



A novelty for cultural heritage material analysis: Transmission Electron Microscope (TEM) 3D electron diffraction tomography applied to Roman glass *tesserae*

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ABSTRACT

We present a novel electron diffraction technique (Automated precession 3D diffraction tomography - ADT) based on a Transmission Electron Microscope (TEM) to precisely determine unit cell parameters, Space Group symmetry and atomic structure of various pigment/opacifier crystallites of submicron dimensions and commonly present in colored Roman glass *tesserae*. Such technique can operate at nanometer scale and it is possible to distinguish even between mineralogical phases of similar/same chemical composition, but different crystal structures.

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1. Introduction

The scientific study of colors and constituent materials in ancient glasses, ceramics, decorated pottery etc., is an issue of great importance in archaeometric research due to its association with manufacturing and production information and finally to the so-called *chaîne opératoire* choices and processes.

To tackle the above issues, the field of archaeometry makes use of the analytical information of an array of instrumentations, (e.g. X-ray Fluorescence (XRF), Raman spectroscopy, X-ray Diffraction (XRD), Secondary Image Mass Spectrometry (SIMS) or Electron Probe Microscopy Analysis (EPMA)); in all such techniques when the research aims are towards the study of the various phases and their association to the final coloration there is lack of straightforward answers due to the

complexity and heterogeneity of the historical materials exhibit. All the previous mentioned analytical techniques operate only at 1–0.3 micron resolution scale, where the acquired data are usually not conclusive due to the possible co-existence of many (nm size) phases present and probably interfering within the analyzed (micron size) volume; as a result, data/signals coming from a particular crystal location may in fact be influenced from a number of other surrounding crystals contribution.

Archaeological glass is an overall homogeneous material and even small fragments may generate secure results for the chemical composition of a finished product. However, glass mosaic *tesserae* and especially the opaque ones, are often complex in nature; several phases can be identified in the glass matrix of a single specimen. Mosaic *tesserae* were cut from various materials including glass; the advantages of using glass versus stone or ceramic material being the ability to offer a range of colors and a glittering quality which could heighten bold contrasts in pictorial representations. Though the earliest evidence for the

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use of glass *tesserae* was identified on the Greek island of Delos, dating back to the second century BC [1], their widespread use in mosaics is significantly noticed as of the mid-first century AD and onwards [2]. Hellenistic till Late Roman glass *tesserae* was a soda-lime-silica base glass, having initially antimony-based opacifiers while tin based opacifiers initially introduced during the second century BC and gradually prevailed by the Late Roman/Early Byzantine period. In addition, calcium phosphate was occasionally used since then and onwards. By adding opacifying agents and with the combination of coloring elements, such as iron, copper, manganese and cobalt, a very wide range of colors was achieved [3].

A large collection of Late Roman colored mosaic glass *tesserae*, excavated in 2008 at the sanctuary of Isis and Sarapis, within the archaeological site of ancient Messene (Peloponnese, Greece) was analyzed by SEM/EDS aiming at the characterization of its base glass composition and pigments [4]. The *tesserae* studied within the present work, cover the yellow and blue colors while their composition and structure is representative of the Late Roman glass *tesserae* technology [3,4]. The aim of the present work is to exploit a novel TEM and electron diffraction (ED) based technique (Fig. 1), which allows obtaining accurate information regarding the crystal structure of the pigments/opacifiers of the glass mosaics and more specifically the study of their composition, crystal structure and its relationship with the glass matrix.

2. Materials and methods

2.1. Sample preparation

Three different thin/electron beam transparent lamellae (4×4 micron size and approximately 100 nm thick) were removed by using the Focused Ion Beam (FIB) sample preparation technique (Fig. 1S). Those three slices were FIB cut using Ga ions, during a time-consuming process, from larger *tesserae* fragments having yellow, deep blue and light blue colors. All samples were lifted out from FIB to specific TEM grids for subsequent observation and examination. For SEM observation and EPMA analysis several typical SEM slab containing

various colored *tesserae*, embedded in epoxy resin and carbon coated, were examined (Fig. 2).

3. Technique and instrumentation

For FIB specimen preparation the FEI Dual Beam Helios NanoLab 600 was used at LMA Zaragoza using Ga + ions source at 30 keV. For electron diffraction tomography experiments, a TEM Jeol 2010 LaB6 (200 keV) was used equipped with “spinning star” precession system [5] at the University of Patras. TED EDS measurements were performed with TEM Jeol 2100F equipped with Jeol Centurio detector at Si Map Grenoble University. SEM measurements were performed at the University Rey Juan Carlos Madrid (model Philips XL30-EDAXdax). Polished glass cross sections were analyzed by EPMA using a JEOL JXA-8230 at the Science and Technology Centres of the University of Barcelona. The measurement conditions were 20 keV, at 15 nA probe current, a spot size of ca. 2 μm , and a counting time of 20s per element. The calibration standards used were: hematite (Fe, LIF, $K\alpha$), rutile (Ti, PET, $K\alpha$), periclase (Mg, TAP, $K\alpha$), rhodonite (Mn, LIF, $K\alpha$), Al_2O_3 (Al, TAP, $K\alpha$), metallic antimony (Sb, LIF, $L\alpha$), metallic tin (Sn, LIF, $L\alpha$), diopside (Si, TAP, $K\alpha$), CuO_2 (Cu, LIF, $K\alpha$), wollastonite (Ca, PET, $K\alpha$), metallic silver (Ag, LIF, $L\alpha$), metallic cobalt (Co, LIF, $K\alpha$), albite (Na, TAP, $K\alpha$), orthoclase (K, PET, $L\alpha$), galena (Pb, LIF, $L\alpha$), AgCl (Cl, PET, $K\alpha$) and celestine (S, PET, $K\alpha$). Point analyses and elemental maps were performed directly on the carbon-coated surface of the sample on selected spots in order to probe both the glaze and the pigments. TEM EDS spatial resolution was of range of 3–5 nm (in our case) although EPMA spatial resolution was 1 μm . On the other hand, EPMA compared to EDS provides much better energy resolution for the selected fluorescent emission lines (5–20 eV vs 130–150 eV for TEM-EDS). Therefore it was very useful in our study to combine high spatial resolution EDS-TEM with high energy resolution EPMA to study crystals composition. Information on the accuracy and detection limits of EPMA is given in Table 4S.

The novel TEM based technique called ADT (Automated precession 3D diffraction tomography) has been employed to analyze nm size crystal structures embedded in ceramic/glass matrix. The technique consists of collecting and processing 3D ED data from single nanocrystals [6] and is based on sampling the reciprocal space for the examined crystal in small steps (usually 1° tilt) without any prior information on the structure and orientation of such crystal. The only essential requirement is that the data should be collected from the same crystal, in such a way that large numbers of ED reflections are typically recorded through a tilt around an arbitrary axis. This way, the 3D reciprocal volume of the given crystal can be reconstructed where diffraction tomography data

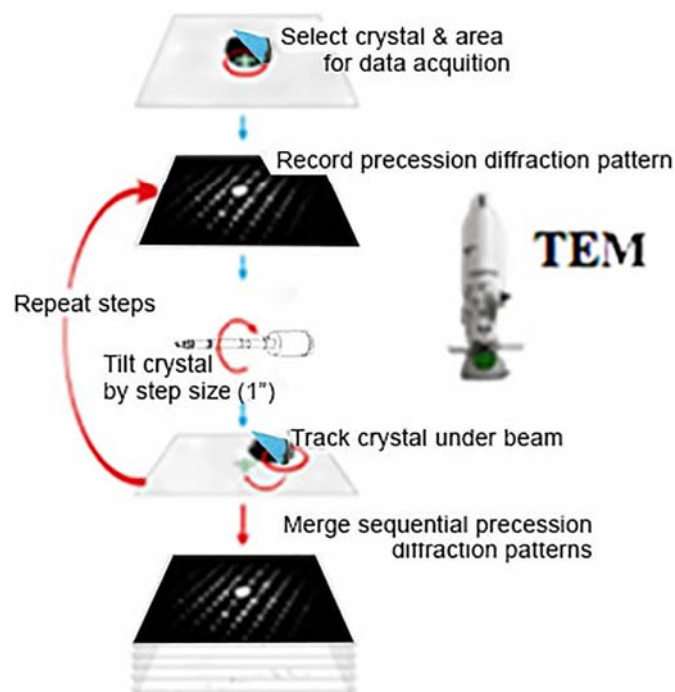


Fig. 1. Set-up for automated 3D precession electron diffraction tomography (ADT) in the TEM.

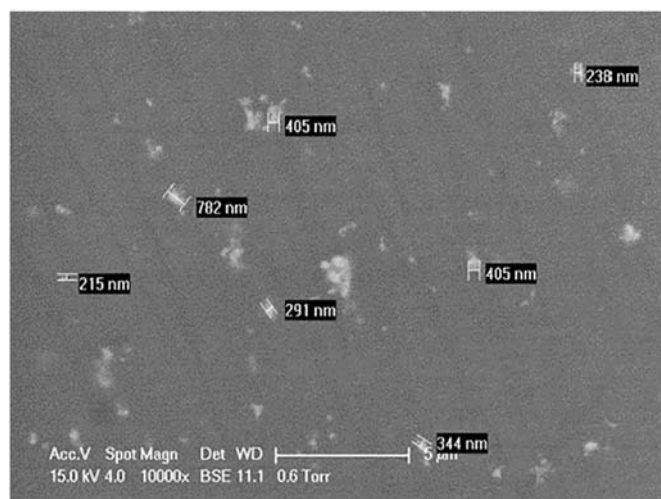


Fig. 2. SEM image of the yellow tesserae showing glass matrix with 200–400 nm precipitates (opacifiers/pigments).

contains nearly all reflections present in the covered wedge of reciprocal space.

ADT diffraction tomography can be performed in any TEM using a standard single tilt or tomography holder. An efficient sampling depends on the crystal symmetry: the higher the symmetry the smaller the minimum required angular range. In general, a tilting range of the specimen from -60° to $+60^\circ$ along the goniometer axis with a tilting step of 1° is an optimal compromise; this way, a total tilt wedge of 120° can be recorded, providing 121 diffraction patterns which are usually enough for unit cell, symmetry and crystal structure determination.

On the other hand, precession electron diffraction (PED) has been developed the last years as technique to solve crystal structures as renders ED intensities with less dynamical effects [7,8]. This method is based on the precession of the incident electron beam, which is inclined away from the optical axis of the TEM and precesses on a cone surface having the vertex fixed on the sample. Due to beam precession, (usually applied at 1° semi-angle) reflection intensities are integrated over diffraction conditions that are far from perfect zone axis orientation, therefore dynamical effects in PED patterns are highly reduced. The use of PED reflections in combination with ADT tomography is important because symmetry related ED intensities are easily revealed helping significantly to symmetry (Space Group) determination. Therefore, PED intensity comparison between possibly symmetry related ED reflections allows to distinguish between crystals having similar unit cell but different crystal symmetries. In addition, during crystal tilt in ADT (-60° to $+60^\circ$), the use of PED (at 1° semi-angle) helps to recover more reliable “quasi-kinematical” ED reflections intensities of reciprocal space sections taken every 1° tilt step as 3D diffraction tomography sweeps through the reciprocal space of the crystal under examination. Use of such quasi-kinematical PED intensities is essential also to solve crystal structures at atomic scale [8].

4. Results and discussion

4.1. Yellow tesserae

In this work we analyzed FIB lamellae from different colored glass tesserae (yellow, deep and light blue). Regarding the yellow color sample, SEM examination study revealed the presence of small precipitates (200–400 nm) embedded in an amorphous glassy matrix (Fig. 2).

We performed ADT analysis on 3 different crystallites and reconstructed reciprocal space as shown in Fig. 3a and b respectively. For ADT analysis, TEM goniometer was tilted about $\pm 80^\circ$ to collect $\times 160$ ED patterns for every 1° of tilt from every crystallite. Symmetry and extinction rules analysis of $\times 3$ ED dataset intensities for all 3 analyzed crystallites were consistent to a cubic cell with Fd-3m symmetry (Fig. 3c) and cell parameter ($a = 10.53 \text{ \AA}$, $\alpha = \beta = \gamma = 90^\circ$).

The TEM EDS mapping shows that crystallites contain Sb, Pb and O as major elements, however the presence of Cu, Fe, S, Na and Mn was also detected (Fig. 2S). A detailed search in the COD (Crystallography Open Database [9]; of possible compounds having a similar cubic unit cell of $a = 10.53 \text{ \AA}$ ($\pm 2\%$), Fd-3m symmetry and containing (at least some) of the elements found by TEM EDS mapping, led to the unique solution that corresponds to **Pb₂Sb₂O₇** compound; Yellow lead antimonate has a long history, in particular regarding its use as a glaze colorant and opacifier in Egypt and Mesopotamia in the 2nd millennium BC [10]; this compound is one of the earliest artificial pigments, and was also used as a colorant and opacifier in the Roman world [11].

A more detailed structure determination was performed with Endeavour software [12] which uses combined global optimization of the difference between calculated and measured ED intensities and global optimization of the energy potential system (simulated annealing); having as input the 315 ED reflections found from ADT

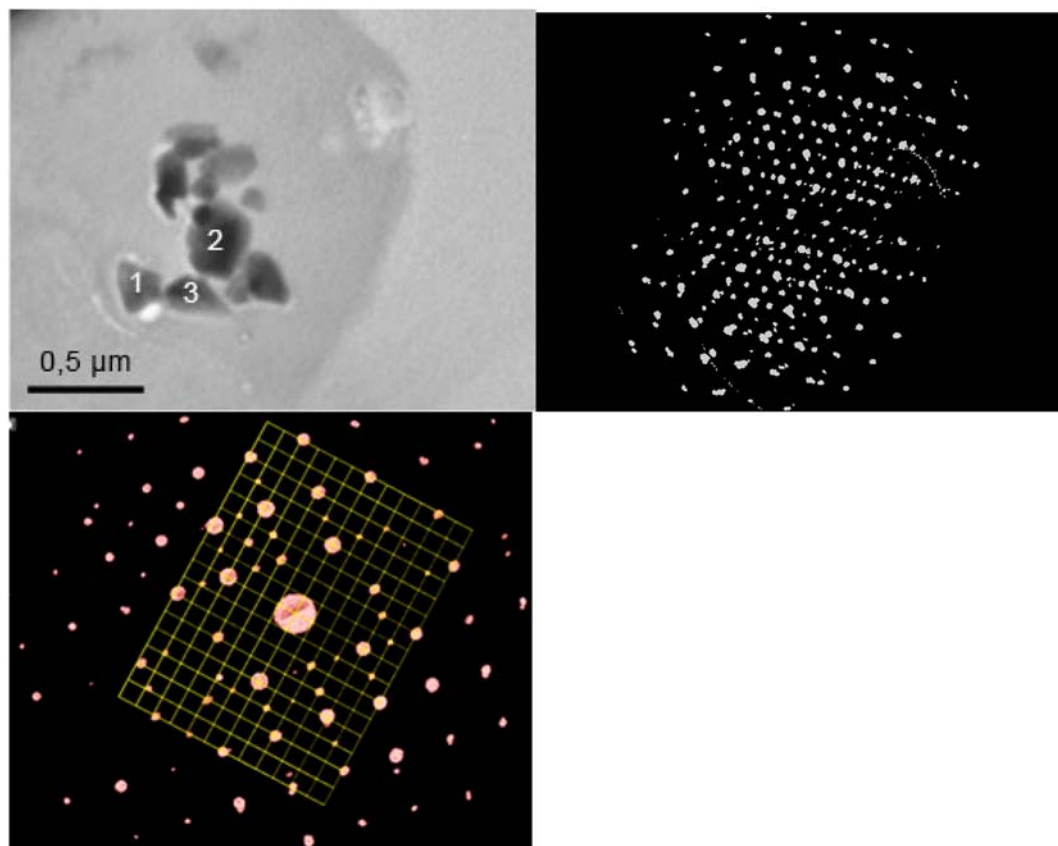


Fig. 3. (Clockwise). Yellow tesserae (a) FIB thin slice of yellow tesserae containing several pigment/opacifier crystals (crystals 1, 2 and 3 selected for ADT diffraction tomography) (b) reconstructed 3D diffraction volume of $\text{Pb}_2\text{Sb}_2\text{O}_7$ opacifier obtained by ADT (c) reciprocal space projection of the cubic structure unit cell along main a^* direction.

experiment, Fd-3m symmetry and **Pb₂Sb₂O₇** as chemical formula, Endeavour led to the determination of all Pb, Sb and O atomic positions of the structure (Fig. 4, Table 1). From those analyses, we conclude that the **Pb₂Sb₂O₇** yellow lead antimonite may contribute to the yellow color of the tesserae (Table 1), (Fig. 4).

On the other hand, a closer look at the EPMA analysis data, confirms the presence of Pb, Sb and O in the crystallites in addition to minor amounts of Cu, Fe, S, Na and Mn (Table 1S). Since Cu, Fe, S, Na and Mn are also present not only within the opacifying crystallites, but also in the composition of the glass matrix (Table 1S) and due to the fact that the **Pb₂Sb₂O₇** structure type is of pyrochlore, we assume that the pigment/opacifier accommodated minor amounts of Fe, Cu and Mn in the main framework. These elements have been introduced as a result of an ionic exchange between the pigment and the glass matrix during the firing process. Ion substitution in pyrochlores through ionic exchanges is well known in solid state chemistry and is used in modern material science applications [13].

4.2. Deep blue tesserae

Regarding the deep blue color sample, SEM examination studies reveal the presence of large crystals (1.3–2 μm) embedded in an amorphous glass matrix. (Fig. 5) are responsible of the glaze coloration. We examined with ADT analysis on 3 different crystallites (Fig. 6a) and reconstructed its reciprocal space (Fig. 6b). TEM goniometer was tilted about ± 70° to collect × 140 ED patterns for every 1° of tilt, for each crystallite. Symmetry and extinction rules analysis of 3 ED dataset intensities from all 3 different crystallites were consistent with hexagonal unit cell having P-31 m symmetry (Fig. 6c) and cell parameter ($a = b = 5.24 \text{ \AA}$, $c = 5.02 \text{ \AA}$, $\alpha = \beta = 90^\circ$, $\gamma = 120^\circ$). TEM EDS mapping shows that crystallites contain Ca, Sb and O as principal elements, whereas presence of Mn was also detected in (Fig. 3S).

A detailed search in the COD Database of possible compounds having similar hexagonal unit cell ($a = b = 5.24 \text{ \AA}$, $c = 5.02 \text{ \AA} (\pm 2\%)$, P-31m symmetry and containing (at least some) of the elements found by TEM EDS mapping, led to the unique conclusion that the sample corresponds to **CaSb₂O₆**. This material is well known as white color pigment/opacifier since ancient times [11–14].

In addition, a detailed structure determination with simulated annealing (Endeavour software) having as input 327 ED reflections as

Table 1

Atomic positions of **Pb₂Sb₂O₇**, determined using simulated annealing.

1	Pb	0.62500	0.62500	0.62500
2	Sb	0.12500	0.12500	0.12500
3	O ₁	0.3129	0.00000	0.00000
4	O ₂	0.00000	0.00000	0.00000

extracted from ADT data collection, P-31m symmetry and **CaSb₂O₆** chemical formula, led to determination of all Ca, Sb and O atomic positions in the structure (Fig. 7).

A closer look at the EPMA analysis data, besides the presence of Ca and Sb, the presence of minor quantities of Al, K, Fe, Mg and Mn in the crystallites are also revealed (Table 2S). Since Al, K, Fe, Mg and Mn are also present in the glass matrix and the **CaSb₂O₆** structure is also a pyrochlore related type, we assume that crystallites can accommodate minor amounts of Fe, Mg, Mn in the main crystal framework though an ionic exchange between the pigment and the glass matrix at high firing temperatures as observed with the yellow tesserae. As **CaSb₂O₆** corresponds to a white color pigment the observed deep blue color of the tesserae is likely due to the presence of Co in the glass matrix as revealed by EPMA (0.82–1.11 wt% approx.).

4.3. Light blue tesserae

For the light blue color sample, SEM examination study revealed the presence of large precipitates (2–5 μm) embedded in an amorphous glassy matrix. As in the case of deep blue sample, the presence of such large crystallites (Fig. 8) act as pigments and are responsible for glass coloration. We performed ADT analysis on 3 different crystallites (Fig. 9a) and reconstructed its reciprocal space (Fig. 9b). TEM goniometer was tilted about ± 70° to collect × 140 ED patterns for every 1° of tilt, from each crystallite. Symmetry and extinction rules analysis of 3 ED dataset intensities from all 3 different crystallites was consistent with cubic unit cell having Fd-3m symmetry and cell parameter ($a = b = c = 10.26 \text{ \AA}$, $\alpha = \beta = \gamma = 90^\circ$) (Fig. 9c) (Fig. 10).

The TEM EDS mapping shows that crystallites contain Ca, Sb and O as major elements, but presence of Cu, Fe, Mn and Na was also detected (Fig. 4S). A detailed search in the COD Database of possible compounds having similar cubic unit cell ($a = 10.26 \text{ \AA} \pm 2\%$), Fd-3m symmetry and containing (at least some) of the elements found by EDS TEM mapping, led to the unique solution that the compound corresponds to **Ca₂Sb₂O₇** which is also a known white pigment/opacifier in antiquity [11–14].

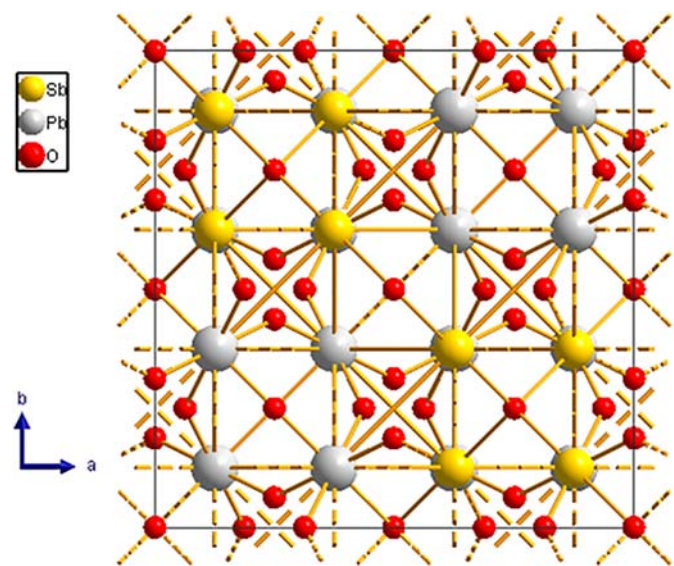


Fig. 4. Yellow tesserae: schematic representation of a cubic crystal structure projection of **Pb₂Sb₂O₇** opacifier obtained with simulated annealing from 315 3D reflections intensities and having Pb, Sb and O atomic positions. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

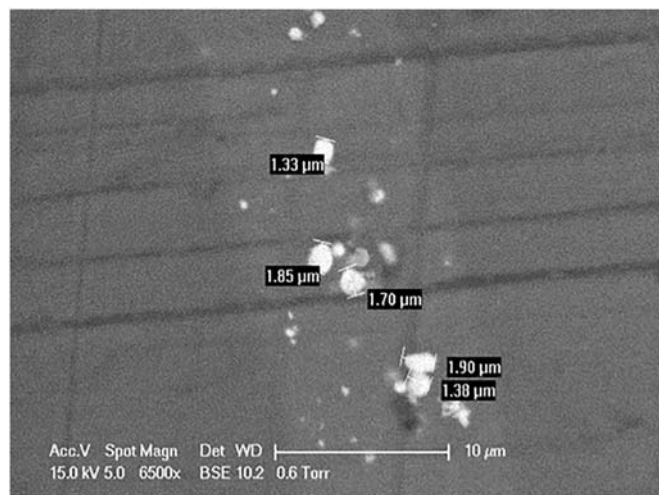


Fig. 5. SEM image of deep blue tesserae showing glass matrix including 1–2 μm precipitates (pigments/opacifiers).

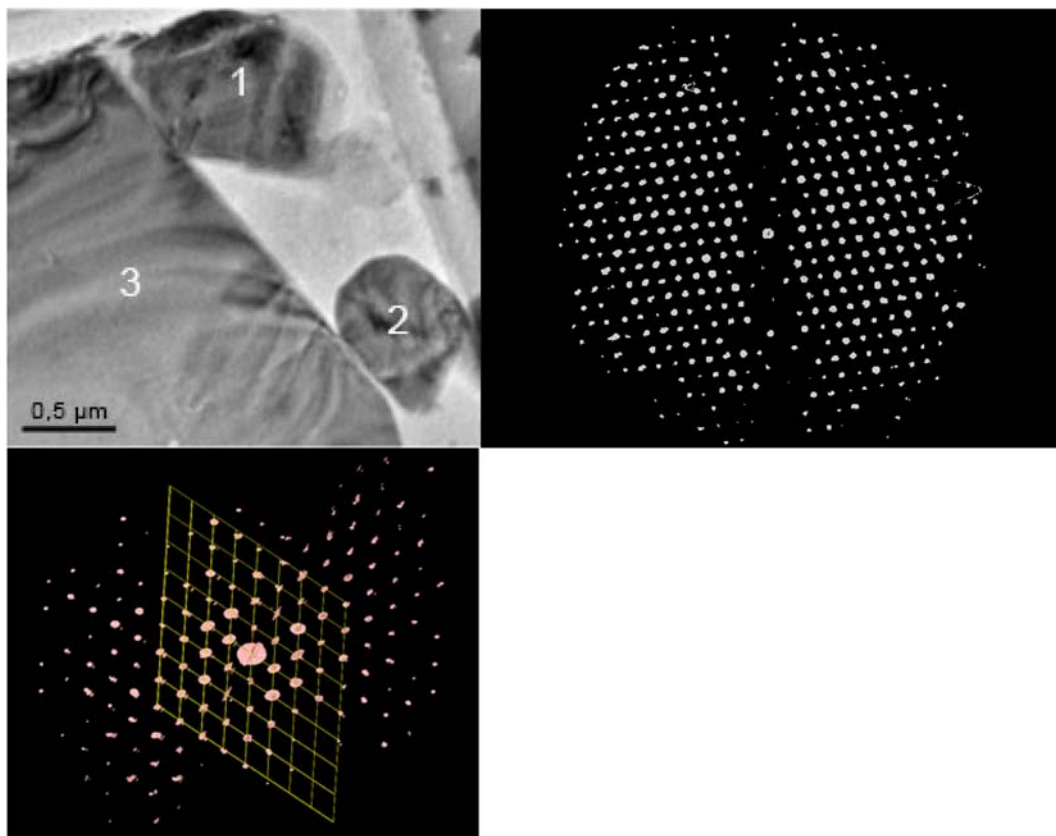


Fig. 6. (Clockwise). Deep blue sample (a) FIB thin slice of deep blue tesserae containing several large pigment/opacifier crystals (crystals 1, 2 and 3 selected for ADT diffraction tomography) (b) reconstructed 3D diffraction volume of CaSbO₆ opacifier obtained by ADT (c) reciprocal space projection of the hexagonal unit cell along main c* direction.

Crystallographic structure determination with simulated annealing (Endeavour software) having as input 2061 ED reflections from ADT experiments and **Ca₂Sb₂O₇** chemical formula, led to determination of all Ca, Sb and O atomic positions in the structure. The EPMA data analysis, confirms the presence of Cu, Fe, Mn and Na in the crystallites as well in the glass matrix (Table 3S). As the **Ca₂Sb₂O₇** structure is also of pyrochlore type, it can accommodate other cations (like Fe, Cu) in the main framework that can enter the structure at high temperatures through ionic exchanges.

As in the previous sample, the light blue color of the tesserae may occur due to the presence of Co in the glass matrix as revealed by

Table 2

Atomic positions of CaSb₂O₆ determined using simulated annealing.

1	Ca ₁	0.00000	0.00000	0.00000
2	Sb ₁	0.33333	0.66667	0.50000
3	O ₁	0.36800	0.00000	0.2951

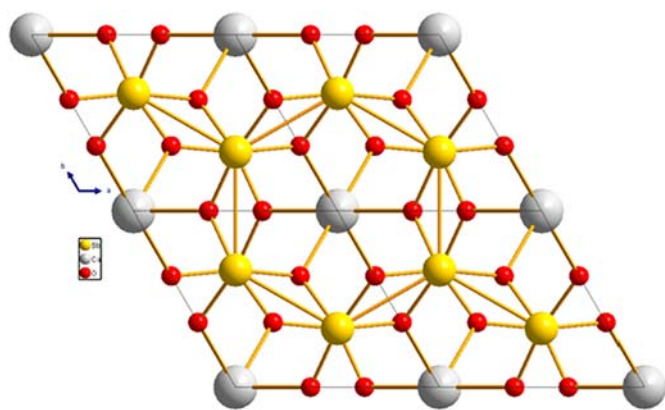


Fig. 7. Deep blue tesserae: schematic representation of a hexagonal crystal structure projection of CaSb₂O₆ opacifier obtained with simulated annealing from 327 3D reflections intensities and having Ca, Sb and O atomic positions.

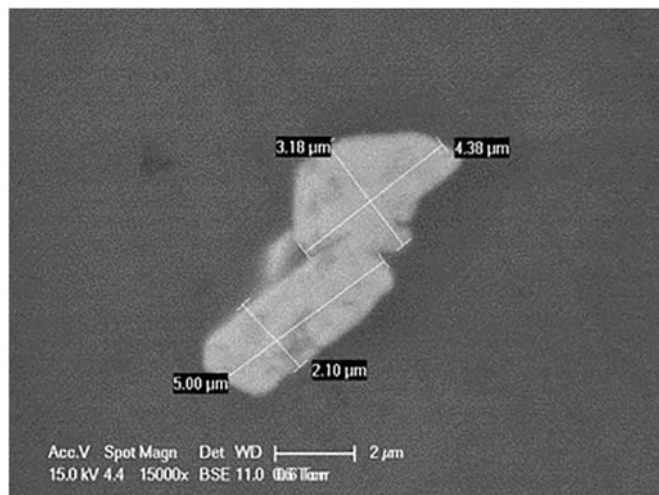


Fig. 8. SEM image of light blue tesserae showing glass matrix with micron size precipitate (pigment/opacifier).

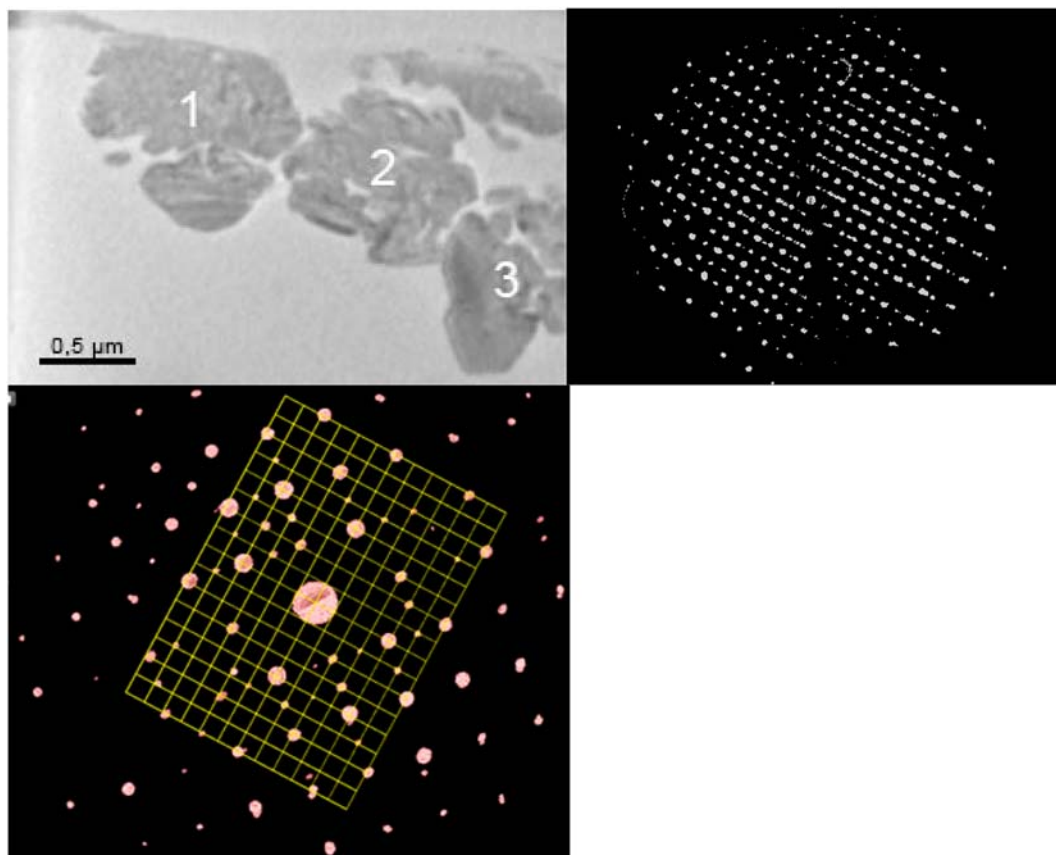


Fig. 9. (Clockwise). Light Blue tesserae a) FIB thin slice of light blue tesserae containing several large opacifier crystals (crystals 1, 2 and 3 selected for ADT diffraction tomography) (b) reconstructed 3D diffraction volume of $\text{Ca}_2\text{Sb}_2\text{O}_7$ opacifier obtained by ADT (c) reciprocal space projection of the cubic unit cell along main c^* direction.

EPMA (0.23–0.41 wt%) and not from the pigment itself. However, its concentration is lower than the deep blue tesserae, which could explain the less intense blue color saturation.

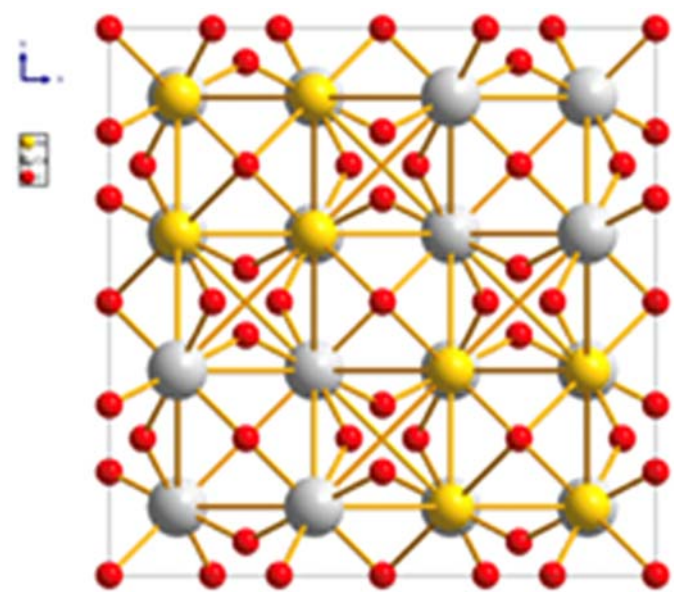


Fig. 10. Light blue tesserae Schematic representation of a cubic crystal structure projection of $\text{Ca}_2\text{Sb}_2\text{O}_7$ opacifier obtained with simulated annealing from 2061 3D reflections intensities and having Ca, Sb and O atomic positions.

5. Concluding remarks

The introduction of novel precession electron diffraction tomography technique (ADT) in the field of cultural heritage allows to obtain very precise crystallographic data (unit cell, symmetry and atomic positions) of different phases that may exist in ancient glass and pottery. This technique can be used easily in any TEM (100–300 kV) having sufficient angular tilt ($\pm 45^\circ$), precession electron diffraction hardware, and 3D electron diffraction tomography software. Although TEM has been scarcely used for archaeometry studies [15].

Our work stands as one of the first in the field of cultural heritage studies [16] that makes use of PED 3D electron crystallography tomography techniques to finely distinguish between different crystal structure phases present in a glass. Such analysis can be performed at nm scale and it has strong advantages over conventional analytical techniques like e.g. XRF, Raman, XRD, or EPMA which lack spatial resolution (micron instead of nm probe size) over the analyzed volume area. On the other hand SIMS may reach $10\ \mu\text{m}$ – $10\ \text{nm}$ resolution and map elements in crystallites [17] at nm scale but cannot identify crystal structure of individual crystallites. Using ADT technique it has been possible to precisely distinguish in opaque, colored Roman tesserae between different pigments/opacifiers having similar/same chemical

Table 3
Atomic positions of $\text{Ca}_2\text{Sb}_2\text{O}_7$ determined using simulated annealing.

1	Ca	0.12500	0.12500	0.62500
2	Sb	0.12500	0.12500	0.12500
3	O ₁	0.31120	0.00000	0.00000
4	O ₂	0.00000	0.00000	0.00000

composition, but different crystal structures. The accurate crystallographic structure of the phases that are present in a glass may be important in order to establish e.g. precise firing conditions, as different phases are formed at different temperatures.

We revealed also that each type of pigment/opacifier in the studied colored tesserae has a pyrochlore related type crystal structure which may host additional cations like Fe, Cu and Mn within the structural framework through ionic exchanges that may happen at high firing temperatures during glass melting. On the other hand, the question of how the overall glass color can change as result of the opacifier crystals hosting other elements (e.g. Copper in Pb₂Sb₂O₇ crystals in yellow glass) is a complex issue beyond the scope of our work. A recent review information on color glass change as result of element substitution in crystals can be found at [18]. The study presented herein is a part of a wider research towards shedding light into the structural origin of wide palette of colors used in the Ancient World.

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.microc.2017.12.023>.

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