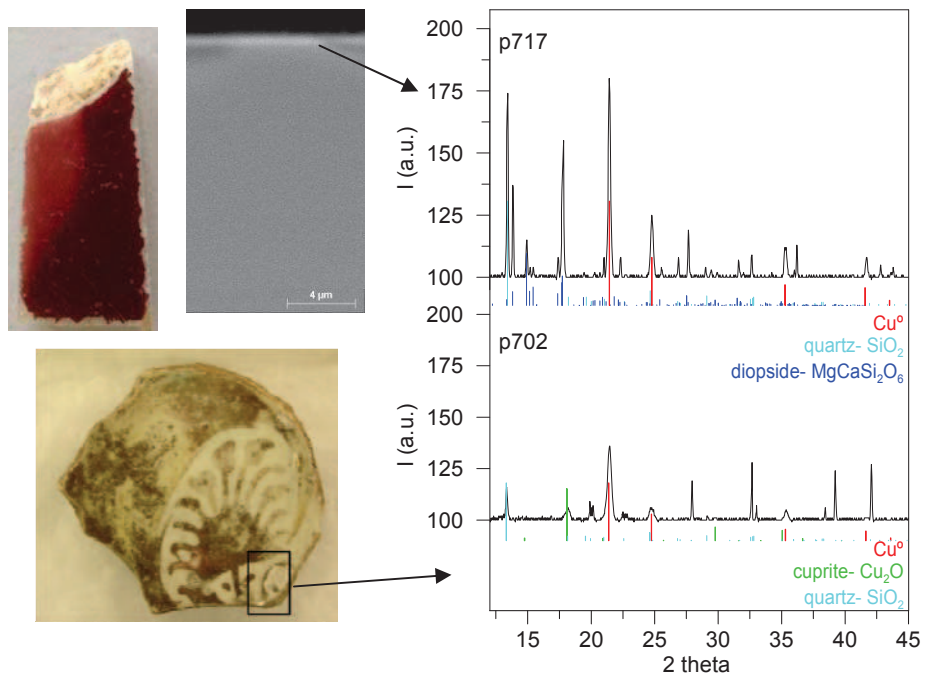


Figure 5

