

G. PADELETTI¹,
P. FERMO²

How the masters in Umbria, Italy, generated and used nanoparticles in art fabrication during the Renaissance period

¹ Istituto per lo Studio dei Materiali Nanostrutturati – CNR, cp 10, 00016 Monterotondo Staz., Roma, Italy
² Dipartimento di Chimica Inorg. Metallorganica e Analitica, Università degli Studi di Milano, Via Venezian 21, 20133 Milano, Italy

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ABSTRACT Lustre was one of the most sophisticated techniques for the decoration of majolicas during the Renaissance period. Lustre consists of a thin metallic film containing silver, copper and other substances like iron oxide and cinnabar applied in a reducing atmosphere on a previously glazed ceramic. In this way, beautiful iridescent reflections of different colours (in particular gold and ruby-red) are obtained. The characterisation and the study of lustre-decorated majolicas is of great interest for archaeologists, but also offers possibilities for producing pottery with outstanding decoration today, following ancient examples, since nowadays Italian artisans are interested in the reproduction of the ancient recipes and procedures. Moreover, it can even suggest new procedures for obtaining uniform thin metallic films for technological applications. A study has been carried out on ancient lustre layers using numerous different analytical techniques such as XRD, SEM-EDX, TEM-EDX-SAED, ETAAS, ICP-OES, UV-vis reflectance spectroscopy and SAXS. Lustre films were shown to be formed by copper and silver clusters of nanometric dimension. The colour and the properties of the lustre films depend on the elemental composition of the impasto applied to the ceramic surface as well as on other factors like the metallic nanocluster dimension, the firing conditions, the underlying glaze composition and the procedure used.

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1 Introduction

During different ages, ceramic concerned for every form of useful object, being a matter for experimentation with techniques and styles. For these reasons, every object contains aspects of the cultural heritage of its civilisation.

Amongst all the ware produced by man, pottery resists time and weathering even better than metals. In spite of its brittleness, the shard found in the ground allows us to attribute names and characters to cultures and civilisation.

In Italy, a more remarkable evolution took place during the XIV century, when a new technique concerning glaze preparation was developed. Due to the contemporary presence of

tin and lead oxides, a white and waterproof coating was obtained and it was possible for the pottery painters to use this as a canvas. For this reason, real works of art were produced, representing portraits of noblewomen and noblemen, mythological and religious scenes, sayings, loving dedication, heraldic symbols and coats of arms. All these motifs were inspired by the masterpieces of Renaissance artists and were requested by cultured and refined customers.

This moment represents the origin of “majolica” in its actual meaning, which is referred generally to glazed production. It is characterised by a ceramic body with a porous structure, and over it there is a glazed layer, generally white, that is decorated. But during the XV and XVI centuries, the Italian potters only named “majolica” (of Mallorca) the objects decorated with metallic reflections (i.e. lustre), reminding the beautiful pieces of this kind firstly obtained by Arabs and Hispano-Moors, and imported into Italy through Mallorca island.

The lustre technique, which will be the object of our study, was introduced to the Mediterranean basin from Islamic potters, in order to deceive the religious prohibition of using gold and silver vessels at the table. In fact, covering the pottery with a golden-like or copper-like coating, a precious metal aspect was conferred.

The lustre technique was first made in Iraq, then spread to Egypt, Persia and Spain, following the expansion of Arabian culture during the medieval times [1]. From Spain (Valencia, Manises and Malaga), lustre was introduced to the Italian peninsula, where it was used mostly in central Italy to decorate the most beautiful majolicas. Important centres for this activity, were Gubbio and Deruta, located in Umbria.

It has to be pointed out that the Italian artisans developed their own style for the decorative motifs, as well as for what concerns the metallic colours obtained.

For this reason, the local artisans became keepers of refined and secret recipes and techniques for decorating ceramic objects.

The most important artist in this field was Mastro Giorgio Andreoli da Gubbio [2, 3], whose works can be found in the most important museums of the world and are very well known in the antique trade market as well. His fame is due to the fact that by optimising the lustre technique, he obtained outstanding results, which were not possible to replicate during his time or now. He specialised mainly in two kinds of

reflections: an intense golden-yellow and a ruby-red colour, but the original recipes and technological procedures used at that time were and have remained a secret after his death until today. Probably, the process of lustre-making was jealously kept and handed on only within the Andreoli family, the secret recipes differentiating the production and helping to guard against competition.

In the specific case of the Renaissance, information on majolica production technology has been passed on by the Knight Cipriano Piccolpasso from Casteldurante, who wrote a treatise entitled “The three books on the art of the Potter” (1558) [4]. It has to be taken into account that the information reported by Piccolpasso could not be entirely correct, due to the aforementioned reasons regarding secrecy. Referring to his work, the objects were obtained in the desired form and fired in a first step at 1000 °C.

Once cooked and cooled down, the object was immersed in the glaze, which consisted of sand, potassium carbonate, salts and oxides, such as lead and tin oxides, finely ground and mixed with water. After drying in air, it was possible to decorate the glaze surface using very soft brushes, made from bristles of goat, and sometimes, for very fine details, whiskers of cats and mice too. After that, it was sprayed with a transparent paint and the object underwent a second firing at 900 °C. At the end of this process, the object was complete.

However, if we refer to lustre, another step was required to achieve the result of producing reflections and iridescences on majolica. Ancient documentation indicates that the lustre was obtained using a mixture of copper and silver salts, clays, ochre and other optional substances dissolved or dispersed in vinegar, and firing it in a reducing atmosphere in special kilns made for this purpose (Fig. 1), where probably it was easier to control both the temperature and atmosphere.

The reducing atmosphere was achieved by burning smoke materials, horse hoof or broom, which is very common in this geographic area (see Fig. 2), at temperatures around 500–600 °C (just to soften the glaze a little, so that the metal particles are allowed to penetrate inside). The reducing atmosphere is thought to be responsible for the reduction of copper and silver compounds to metals, forming a metallic film.

From this brief description, it emerges that in this procedure, too many variables are present and some of them are really complex and difficult to reproduce. Piccolpasso himself defined this step as “arte fallace” (i.e. fallacious art).

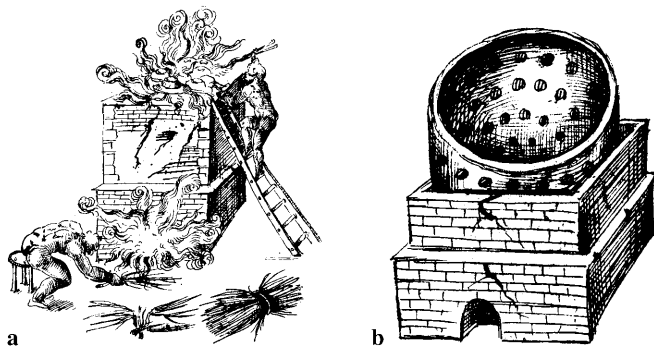


FIGURE 1 Kilns (a) and (b) used for the firing of lustre pottery (figures from [4] by courtesy of Edizioni all’Insegna del Giglio, Firenze, Italy)



FIGURE 2 A broom bush in Gubbio (Umbria, central Italy)

Because of such difficulties, this technique was only used for the realisation of valuable objects and became the line between the artisan and the artist, since realising lustred objects was an exhibition of the personal skillfulness of the master.

For this reason, during the Renaissance, the lustred majolicas were in a dominant position, golden and ruby effects reminiscent of richness, and were requested as status symbols from Courts all over Europe.

Mastro Giorgio became so famous that masters from other towns (for instance Casteldurante and Urbino) used to bring their production to Gubbio for the final application of lustre decoration. Typical examples of this kind of cooperation are the “istoriato” dishes, decorated with the representation of stories from drawings or engravings by means of a perforated pattern on the glazed surface. In this scenery, the lustre touches are distributed very skillfully and marvellously inserted in the pictorial decoration, assuming different colour variations.

Confirming the particular ability required in lustre procedure, on the back of majolica dishes, it is possible to find two signatures, those of the painter and Mastro Giorgio. A wonderful example of this kind of cooperation is depicted in Fig. 3. In Fig. 4, a dish entirely decorated and lustred in Mastro Giorgio’s workshop is shown.

A great historical and technological interest surrounds lustre. It is also important to point out that lustre is one of the most ancient nanophase materials produced in the past, together with gold-ruby glasses, Lycurgus cup and Maya blue [5–7].

Detailed information on chemical composition and physical properties are important for archaeologists, but also offer possibilities for producing today, following ancient examples, pottery with outstanding decoration, or even may suggest new procedures for obtaining uniform and reproducible thin metallic films for technological applications. Information on lustre is still little and fragmentary, and for these reasons it is of particular interest to study this subject with techniques that are now available for advanced research on materials.

The scientific studies carried out on this subject to date [8–14] have concerned the chemical and physical characterisation of the lustre films and have principally pointed out the nanostructured nature of the lustre layers. In particu-



FIGURE 3 Majolica dish. “Pico, Circe e Canente” painted by Xanto Avelli da Urbino and lustred by Mastro Giorgio Andreoli; by courtesy of Museo Civico – Palazzo dei Consoli, Gubbio

lar, it has been demonstrated that lustre is a thin film (about 1 μm) containing high-density silver and copper nanocrystals dispersed in a glassy matrix. Concerning the elemental analysis performed on the lustre samples, it was found that the colour depends not only on the chemical composition of the impasto used in the lustre-making process, but also on other factors such as the particle dimensions, which can be strongly influenced by the firing conditions (temperature and reducing atmosphere) [12].



FIGURE 4 Majolica dish. “La caduta di Fetonte” painted and lustred by Mastro Giorgio Andreoli; by courtesy of Museo Civico – Palazzo dei Consoli, Gubbio

The aim of this work is to gain a further insight into the technological procedure and into the recipes employed by the ancient Umbrian potters for the production of both the gold and the more uncommon ruby-red lustre. For this purpose, the following analytical techniques have been employed: X-ray diffraction (XRD), atomic absorption spectrometry with electrothermal atomization (ETAAS), inductively coupled plasma optical emission spectrometry (ICP–OES), scanning electron microscopy/energy-dispersive X-ray spectroscopy (SEM–EDX), scanning electron microscopy equipped with a back-scattered electron detector (SEM–BSE), transmission electron microscopy/energy-dispersive X-ray spectroscopy/selected-area electron diffraction (TEM–EDX–SAED), small-angle X-ray scattering (SAXS) and UV–vis diffuse reflectance spectroscopy.

2 Experimental details

2.1 Sample descriptions

The samples examined in this work (Table 1) are lustre-decorated majolica shards dating back to the 15th and the 16th centuries and coming from the two major centres of production of this ware, i.e. Gubbio and Deruta, both located in central Italy. The samples are plates, dishes, basins or bowls fragments, decorated with simple and geometrical motifs showing gold or ruby-red lustre, or both. Often, lustres were applied within areas delimited with blue drawings or, sometimes, over the blue decorations. As decorations, simple motifs were often employed, such as flowers (and in particular sunflowers), spreading leaves or wolf-teeth, which can simulate sun beams. In fact, all these themes remind us of the sun and the light [1].

The samples have been provided by private collectors, or have been found during restructuring works or archaeological surveys carried out in Gubbio and supplied by Gubbio Town Council.

Ceramic shard description	Examined sample colour
Lat, shard decorated by a typical Gubbio motif	red
G50r, shard decorated by gold and red motifs, Gubbio	red
G50g, shard decorated by gold and red motifs, Gubbio	gold
L22r, shard decorated by blue, gold and red motifs with the typical Gubbio design a settori, Gubbio	red
L22g, shard decorated by blue, gold and red motifs with the typical Gubbio design a settori, Gubbio	gold
L2, shard decorated by gold and red motifs, Gubbio	red
L2, shard decorated by gold and red motifs, Gubbio	gold
L8r, shard decorated by gold and red motifs, Gubbio	red
L8g, shard decorated by gold and red motifs, Gubbio	gold
Lamr, shard decorated by gold and red motifs, Gubbio	red
Lamg, shard decorated by gold and red motifs, Gubbio	gold
L19, shard decorated by blue and gold motifs, Deruta	gold
L24, shard decorated by blue and gold motifs, Deruta	gold
L25, shard decorated by blue and gold motifs, Deruta	gold
Lq, shard decorated by flowers and bands, Deruta	gold
Ly, shard decorated by wolf-teeth, Deruta	gold
Lz, shard decorated by botanical motifs, Deruta	gold

TABLE 1 Description of the Italian Renaissance lustre-decorated ceramic shards analysed

2.2 Analytical techniques used

2.2.1 XRD. X-ray diffraction analyses were performed by a Bragg–Brentano diffractometer (STEIFERT ID 3000) equipped with a Ge focussing primary monochromator ($\lambda = \text{Cu } K_{\alpha}$). The diffractograms were acquired directly on the sample surfaces, being careful to select flat areas.

2.2.2 ETAAS. The determination of Cu and Ag content in the lustre layers was performed by ETAAS analyses using a Perkin–Elmer 4000 atomic-absorption instrument equipped with a Perkin–Elmer HGA 500 graphite furnace. This choice was dictated by the small amount of sample we could cut off from the ceramic shards and because of the numerous measurements that each fragment underwent. In fact, one of the advantages provided by ETAAS is the small quantity required for analysis, even less than ICP-OES [12].

Samples consisted of lustre + glaze and glaze scales only, taken from the shard surface by means of a bistoury in order to separate the decorated part from the ceramic body. Obviously, it was not possible to separate the lustre from the underlying glaze where it was embedded. For this reason, as copper was one of the elements present in the glaze underlying the lustre layer, in order to determine the copper concentration in the lustre layer it was necessary to analyse both the glaze and the lustre + glaze samples and subsequently make a subtraction [12, 13].

The samples were submitted to a total digestion procedure in a microwave oven (Milestone 1200) in order to facilitate complete dissolution in about 20 min. About 2 ml of 40% HF (Merck, Germany) and 2 ml of 65% HNO₃ (Merck), both of ultra-pure grade, were added to a small quantity of sample, exactly weighed (3 mg down to less than 1 mg), in a PTFE vessel that was subsequently put in the microwave oven pressure device and heated. Then the solution obtained was transferred into a platinum crucible, 2 ml of ultra-pure HClO₄ 65% (Merck) was added and the crucible heated to allow HF to evaporate off. After cooling to room temperature, the solution was diluted to 10 or 5 ml (depending on the weighed sample quantity) with high-purity water and transferred to a plastic flask. All the solutions were prepared using water purified with a Milli-Q water purification system (Millipore, USA). 10 or 20 μl (respectively for Ag or Cu) were injected into the furnace using a fixed-volume micropipette. For Ag determination, 10 μl of a solution of a matrix modifier (Pd 1.5 g/l and Mg(NO₃)₂ 1.0 g/l) were added in the graphite tube to 10 μl of the sample solution.

Blank samples were prepared following the same procedure used for sample preparation. Samples containing PbO, SiO₂ and Ag in the same concentration ranges as those present in lustre samples were prepared to be used as references.

2.2.3 ICP–OES. ICP analyses were performed on the glazes underlying the lustre layers using a Jobin–Yvon instrument, model Ultima. A plastic Scott chamber equipped with a cross-flow nebulizer allowed the analyses of hydrofluoric acidified solutions. The analyses were carried out on solutions obtained by submitting the glazed samples to total acidic digestion by means of HF and HNO₃, as has been described in previous work [12].

2.2.4 Optical microscopy. For each shard examined, a resin-impregnated polished cross section was prepared in order to observe the ceramic shards (lustre + glaze + ceramic body) by optical microscopy. The observations were performed by means of a Leitz Ortholux optical microscope equipped with a Ultrapack illuminator.

2.2.5 SEM–EDX–BSE. SEM–EDX analyses were performed on lustre scales cut off from the ceramic shard surface or directly on the shard surfaces using a Hitachi 2400 scanning electronic microscope equipped with a Quantum Kevex energy-dispersive X-ray micro-analyser (EDX). Polished cross sections were also examined in order to analyse the glaze.

Secondary electron micrographs (SEM–BSE) were acquired by means of a Leica (Cambridge) Stereoscan 420 scanning electron microscope equipped with a back-scattered electron detector. In this case, the shard surfaces were coated with a thin carbon layer deposited by means of a Balzers sputter coater SCD 050.

2.2.6 TEM–EDX–SAED. TEM images, EDX analyses and SAED patterns were acquired using a Philips model 400 T instrument operating with a maximum accelerating voltage of 120 kV and equipped with an energy-dispersive X-ray micro-analyser (EDX) and a C–U detector. The analyses were acquired from electron-transparent samples prepared from sections having a thickness of about 100 μm and made thinner by ion-beam bombardment. In order to protect the lustre layer while making it thinner, a monocrystalline silicon slide was pasted by means of an oven-curing resin over each sample before cutting the sections to be submitted to the bombardment.

2.2.7 SAXS. The SAXS measurements were acquired from some lustre scales by means of the apparatus already described in detail in a previous work [10].

2.2.8 UV–vis diffuse reflectance spectroscopy. Diffuse reflectance spectra were acquired in the UV–vis spectral range from 800 to 350 nm using a JASCO/UV/vis/NIR spectrophotometer model V-570.

The lustre samples were selectively irradiated using black masks having a suitable size aperture and applied to the shard surfaces. In this way it was possible to acquire the spectra on sufficiently flat and homogeneous areas. The baseline was previously registered on a little white block of Mylar, to which each mask had been applied. The same block of Mylar was also used as a reference sample.

3 Results and discussion

3.1 Glaze morphology and chemical composition

It is well known [1] that, in order to obtain a satisfactory lustre film, there must be a suitable glaze/lustre interaction. In particular, it has been pointed out [15] that tin-opacified lead-alkali glazes are preferred in order to obtain a good quality lustre decoration. For this reason, both morphological and chemical investigations were carried out on the glazes underlying the lustre films.

The glazes were typically from 100- to 300- μm thick, as could be observed by SEM micrographs acquired from two

sample cross-polished sections (Fig. 5) where the two components, glaze and ceramic body, were present. Bubbles and numerous un-reacted quartz grains may be observed throughout the glaze thickness.

Because of the small thickness of the lustre film (0.1–2 μm), it could not be easily observed in the SEM micrographs. It has been reasonably supposed by Fabbri et al. [16] that a homogeneous glaze thickness, such as that observed for the ceramics studied in this work, probably indicates the use of the immersion technique for the application of the glaze, i.e. during the glazing process the object was completely immersed into the slip.

A group of about 30 glazes was analysed by ICP–OES in order to obtain information on the raw materials used. The ranges of variation of elemental compositions, reported in Table 2, are in good agreement with data previously obtained [8, 12].

The analysed glazes, which were of the lead-alkali type, show in some cases a relatively high soda (Na_2O) content if compared with the glazes produced according to the recipes reported by Piccolpasso [4], where soda content varies between 1 and 4% [15, 17]. The glazing mixture was commonly prepared starting from marzacotto (sintered sand and calcined wine lees providing potash and salt), which furnished a high potash (K_2O) quantity. On the contrary, the marzacotto used for the production of some shards examined in this work is more similar to that typical of some Islamic ceramic wares, due to its high Na_2O content. The use, during the Italian Renaissance, of a recipe characterised by such a high soda content has also been reported by Tite [17].

The presence of tin oxide, commonly used to obtain the glaze opacity, has been revealed by means of XRD, SEM–EDX and TEM–EDX analyses. It is important to point out

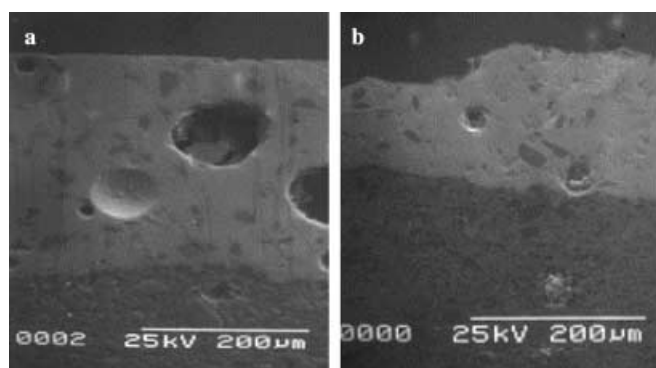


FIGURE 5 SEM micrographs (a) and (b) of polished sections obtained from lustrated ceramic shards showing the presence of bubbles and unreacted quartz grains (dark grey)

Glaze composition (wt.%)	Glaze composition (wt.%)	Glaze composition (ppm)
PbO 15.0–29.8	MgO 0.1–1.4	Cu 76–2800
K_2O 5.7–9.6	Fe_2O_3 0.3–3.9	Mn 30–385
Na_2O 0.9–12.7	TiO_2 0.1–0.3	Cr 10–134
Al_2O_3 1.1–5.7		Ni 6–293
CaO 1.1–8.7		Zn 0–974

TABLE 2 Range of variation in Italian Renaissance glaze chemical composition determined by ICP–OES quoted as wt. % of oxide (major and minor elements) or ppm (trace elements)

that Sn, and likewise Si, was not quantitatively determined by ICP–OES because of the sample dissolution procedure used [12]. In Fig. 6, a SEM image acquired from a polished section showing some crystals of tin oxide is reported.

SAED analyses performed on some glaze areas have shown that the glaze is an amorphous material where occasionally crystalline grains are observable. In particular, some cassiterite (SnO_2) crystals have been evidenced (Fig. 7a) in a TEM image. The identification of the phase in this case was made on the basis of the chemical composition (TEM–EDX analysis) and taking into account the morphology of the crystal, which is of the typical twinning type observed for the cassiterite crystals and known as “tin beak” (Fig. 7b).

The observations carried out on polished sections of ceramic shards by optical microscopy (Fig. 8) have evidenced the presence of some blue areas where small, a pigment consisting of a potassium silicate glass containing cobalt oxide, has been applied over the glaze to obtain the characteristic blue decoration [9, 11]. It is interesting to notice how, during the firing process, the pigment has been completely incorporated into the glaze.

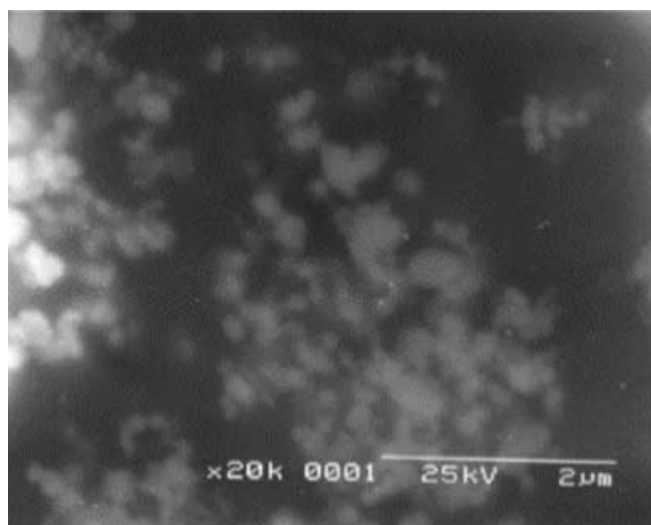


FIGURE 6 SEM micrograph acquired from a polished section obtained from a lustrated ceramic shard, showing the presence of tin oxide crystals inside the glaze

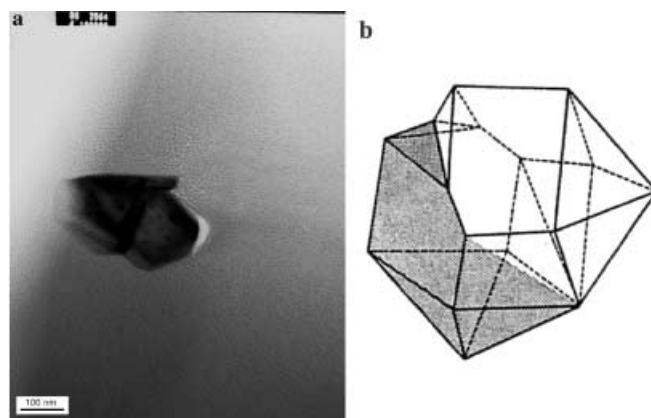
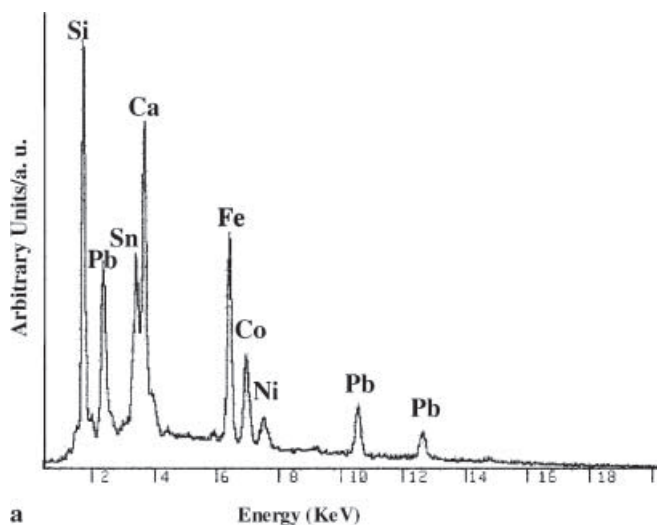


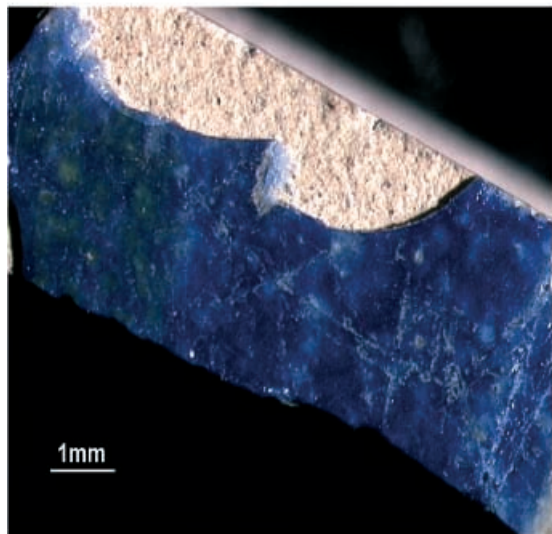
FIGURE 7 TEM image acquired from a glazed area showing a cassiterite (SnO_2) crystal (a) characterised by the typical cassiterite “tin beak” twinning (b)



FIGURE 8 Optical microscopy image acquired from a polished section obtained from a lustrated ceramic shard: the ceramic body (*bottom*) and the glaze (*top*) decorated with the blue pigment smalt are visible



a



b

FIGURE 9 SEM-EDX spectrum showing the composition typical of smalt pigment (**a**) acquired from a blue area present on a ceramic shard (**b**)

The smalt chemical composition has been successfully disclosed by SEM-EDX (Fig. 9a), analyzing a shard characterised by the presence of a very deep blue decoration (Fig. 9b). Cobalt as well as iron and nickel signals are present. In fact, it is well known that the pigment was prepared starting from minerals containing Co, Fe and Ni: the oxides of cobalt, nickel and iron were melted together with siliceous sand and the resulting pigment sold to the ancient potters with the name of Zaffre or Zaffera [18].

3.2 Lustre chemical composition

As has been already pointed out in the introduction, lustre is a decorative metallic film applied to the surface of previously glazed majolicas. Some analytical studies [8, 9, 11, 12] have shown the presence in the lustre layer of copper and silver metallic nanocrystals embedded in a glassy matrix. The lustre film is typically from 0.1–0.5 to 2- μm thick, as can be observed in the image acquired by an optical microscope of a thin section prepared for TEM analysis (Fig. 10).

By means of XRD analyses (not shown) performed on the lustre-decorated surfaces, the following crystalline phases were observed: cassiterite (SnO_2), present in the glaze, metallic silver and copper, silver oxide, copper oxide (indicating that the reduction process was not complete) and cosalite, a compound containing bismuth combined with lead and sulphur, whose presence is a peculiar characteristic of the Italian lustre decorations [13].

Two EDX spectra acquired from the lustre surfaces are shown in Fig. 11. Generally, silver and copper signals are more intense in gold-yellow and ruby-red lustres, respectively. The Si, Pb, K and Ca signals are due to the glassy matrix where the lustre is embedded.

As one of the aims of the present research was to acquire further information on ancient recipes, it is of fundamental importance to detect and quantify the elements present in the lustre, to go back to the impasto preparation. It was previously found by EDX analysis that ruby-red lustre showed Cu/Ag ratios > 1 , whereas the gold ones, for the most part, were characterised by Cu/Ag < 1 [8]. Moreover, in a recent work Molera et al. [19] have found that gold-brown lustre decorations show a higher Ag content compared with red ones. However, to perform a satisfactory quantitative analysis, EDX

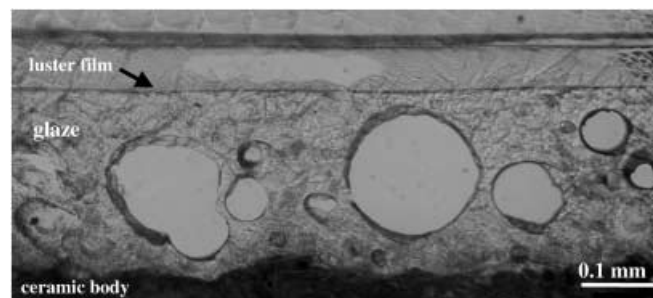


FIGURE 10 Optical microscopy image acquired from a thin section prepared for TEM analysis of a lustrated ceramic shard; starting from the *bottom*, the following sequence is observable: ceramic body, glaze, lustre layer and, *on the top*, the glue layer and the thin slide used for the sample preparation; large air bubbles are observable inside the glaze

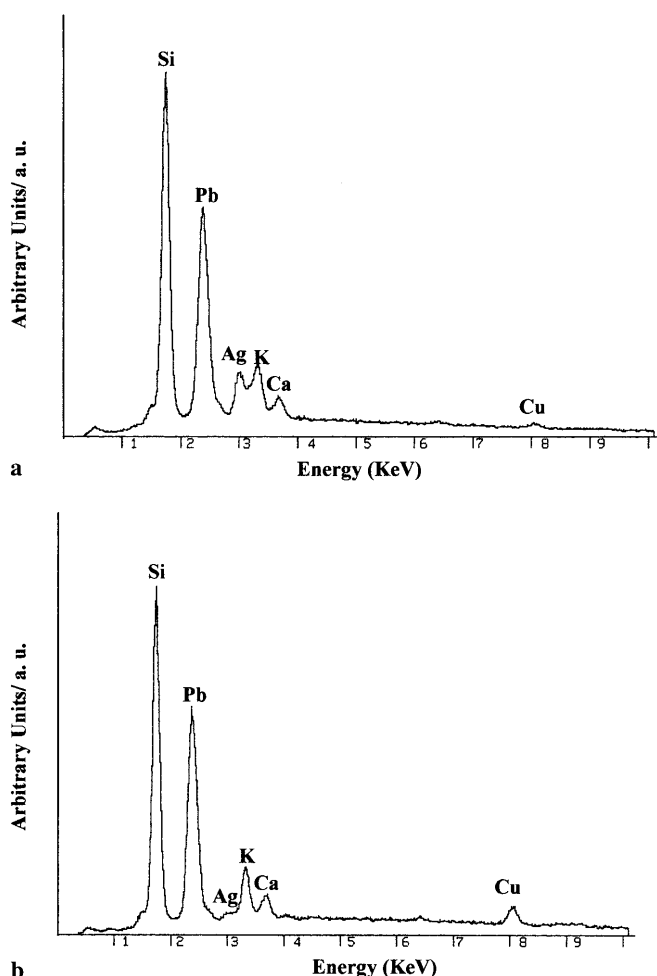


FIGURE 11 SEM-EDX spectrum acquired from a gold lustre (a) and from a ruby-red lustre (b), respectively

was not accurate enough since it is characterised by a detection limit of about 1 wt.%. This represents a quite restrictive condition as, due to small thickness of the lustre (see Fig. 10), in many cases the copper or silver concentration may be under this value. For this reason, we decided to perform the quantitative analyses by means of ETAAS, which, due to the lower detection limits, allows one to work on very small sample quantities, down to 1 mg. As it is impossible to separate the lustre layer from the underlying glaze, the analysed samples consisted of lustre plus glaze (see Sect. 2.2.2 ETAAS). Therefore only Ag/Cu ratios and not absolute concentration values are shown. The results are summarised in Table 3, where for the most representative samples, the colour and the relative Cu/Ag ratio are reported.

An important aspect that can be seen is that the colour is not unambiguously determined by the chemical composition. In fact the two gold lustre samples named Lz and L19 are characterised by high Cu/Ag ratios. Therefore, other parameters, different from the chemical composition, have to be co-responsible for the lustre colour. Comparing the two colours, for compositions present simultaneously on the same shard (samples G50, L22, L2, L8 and Lam), higher Cu/Ag values are always associated with ruby-red colour. This is an important consideration, because only in this case we can assume that both colours have undergone the same process

Sample name	Colour	Cu/Ag
Lat	red	Ag absent
G50r	red	Ag absent
G50g	gold	8.00
L22r	red	4.07
L22g	gold	0.12
L2r	red	0.4
L2g	gold	Cu absent
L8r	red	3.34
L8g	gold	0.10
Lamr	red	4.02
Lamg	gold	1.01
L19	gold	9.17
L24	gold	0.40
L25	gold	Cu absent
Lq	gold	Cu absent
Ly	gold	0.17
Lz	gold	11.33

TABLE 3 Cu/Ag ratios determined by ETAAS in some Italian Renaissance lustre samples

conditions and the only difference should derive from the impasto stoichiometry.

3.3 Lustre nanostructure

In the present work, the nanostructure of a quite large number of lustre samples has been analysed by means of UV-vis diffuse reflectance spectroscopy, TEM-EDX-SAED, SEM-BSE and SAXS.

In order to gain a further insight into the lustre film nature, the optical properties of these films have been investigated, and UV-vis reflectance spectroscopy was employed. The spectra acquired from the lustre surfaces allow us to point out the metallic colloidal nature of Cu and Ag particles. In fact, colloidal dispersions of metals exhibit absorption bands in the ultraviolet-visible range typical of the metallic nature of the particles. As has been previously observed [8, 9, 11, 12], the spectra corresponding to the gold lustre samples show a maximum at about 420–440 nm, due to the silver SPR (surface plasmon resonance) band (see Fig. 12a), while the spectra acquired from ruby-red lustre decorations show a maximum at about 560 nm due to the copper SPR band and, in most cases, a maximum due to the Ag SPR band (see Fig. 12b).

The particle nanodimensions are responsible for the beautiful colours and the iridescent effects typical of this kind of decoration [20, 21].

More detailed interpretation of the optical absorption spectra can be obtained taking into account the analogy existing between the lustre films and some metal-nanocluster composite glasses, widely studied in the literature because of their application in the material science field [22–29]. Particularly interesting is the case of silver, copper and silver-copper nanostructured films obtained by different preparation techniques such as ion-bombardment, sol-gel deposition or the ion-exchange process.

On the basis of the studies concerning these metallic composites, it is also possible to hypothesise a lustre formation mechanism which may start from an ion exchange between the alkali present in the matrix and the metallic ions (copper and silver) present in the impasto used for the lustre prep-

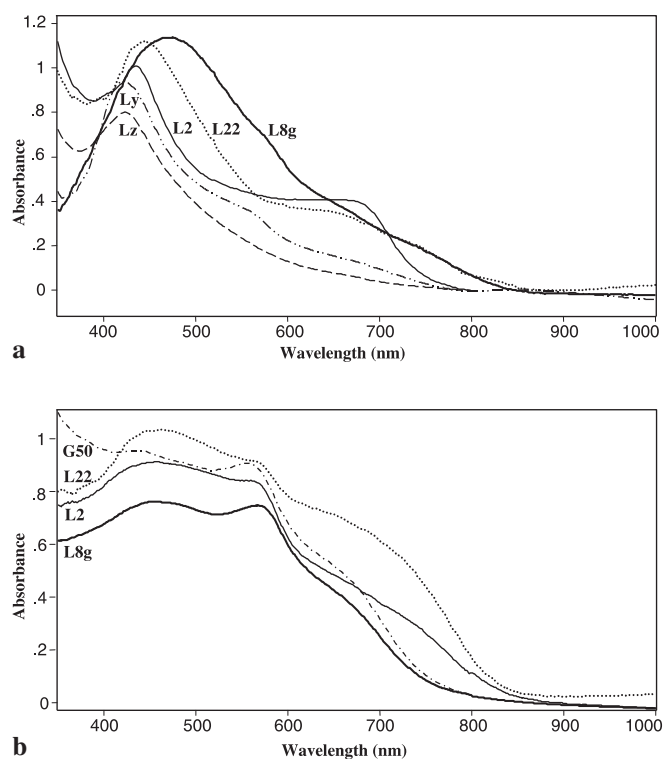


FIGURE 12 UV-vis diffuse reflectance spectra acquired from gold lustre samples (a) and ruby-red lustre samples (b), respectively

ation, followed by the precipitation of metallic particles of nanometer size near the surface [25, 27]. Therefore, alkali glazes characterised by a high soda content, such those employed in the case of the lustre samples examined, may be particularly suitable for the preparation of a good-quality lustre.

Examining the spectra reported in Fig. 12a and comparing them with the results in Table 3, it is evident that even if the lustre film is characterised by $\text{Cu}/\text{Ag} > 1$ (sample Lz), the related copper SPR band may be not evident. Meanwhile, in the spectra acquired for red decorations, the silver SPR band is always present, if Ag is present, independent of its concentration. The spectrum acquired from sample G50r (Fig. 12b), which does not contain silver (see Table 3), does not show a silver SPR band; the broad absorption observable between 400 and 500 nm is common in UV-vis optical absorption spectra acquired from Cu-nanocluster-doped silica films prepared by the sol-gel technique or ion implantation [22, 29].

For lustre films, it is not simple to find a correlation among the SPR band maximum wavelength in the optical absorption spectra and the metallic particle dimensions because of the numerous variables which have to be taken into account. The same problems have been observed with the optical absorption spectra acquired from films containing nanometer metallic particles prepared nowadays [22–29].

It has been demonstrated that the optical absorption clearly depends on the metallic nanoparticle dimensions. In fact, from Mie theory [30, 31], the SPR maximum shifts to longer wavelengths with increasing particle size.

Furthermore, it has been observed that when the particles are very small, a considerable decreasing of the peak height may also occur. For example, for silver particles of 5-nm

diameter dispersed in glass, the peak height correction may be about 60% [31]. Furthermore, metal clusters smaller than 1 nm cannot contribute to the SPR absorption. In particular, in the case of sample Lz (Fig. 12a), it can be supposed that the considerable decrease in copper signal height is due to the small copper particle dimensions. In fact, by both SAXS and TEM measurements, it has been observed that copper nanocrystals are smaller than the silver ones.

Several factors, such as the metal concentration, the firing conditions (temperature and annealing atmosphere) and the nature of the matrix have been found to influence the lustre formation.

As concerns the firing conditions, both temperature and annealing time can influence the metallic film features, at a given temperature. In fact, increasing both these two parameters, the formation of a large number of larger clusters was observed [22, 25], producing an increase of the SPR 440-nm band, attributed to the dissolution of smaller clusters and to the coarsening of the bigger ones. To this purpose, it is interesting to observe the optical absorption spectra acquired from lustre samples characterised by similar metal concentrations, such as Ly, L22g and L8g (Cu/Ag about 0.1, Table 3). Looking at Fig. 12a, it is possible to notice how the SPR Ag band shows an increasing intensity going from Ly to L8g, together with a red shift and increasing broadening. Therefore, it is possible that sample L8g has been fired at a higher temperature or, alternatively, annealed for a longer time, with respect to the other two samples. It is important to stress that the differences observed in the optical absorption spectra correspond to appreciable changes in the lustre colour tone of these three samples. Therefore, we can conclude that starting from the same impasto recipe, i.e. the same Cu/Ag ratio, it is possible to obtain different results by just varying the firing conditions.

It has also been observed [22] that if the temperature is further increased, a decrease of the SPR band occurs, due to the dissolution of Ag clusters. At temperatures above 700 °C, a high metal fraction may volatilise even if a partial metal volatilisation may occur at lower temperature (550 °C) too, increasing the annealing time. In fact, some of the observed majolica shards were characterised by dark and bad-quality lustres, clearly indicating that they had been over-fired. The metal volatilisation was therefore responsible for these bad results.

Also, the annealing atmosphere may influence the cluster dimensions: using a reducing atmosphere, such as that employed for producing lustre films, the relative amount of big clusters was lower than that obtained with air annealing. It is also important to point out that metallic silver cluster formation occurred also when the films were annealed in air, while, on the contrary, copper metal clusters formed only in a reducing atmosphere [22, 32]. Nevertheless, for both colours, the use of a reducing atmosphere helps in obtaining particles of nanometer dimension, i.e. the lustre nanostructure being responsible for the good-quality lustre giving the beautiful iridescent and metallic effects.

Finally, metal concentration is another important parameter influencing the cluster dimensions [22, 24]: the cluster mean size decreases, lowering the metal concentration.

In a previous paper [10], we used small-angle X-ray scattering to investigate the lustre film particle shape, the particle

size distribution (polydispersity), the mean particle radius, the interparticle distance and the packing density. In fact, by means of the SAXS technique, it is possible to investigate lattice distances having a size of the order of 10–100-times the interatomic distances, typical of colloids and consequently of lustre films. SAXS measurements confirmed that the lustre films consisted of nanoparticles having generally a mean radius ranging from 14 to 30 nm, the copper particles generally being smaller than the silver ones [10]. An interesting parameter, which can be easily determined by SAXS measurements, is the polydispersity (g_y). For example, sample Lz is characterised, with respect to the other samples, by a high value of g_y , by a small average particle radius and a high Cu/Ag ratio, but, in the optical absorption spectrum, only the silver SPR band can be observed, giving rise to a gold colour. Therefore, it can be assumed that the very small copper nanocrystals are present, whose SPR band has such a low intensity, that do not contribute to the colour.

A direct observation of metal nanoparticles has been performed by SEM–EDX–BSE. Silver particles having dimensions ranging from 30 to 100 nm have been observed (Fig. 13a). As silver particles generally have a higher dimension than the copper ones, sometimes they are enough large to be observable by SEM.

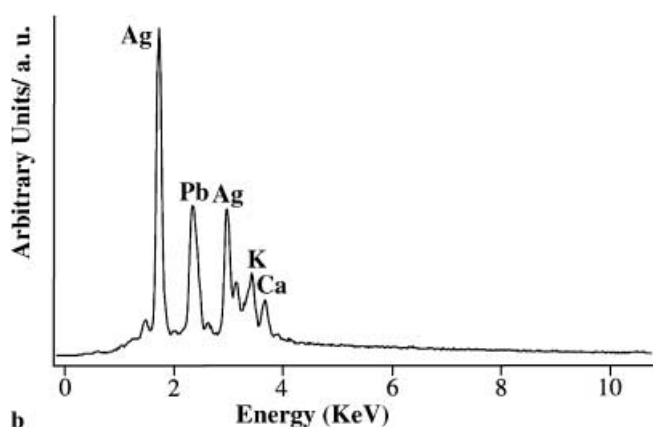
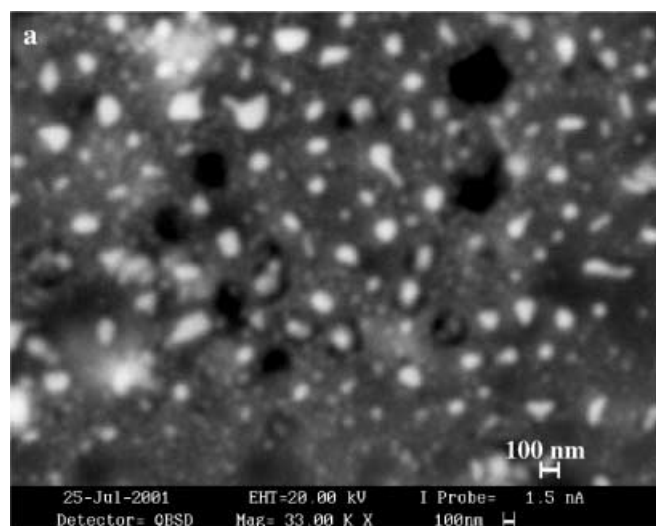


FIGURE 13 SEM–BSE micrograph acquired from the surface of a gold lustre sample and showing the presence of nanoparticles (a); SEM–EDX spectrum acquired from the nanoparticles (b)

TEM analyses, too, have evidenced the presence of both silver and copper nanoparticles inside a quite thin region ranging from about 70 nm to about 2 μm . It is difficult to define an average thickness for the lustre layers as they are quite heterogeneous. Some examples of lustre films are shown in Fig. 14a and b.

The TEM image reported in Fig. 14a has been acquired from a ruby-red lustre while the image of Fig. 14b has been acquired from a gold lustre. In the first case, it has been found from EDX analysis that the nanoparticles are mostly of copper, while in the second case (Fig. 14b) the particles are mostly of silver. In both cases, the particle size is quite variable (5–25 nm for copper particles and 5–50 nm for silver particles); both particle dimensions and density are higher toward the outermost layer.

It is interesting to note that the observable particles have a spheroidal form, as already supposed from SAXS analyses [10].

The metallic nature of the nanoparticles has been confirmed by selected-area electron diffraction (SAED) patterns. Two examples of SAED patterns acquired from copper particles are shown in Fig. 15a and b. The structure identified is the face-centred-cubic (fcc) arrangement, typical of metallic copper with a cell parameter of 3.60 Å. In Fig. 15b, the polycrystalline ring pattern from metallic Cu is superimposed on the diffuse diffracted intensity from the amorphous silica matrix.

The cell parameter identified for silver particles was 4.0 Å.

In the case of the area shown in Fig. 14a, it has been observed from the SAED pattern (reported in Fig. 16) that both Cu and Ag (spotty) rings are present, suggesting the separation, instead of alloying, of the two crystalline species, as is expected from the copper–silver phase diagram.

In fact the formation of phase-separated aggregates in the Ag–Cu/SiO₂ systems obtained by the sol-gel technique has also been observed [22, 24].

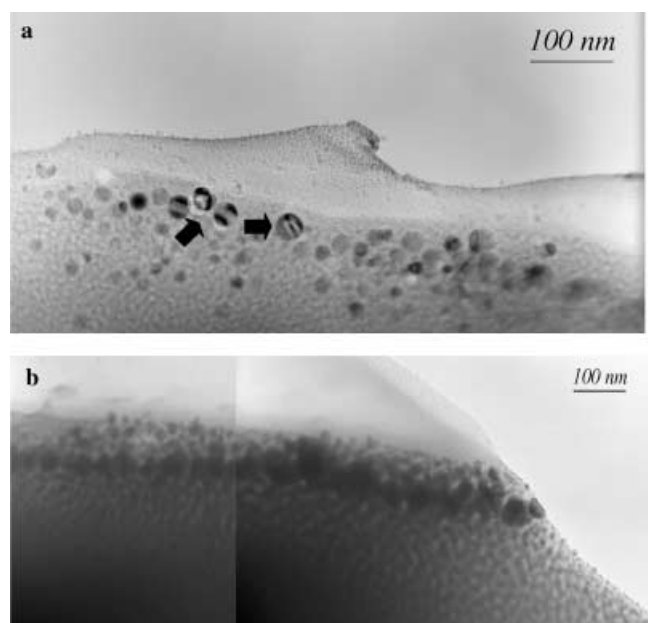


FIGURE 14 TEM images acquired from ruby-red (a) and from gold (b) lustre samples, respectively. The arrows indicate the presence of stacking faults

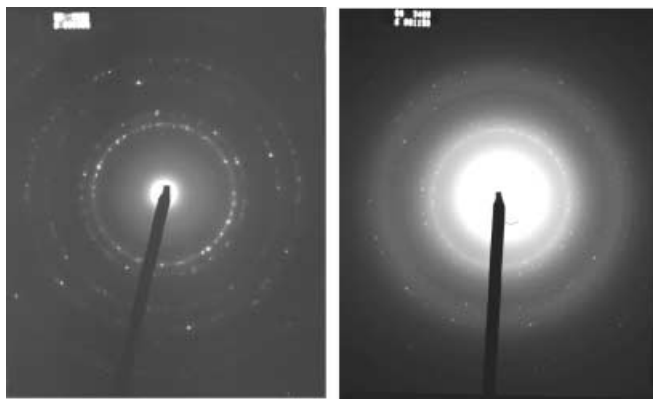


FIGURE 15 SAED patterns acquired from a lustred area showing the presence of metallic copper (fcc arrangement; cell parameter 3.60 \AA) (a); SAED patterns acquired from an area characterised by the presence of both metallic copper (polycrystalline rings) and an amorphous silica matrix (diffuse rings) (b)

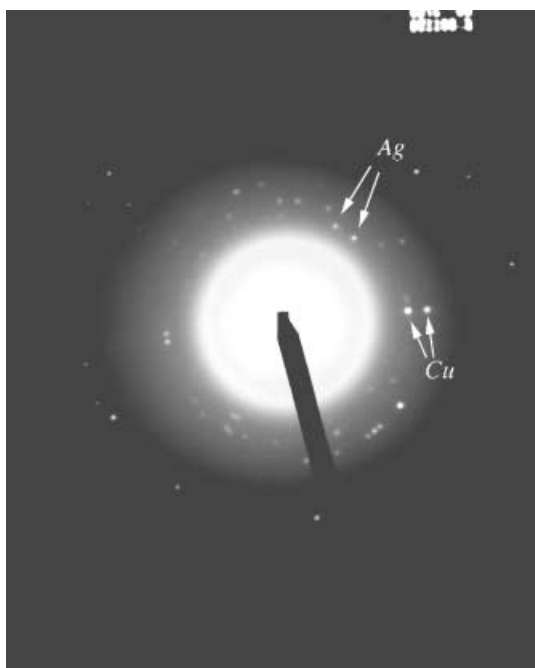


FIGURE 16 SAED patterns acquired from a lustre sample area showing the presence of phase-separated aggregates of copper and silver metallic particles

As for the nanocrystal morphology, it is also interesting to note the presence of numerous multiple twinned particles (MTPs), indicated by an arrow in Fig. 17 and of particles characterised by evident stacking faults, indicated by arrows in Fig. 14a and by double arrows in Fig. 17. Both these structures (MTPs and stacking faults) are quite common in nanometer-sized particles and are well documented in the literature [33, 34]. The study of particle shape in the nanometer size regime is of great importance for developments in nanotechnology. A high surface tension, together with a high constriction due to the presence of the matrix where the crystals nucleate, have to be taken into account to explain the formation of the faults.

The case of MTP particles which are formed by five tetrahedra, bounded by $\{111\}$ planes and twin-related to one another to form a decahedron (Fig. 17, inset), very common in the case of metals with a fcc arrangement like copper, sil-

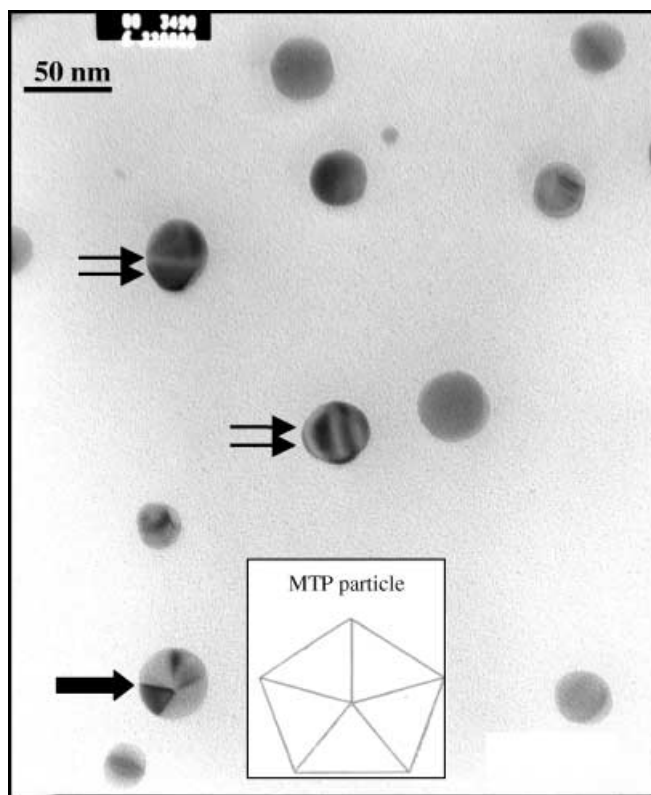


FIGURE 17 TEM image acquired from a lustre sample area where both MTPs (multiple twinned particles) (indicated by an arrow) and stacking faults (indicated by double arrows) are present; in the inset, the decahedron structure typical of MTPs is shown

ver or gold, is very interesting. Pentagonal symmetry such as that typical of the decahedron is energetically favourable as it allows the nanocrystallites to have facets along the lattice planes [34]. It is worth noting that the dimensions of the MTPs observed in the lustre layers are in good agreement with the dimension reported for such particles in the literature [36]. The temperature range more suitable for the growth of these crystals depends on the metal and seems to vary from room temperature to about $400 \text{ }^\circ\text{C}$. For example, in the case of gold particles [35] at temperatures above $400 \text{ }^\circ\text{C}$, only a few twinned particles are found and normal particles mainly grow up. As in the case of lustre films, the firing temperature is about $650 \text{ }^\circ\text{C}$, and very few MTPs are to be expected, as has actually been observed. The presence of faulted particles depends on the metal concentration too: in fact, if a high particle density is present (as in the case of the lustre film reported in Fig. 14b), the growth of the particles is favourable and small crystals touch each other and coalesce by surface diffusion to form large crystals ($> 50 \text{ nm}$), generally free of twins [33]; in this way a continuous film is formed.

As concerns the relation between the lustre chemical composition and the nanostructure, it has been observed that if the metal concentration increases, generally both the particle dimensions and the particle density increase [24]. To this end, we have compared two red lustre films, such as L8r and L22r, characterised by different Cu percentage values (0.025% and 0.049% respectively). The higher Cu value is associated with

higher packing density and particle dimension, observed by TEM images (not shown).

TEM–EDX analyses acquired from the outermost portions of the lustre layers show that the lead content is lower than that found inside the glaze, as has been already observed by XPS analyses [8].

Another interesting observation made by TEM–EDX analysis concerns the assessment of the carbon to oxygen ratio. For example, in one of the examined samples it has been found that the C/O ratio varies from about 16 to 0.1, going from the outermost layer (lustre) towards the inner layer (glaze). This allows us to acquire information on the annealing atmosphere during lustre firing and it confirms the presence of a strongly reducing atmosphere, as reported in the ancient recipes [4].

4 Conclusions

A study of lustre, one of the most sophisticated techniques for the decoration of majolicas during the Renaissance period, has been carried out. Lustre is the very thin outermost decorative layer consisting of silver and copper nanoparticles, which are responsible for the beautiful metallic and iridescent effects.

The analysed glazes show a composition typical of lead-alkali glazes commonly used for the production of lusted majolicas.

The colour, and consequently the optical absorption spectra, depend not only on the metal concentration but also on the particle size, which is influenced by the technical conditions employed in the lustre production.

Both TEM and SAXS analyses have shown that the copper and silver nanoparticle dimensions range from about 5 to 100 nm, the copper particles having smaller dimensions than the silver.

By TEM analysis, growth faults, such as multiple twinned particles and stacking faults, typical of metallic nanoparticles, were evidenced. Generally, the gold colour is associated with the presence of silver together with copper, whilst the ruby-red colour could be associated with the presence of copper only. However, this general assumption presents several exceptions, which have been previously discussed.

The differences encountered in the lustre and glaze chemical compositions (i.e. Cu/Ag ratio) suggest experimentation with different recipes.

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