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Unraveling the role of lattice substitutions on the stabilization of the intrinsically unstable Pb₂Sb₂O₇ pyrochlore: explaining the lightfast-ness of lead pyroantimonate artists' pigments

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ABSTRACT: The pyroantimonate pigments Naples Yellow and lead tin antimonate yellow are recognized as some of the most stable synthetic yellow pigments in the history of art. However, this exceptional light-fastness is in contrast with experimental evidence suggesting that this class of mixed oxides is of semiconducting nature. In this study the electronic structure and light-induced behavior of the lead pyroantimonate pigments were determined by means of a combined multi-faceted analytical and computational approach (photo-electrochemical measurements, UV-Vis diffuse reflectance spectroscopy, STEM-EDS, STEM-HAADF and density functional theory calculations). The results demonstrate both the semiconducting nature and the lightfastness of these pigments. Poor optical absorption and minority carrier mobility are the main properties responsible for the observed stability. In addition, novel fundamental insights into the role played by Na atoms in the stabilization of the otherwise intrinsically unstable Pb₂Sb₂O₇ pyrochlore were obtained.

Introduction

Lead antimonate yellow (Pb₂Sb₂O₇), commonly referred to as Naples Yellow, is one of the synthetic yellow pigments most frequently encountered in pre-20th century Western European art¹⁻⁴. The reason behind the appreciation of artists for this pigment lies not only in its intense bright hue and high opacity, but also in its reported lightfastness and overall stability².

Lead antimonate yellow has been lost and rediscovered several times throughout history. After enjoying a great popularity in ancient Egyptian, Mesopotamian and Roman cultures^{2,5,6}, where it was the main yellow colorant and opacifier used in glass and glazes, by the end of the 4th century A.D. the pigment fell into disuse throughout Europe. From that moment on, during the Middle Ages, the utilization of lead antimonate yellow was limited to the Slavonian, Islamic and Byzantine world^{3,7}. Only in the 16th century the pigment returned to Western Europe, reappearing in the Italian art of the beginning of the century. The reasons for the resurgence of interest for this pigment is still not clear. The most likely hypothesis is that the knowhow on the production of lead antimonate was introduced to the

Venetian glass workshops by foreign glassworkers, mostly Arab, during large waves of immigration from the Eastern Mediterranean^{1,3}. Throughout the 16th century, the production of Naples yellow remained intimately related to the glass and ceramic industries⁸. Several recipes from this period of time describe the synthesis of yellow pigments to be used as colorants and opacifiers in glass. However, the complex terminology used in the sources and the tendency to refer to different pigments with the same name of Giallolino created a certain confusion on the topic in the past⁸⁻¹⁰. In 1540, Biringuccio, in his treatise Pirotechnia wrote about the use of antimony in making yellow glass enamels. Few years later, in the late 1550s, Piccolpasso published a treatise on the potter's craft (Li tre libri dell'arte del vasaio), where he reported a series of central Italian recipes for the synthesis of lead antimonate pigments, used to obtain yellow glazes on majolica. The largest concentration of manuscripts containing recipes for the production of this yellow pigment for the glass industry, however, may be found in Venice and Murano $^{1,11-16}$, where the glass manufacture was concentrated. A great amount of examples of the use of Naples Yellow in colored glass and pottery glazes exist in literature^{6,17–23}.

The first reference to Naples yellow as a painting pigment dates back to the early 17th century, when Valerio Mariani da Pesaro (1568-1625?) in his treatise about miniature painting, gives a detailed description of the production of so-called giallo de' vasari (potter's yellow), corresponding to lead antimonate yellow²⁴. Before this time Naples yellow was already but sporadically used by some Italian artists like Giovanni Bellini (1430-1516), Lorenzo Lotto (1480-1556/7), Raphael (1483-1520), and Titian (1490-1576)^{8,25}, that however still preferred the use of other yellow pigments in most of their paintings. In some of these cases of early use of Naples yellow in easel paintings, namely Feast of the Gods by Bellini (1514) and The nativity by Lotto (1523), Berrie²⁵ observed how the lead-antimony mixed oxide is found in the form of crystallites suspended in a siliceous glass matrix. It is not clear if in this case the pigment was produced by grinding of a yellow lead-antimony glass (in a similar fashion as with blue smalt) or if a glassy frit was rather used, but the presence of silicon confirms the close relationship of this pigment with the glass and ceramic industries. The Naples Yellow commonly found in later paintings, however, does not contain silicon, indicating a complete transition from the glass to the easel painting world. Whether embedded in a glass matrix or directly mixed with siccative oil, lead antimonate yellow is always regarded as extremely stable and lightfast².

In the last decade of the 20th century, a variant of Naples Yellow was rediscovered and identified in a series of 17th century Italian paintings²⁶ and 18th-19th century Mid-European paintings²⁷. The new form, called lead tin antimonate yellow, contains tin as an additional cation (Pb₂SnSbO_{6.5}). The effect of the Sn substitution on the overall properties of the material is still unclear, mostly due to the recent rediscovery of this pigment².

From a structural point of view, lead (tin) antimonate yellows belong to the pyrochlore class, a group of cubic compounds described by the general formula $A_2B_2X_6Y$ (where A and B are metals and X and Y are most of the time oxygen atoms, X=O and Y=O')^{28,29}. The "backbone" of this structure is constituted by a network of corner shared octahedra formed by B_2X_6 units. This interpenetrates a second network of A_2Y units, where every oxygen atom is surrounded by four A atoms in a tetrahedral coordination. In the case of lead antimonate $A=Pb^{2+}$ and $B=Sb^{5+}$, while in the case of lead tin antimonate half of the B sites are occupied by Sb⁵⁺ and half by Sn⁴⁺.

The pyrochlore structure tolerates a wide range of substitutions at the A, B and Y sites, as well as vacancies at the A and Y sites, which leads to a large diversity of electrical properties for the compounds belonging to this class²⁸. When it comes to the stability and light-fastness of artistic pigments, these electric properties play a major role. A semiconducting behavior, in particular, is generally associated with a poor stability of the paint film^{30–35}. In the specific case of pyroantimonates with $A=Pb^{2+}$, the information in literature is still very limited. Past authors have even questioned the very existence of a $Pb_2Sb_2O_7$ mixed oxide in the pyrochlore structure^{28,36,37}, suggesting that the lattice would either present a rhombohedral distortion (if the composition is exactly $Pb_2Sb_2O_7$) or a partial substitution of Sb^{5+} in the octahedral sites (stabilizing the cubic structure). The UV-Vis reflectance spectra of Naples Yellow reported in literature^{2,38} seem to suggest a semiconducting behavior for this pigment. A steep absorption edge between 400 and 500 nm is in fact observed, in a similar fashion to other light-sensitive semiconducting pigments such as cadmium yellow (CdS) and chrome yellow (PbCrO₄)^{2,31,33}. This hypothesis is supported by the evidence that other pyroantimonates (e.g. Sn₂Sb₂O₇, Cd₂Sb₂O₇, Ag₂Sb₂O₆) show a semiconducting behavior^{39–42}. With the replacement of Sb⁵⁺ by Sn⁴⁺ (in the B sites) causing an additional shrinking of the conduction band and an increase in the band gap⁴¹. However, the extraordinary lightfastness of lead (tin) antimonate seems incompatible with the hypothesis of a semiconducting nature for this pigment.

Several research questions remain therefore still open when it comes to the stability of this family of pigments. Is pure $Pb_2Sb_2O_7$ actually stable in a pyrochlore structure? What is the explanation for the extraordinary stability of Naples Yellow, given the probable semiconducting nature of the pigment? What is the effect of the Sn⁴⁺ substitution on the optoelectronic properties and on the stability of the material?

With these fundamental questions in mind, in-house synthesized lead antimonate yellow and lead tin antimonate yellow powder samples (further referred to as LAY and LTAY, respectively) were studied by means of a combined multi-faceted analytical and computational approach. The synergic experimental and theoretical strategy allowed to probe the chemical composition, crystalline structure, optoelectronic properties and photochemical behavior of the pigments, leading to fundamental insights on the intimate relationship between their composition and stability.

Experimental section

Synthesis

The LAY and LTAY powders considered in this study were synthetized in-house in the laboratories of the Department of Economics, Engineering, Society and Business Organization of Tuscia University (Viterbo, Italy). The choice of the recipes for the two compounds was the result of an in-depth historical research and laboratory testing described in detail in the work of Agresti^{4,9,43,44}. Agresti et al. considered a wide selection of recipes for the production of Naples yellow, with a particular focus on those by Cipriano Piccolpasso⁴⁵, by Giambattista Passeri (*Istoria delle Pitture in Majolica fatte in Pesaro*, 1758⁴⁶) and by Valerio Mariani da Pesaro^{1,24}. For lead tin antimonate yellow the recipes contained in the Danzica Manuscript¹⁶ as well as the modern recipes described by Cascales et al.⁴⁷ were tested.

The LAY sample selected for this study (sample PSAPZ1 in the PhD thesis of Agresti⁴³ and sample 21 in Agresti et al.⁴) was prepared according to the recipes by Piccolpasso *Zalulino A* and *Castelli A*: Sb 1 lb; Pb 1.5 lb; feccia 1 on; salt 1 on. Where 1 lb (Roman libra) = 327.168 g , 1 on (Roman oncia) = 27.267 g and feccia corresponds to lees. The LTAY sample considered in this study (sample APSA1 in the PhD thesis of Agresti⁴³ and APSA in Capobianco et al.⁴⁴) was synthetized following the optimized recipe and the recommendations in the work by Cascales et al.⁴⁷: molar proportion Pb:Sn:Sb=2:1:1 in the starting oxides. The list of ingredients and the experimental conditions for both the pigments are summarized in Table 1. The pure grade chemicals employed in the synthesis were supplied by Sigma-Aldrich (St. Luis, Missouri), Acros Organics (New York City, New

York) and MP Biomedicals (Santa Ana, California). The reagents were mixed in agate mortars and the obtained powders were put in a kiln on a terracotta tile for 5 hours at different temperatures (Table 1).

	Source	Pb	Sb	Sn	Flux 1	Flux 2	Conditions
LAY	Piccolpasso ⁴⁵	Pb ₃ O ₄ 4.91 g	Sb ₂ O ₃ 3.27 g	-	C4H4K2O6 2.76 g	NaCl 2.76 g	800 °C x 5 h
LTAY	Cascales et al.47	РbО 8.90 g	Sb ₂ O ₃ 2.90 g	SnO ₂ 3.00 g	-	-	925 °C x 5 h

Table 1. Reagents and conditions employed in the synthesis of the LAY and LTAY samples.

Chemical and structural characterization

The samples were examined with a Field Emission Gun-Environmental Scanning Electron Microscope (FEG-ESEM) equipped with an Energy Dispersive X-Ray (EDX) detector (FEI Quanta 250, USA), using an accelerating voltage of 20kV, a take-off angle of 30°, a working distance of 10 mm and a sample chamber pressure of 10^{-4} Pa. Imaging was performed based upon secondary electrons (SE) and back-scattered electrons (BSE). EDX point spectra were acquired using a beam current of ~0.3 nA and a dwell time of 30 s per spectrum. The samples were previously coated with a thin carbon layer in order to obtain a conductive surface.

XRPD (X-Ray powder diffraction) measurements were performed using a Cu anode tube as X-ray source, operated at 40 kV and with 30 mA. The diffracted X-rays were detected by a Huber G670 Guinier camera. Of each sample four repetitions were recorded with a 15 min measuring time each. The obtained diffractograms were summed per sample and further analysed using XRDUA, an in-house software package ⁴⁸.

 μ -RS (micro Raman spectroscopy) spectra were acquired with a Renishaw inVia multiple laser Raman spectrometer with a Peltier-cooled (203K), near-infrared enhanced, deep-depletion CCD detector (576x384 pixels) and coupled to a Leica optical microscope. Raman spectra were collected using an aircooled argon laser (Stellar-Pro 514/50) operating at 514.5 nm wavelength (green) in combination with a 1800 l/mm grating with a maximum laser output power of 50mW. The laser was focused onto the samples through a 50x objective achieving a spatial resolution of a few micrometers. A power density of 1.6 kW/cm² and exposure times of 60 seconds were used. Measurements were repeated on different sample grains. Data acquisition was carried out with Renishaw WiRE 2.0 software.

STEM-HAADF (Scanning Transmission Electron Microscopy with High Angle Annular Dark Field detector) imaging and STEM-EDS (STEM with Energy Dispersive X-ray spectroscopy) spectrum imaging were performed using an aberration corrected FEI Titan 60-300 kV transmission electron microscope operating at an acceleration voltage of 300 kV. An aberration-corrected angstrom-sized probe with an electron probe current of 50 pA was used for atomic resolution imaging and 200 pA was used for EDS maps. For EDS mapping 512 × 512 maps were acquired with a dwell time of 10 µs. Such spectra were acquired cumulatively for 12 minutes. The quantification of the EDS spectra was performed using Cliff-Lorimer method. Independent component analysis (ICA)⁴⁹ of the spectrum images was performed using Hyperspy software.

Optoelectronic properties and photostability

The reactivity and light-induced behavior of the two pigments were studied by means of diffuse reflectance UV-Vis spectroscopy (DR-UV-Vis) and photo-electrochemical methods.

DR-UV-Vis measurements were carried out with an Evolution 500 UV-Vis double-beam spectrophotometer with RSA-UC-40 DR-UV integrated sphere (Thermo Electron Corporation, USA). The pigment powders were mixed with KBr dried at 200°C (0.02 g of pigment powders in 0.98 g KBr) and homogenized in a mortar. The mixtures were then positioned in the DR-UV-Vis cell and measured in the 300 to 800 nm range. The Kubelka-Munk function F(R) was then calculated from the diffuse reflectance results⁵⁰ and used as an approximation of the absorption coefficient α for the pigments considered. An estimation of the band gap energy from the experimental data was performed based on the Tauc relation⁵¹:

$$(\alpha h\nu)^{\frac{1}{n}} = A(h\nu - E_g)$$

where α is the absorption coefficient of the material in m⁻¹, which for small homogenous particles is assumed proportional to F(R) and independent on incident wavelength λ , hv is the energy of the incident photon in eV, n is a constant dependent on the nature of the band gap (n=1/2 for direct allowed transitions, n=3/2 for direct forbidden transitions, n=2 for indirect allowed transitions, n=3 for indirect forbidden transitions), A is a constant and E_g is the size of the optical band gap in eV. On the basis of the computational results, the optical band gap for LAY and LTAY was treated as indirect (i.e. n=2 in the Tauc relation used to calculate the experimental band gap).

The electrochemical experiments were performed with an Autolab PGSTAT101 potentiostat (Metrohm, Switzerland) and the software NOVA 2.1. Graphite working electrodes ($\emptyset = 3$ mm) were pretreated by mechanical polishing with a P600 SiC-paper to obtain a rough surface. To remove any adherent SiC-particles, the electrodes were rinsed with deionized water in an ultrasonic bath for 20 s. The working electrode (WE) was modified by drop-casting a 1.50 µL droplet of ethanol-pigment suspension (50 mg/mL). After the evaporation of the solvent, a thin layer of the chosen pigment was left at the electrode surface. A saturated calomel electrode (SCE) and a glassy carbon electrode were used as the reference (RE) and counter electrode (CE), respectively. WE, with the pigment side oriented upward, CE and RE were positioned in an open container. The latter was filled

with a 4 mL solution of electrolyte (1 mM NaCl solution or the nonaqueous ionic liquid 1-butyl-3-methylimidazolium tetrafluoroborate ([BMIM][BF4]). The effect of light on the electrochemical response of the different pigments was tested by exposing the WE to alternating cycles of darkness (~ 20 s) and illumination (~20 s) using different 30 mW laser sources (blue, 405 nm; green, 532 nm; red, 655 nm). Both chronoamperometric measurements (CA, changes of current VS time upon illumination at a constant potential) and linear sweep voltammetry (LSV, current VS potential when the latter is slowly but constantly increased over time) were performed. The light-chopped illumination conditions allowed for a fast and simple correction of the signal for background currents. The recorded photocurrent is a direct indicator of the photoactivity of the pigment considered, allowing for a relative comparison between different species.

Computational section

The density functional theory (DFT) calculations in this work were performed with the VASP code⁵²,using the projector augmented wave (PAW) method to describe electron-ion interactions⁵³. The Cd 4d5s, Na 3s, O 2s2p, Pb 5d6s6p, S 3s3p, and Sb 4d5s5p electrons were treated as valence. The compounds studied using DFT methods are introduced as needed in the Results section. The total energy calculations and geometry optimizations were done using the Perdew-Burke-Ernzerhof (PBE)⁵⁴ exchange-correlation functional in the case of metals, and the Heyd-Scuseria-Ernzerhof (HSE06)⁵⁵ hybrid-functional in the case of semiconductors. The plane wave basis set energy cutoff (optimized) was set to 450 eV, and total energies were converged to within 10⁻⁴ eV. Geometry optimizations were done using the conjugate gradient algorithm implemented in the VASP code, and forces were converged to within 0.05 eV Å⁻¹.

The formation energies of the compounds with Pb partially substituted with Na and/or with O vacancies (in neutral charge state) were calculated via⁵⁶:

$$E_f[D] = E_T[D] - E_T[P] + \sum_i n_i \mu$$

where $E_T[D]$ ($E_T[P]$) is the total energy of the defect (pristine) cell, and n_i is the number of atoms of type *i* introduced ($n_i > 0$) or removed ($n_i < 0$) from the cell, with μ_i the corresponding chemical potential.

Results and discussion

Chemical and structural characterization

The SEM/EDX analysis showed that the LTAY sample consists of a finely distributed powder (Figure S1 a), relatively homogenous in terms of both particle size ($\Phi \approx 0.1$ -2.0 µm) and chemical composition (Table S1). Furthermore, XRPD spectroscopy confirmed the presence of one single cubic pyrochlore phase with a lattice parameter a=10.56 Å (Figure 1 a). This crystalline structure, together with the average chemical composition corresponding to the formula Pb₂SnSbO_{6.5} (Table S1), matches the information available in literature on this pigment^{27,57}.

LAY, on the contrary, showed a more irregular size distribution ($\Phi \approx 0.1$ -20.0 µm, Figure S1 b) and a deviation from the ideal composition (Table S1). Two different pyrochlore phases

with slightly different lattice parameters were in fact observed via X-Ray powder diffraction (Figure 1 b). A similar behavior is observed by Dik et al.¹ in in-house synthesized Naples Yellow samples calcinated at low temperatures (650°C), and it is linked to changes in the Pb/Sb molar ratio. In the study by Dik, no metallic element other than Pb and Sb is present in the sample. In a different fashion, the change in the Pb/Sb ratio observed in the LAY pigment considered in this study is related to the substitution of Pb²⁺ by Na⁺ (originated from the NaCl used as a flux agent in the historical recipe followed for the synthesis). A significant and variable amount of Na is in fact observed in all the pigment grains analyzed with SEM-EDX (Table S1) and while the molar ratio Pb/Sb is systematically lower than 1 (0.69±0.08), the ratio (Na+Pb)/Sb is much closer to 1 (1.06 ± 0.15) . The high tolerance to substitution in the pyrochlore structure and the similarity in the ionic radii of Na⁺ and Pb^{2+58} , support the conclusion that the widespread presence of Na in the sample is caused by a partial substitution of Pb in the A sites of the lattice. The tendency of Na^+ to substitute Pb^{2+} in the A sites is observed also in the naturally occurring mineral oxyplumboroméite (also known as bindheimite⁵⁹), often referred to as the isostructural hydrated analogue of Pb₂Sb₂O₇ ^{29,46,57,60}. On the basis of these results, the average stoichiometry of the LAY powder was calculated following the general recommendations by Atencio et al.²⁹. The resulting average formula is $Na_{0.74}Pb_{1.38}Sb_2O_{6.75}$.

Of the two phases experimentally observed in the LAY sample, the most abundant phase (\approx 55±10%) showed a good match with the diffraction pattern of bindheimite (PDF 42-1355, a=10.40 Å), normally used as an XRD reference for Naples Yellow. The second phase ($\approx 45\pm 10\%$, cubic pyrochlore with lattice parameter a=10.505 Å), on the contrary, showed no perfect match with any reference compound. The presence of dishomogeneities in the composition of LAY was confirmed also by µ-Raman spectroscopy. The presence of two pyrochlore phases intimately mixed in the sample, in fact, leads to variations in the Raman spectra recorded on different LAY grains (Figure 2). In particular, the ratio between the intensities of the peak at 198 cm⁻¹ and the one at 228 cm⁻¹ changes. These two bands have not been univocally identified but, as reported by Rosi et al. 57, additional bands in the Raman spectrum of lead pyroantimonates can be linked to the distortion of the SbO₆ octahedra (very sensitive due to the rigidity of the Sb-O bond). In addition, different spectra show a shift of the most intense scattering peak at about 510 cm⁻¹ towards lower values (\approx 500 cm⁻¹), accompanied by a decrease in intensity and a broadening, with a shoulder appearing at around 455 cm⁻¹. This peak can be ascribed to the totally symmetric elongation of the SbO₆ octahedra (A_{1g} mode). This confirms the relationship between the changes in the Raman spectra and the symmetry of the octahedral sites, suggesting a different degree of distortion of the crystalline lattice for the two phases. An increase in the lattice dimension and distortion of the octahedral sites in Pb pyroantimonates was observed in two cases before: when a different cation such as Sn^{4+} , Zn^{2+} , Fe^{3+} or Pb^{4+} partially substitutes Sb^{5+} in the B sites 57,60 , or when high amounts of K₂CO₃ are used in the synthesis, causing K⁺ to enter the lattice ⁴⁶. In our study, however, Na⁺ is the only additional cation present in detectable amounts. The effect of the Na⁺/Pb²⁺ substitution on the lattice structure has not been described in literature before, but it is likely to be responsible for the structural changes observed. Given the strong relationship observed between the symmetry of the octahedral sites in Sb pyrochlores and their electronic structure^{40,41}, these changes will affect the overall properties of the pigment.



Figure 1. X-Ray diffractograms for the a) LTAY and b) LAY samples. (*) Pb₂SnSbO_{6.5} (PDF 39-928, a=10.56 Å). (•) Bindheimite (PDF 42-1355, a=10.40 Å), (x) unidentified pyrochlore phase (a=10.505 Å).



Figure 2. Micro-Raman spectra from different grains of LAY. Insets: enlarged view of the main band at around 510 cm⁻¹ (upper panel) and of the two peaks at 198 and 228 cm⁻¹ (lower panel) of spectra (a) and (g).

Different binary combinations of compounds with a general formula $Na_xPb_{2-x}Sb_2O_{7-x/2}$ could translate into the experimental results obtained for LAY. According to the results of the DFT calculations (Figure S2), $Na_{0.5}Pb_{1.5}Sb_2O_{6.75}$ (LAY1) and NaP-bSb₂O_{6.5} (LAY2) are the two compounds that show the best

combination between low formation energies and good correspondence with the experimental lattice parameters. The coexistence of these two Na-substituted lead pyroantimonate phases in the LAY sample was experimentally confirmed by means of high-resolution STEM-HAADF imaging and STEM-EDS analysis (Figure 3 and Figure S3). The experimental EDS results show a good agreement with the stoichiometry of the two computed phases. Furthermore, the distribution of Na-rich and Pbrich areas in the STEM-HAADF images, identified by means of independent component analysis (ICA), confirms how intimately mixed the two phases are in the pigment powder.



Figure 3. a) STEM-HAADF image (at a magnification of 115 kX). The quantification of EDS spectra from the area within the green and red rectangles are respectively given in the table. b) EDS map from the same region in (a) showing a Pb-rich and a Na-rich phase identified by independent component analysis (ICA).

It is extremely interesting to notice how the theoretical $Pb_2Sb_2O_7$ pyrochlore phase is not present in the sample. This information is in contradiction with the literature about Naples yellow as an artists' pigment ($Pb_2Sb_2O_7$ with a ≈ 10.4 Å), but is in agreement with the computed information on this compound. The pure lead antimony mixed oxide, in fact, appears to be intrinsically unstable in the cubic pyrochlore structure (instability arising from a sharply peaked density of states at the Fermi level, Figure 4 and Figure S4), as previously suggested by other authors outside the field of conservation science^{28,36,37}.



Figure 4. Computed density of states (a) and crystalline structure (b) for the Pb₂Sb₂O₇ pyrochlore. The spheres represent single atoms in the structure: grey = Pb, brown = Sb and red = O. In evidence in green the charge density isosurfaces of the highly localized states at the Fermi level arising from the O' atom at the center of the Pb₄O' tetrahedra.

In addition, this phase shows a computed lattice parameter much larger than the literature value for this pigment (a=10.87 Å). These results therefore suggest that $Pb_2Sb_2O_7$ is not the correct formula to describe the pyrochlore pigment commonly referred to as Naples yellow. Our computational and experimental approach demonstrates for the first time an alternative pathway for the stabilization of lead antimonate in a pyrochlore structure, with Na⁺ partially substituting Pb²⁺ in the A sites.

Optoelectronic properties and photostability

Once completed the chemical and structural characterization of the pigment powders, the study of their optoelectronic properties was performed.

As a starting point, it is particularly interesting to notice how the partial substitution of both Pb²⁺ with Na⁺ in LAY1 and LAY2 and Sb⁵⁺ with Sn⁴⁺ in LTAY have a similar effect on the overall stoichiometry and band structure for the pigments. First of all, we found that the sharp peak in the density of states at the Fermi energy in LAY (in the pyrochlore structure this compound would be metallic) arises essentially from highly localized O' p-states (O' is the O atom at the center of Pb tetrahedra) (Figure 4). Thus, compositional changes that allow to eliminate these states can lower the energy of the system and result in a stable compound. Because of their lower valency, the partial substitution of Sb^{5+} with Sn^{4+} in LTAY and of Pb^{2+} with Na^+ in both LAY phases allows for the formation of O vacancies and, as expected, these occur preferentially at the O' sites for all the structures (Figure S5). As the states at the Fermi level are eliminated, these substitutions cause the resulting compounds to be semiconductors.

In order to better understand the photostability of these semiconductors, their optical properties were studied both experimentally (DR-UV-Vis spectroscopy) and computationally using CdS as a reference yellow semiconducting compound. Both approaches showed a significantly lower absorption coefficient for the pyroantimonate pigments in analysis than for the reference semiconductor, with a less steep absorption edge in the visible region of the spectrum (Figure 5).



Figure 5. a) Experimental Kubelka-Munk function (proportional to the absorption coefficient) for LAY, LTAY and CdS and b) computed absorption coefficient for LAY 1 (= $Na_{0.5}Pb_{1.5}Sb_2O_{6.75}$), LAY 2 (= $NaPbSb_2O_{6.5}$), LTAY and CdS as a function of the energy of the incident light.

This behavior is explained by the indirect nature of the computed band gap for all the pyrochlore phases (lower probability for the optical transition). Note that phonon-assisted transitions are typically not included in first-principles computational codes. Even though this type of optical transitions in indirect gap semiconductors are of second order, their effect is not negligible and contributes to the difference between the experimental and theoretical spectra. Further differences may arise from the non-perfectly homogenous and relatively large size of the particles ($\Phi_{\text{particle}} > \lambda$ on average), which could increase the unwanted specular reflection contribution in the spectrum.

In general, the size of the computed band gaps is consistent with the results of the optical measurements (Table 2 and Figure S6). Only in the specific case of Na_{0.5}Pb_{1.5}Sb₂O_{6.75}, a significant difference in size between the computed and experimental band gaps is observed. However, as shown in Figure 5 b, the computed absorption at the threshold is extremely weak, and only becomes significant above ~2eV. This behavior is justified by the character of the bands in the vicinity of the valence band maximum and conduction band minimum for this phase (Figure S7). The upper lying valence bands are of p character, while the lower lying conduction bands are of dominant s character. Thus, in principle optical transitions can take place. However, the former arise mainly from the 2p states of the O' atoms at the center of the Pb-Na tetrahedra, while the latter arise mainly from Sb 5s states. These atoms are only third neighbors in the Na_{0.5}Pb_{1.5}Sb₂O_{6.75} structure (Figure S5 c). Thus, the corresponding optical transition matrix elements are small, and the absorption is weak. Most likely too weak to be macroscopically observed and experimentally detected.

Table 2. Nature and size of the experimental (E_g exp) and computed (E_g comp) band gaps for the pigments considered.

	Composition	Band Gap	E _g exp (eV)	E _g comp (eV)
				2.36
I TAN	DL G. CLO	·	2.22	[indirect]
LIAI	F 025115006.5	mulrect	[indirect]	2.91
				[direct]
				0.42
LAY -	Na0.5Pb1.5Sb2O 6.75	in dimont	2.31 ^[a]	[indirect]
		indirect	[indirect]	0.56
				[direct]
				1.96
		indirect	2.31 ^[a]	[indirect]
	NaP050206.5		[indirect]	2.28
				[direct]
CHE	C49	dimont	2.40	2.10
Cus	Cas	arect	[direct]	[direct]

^[a] Experimental value for the mixture of two phases.

The chrono-amperometric measurements under chopped illumination conditions (at the open circuit potential, OCP) showed a positive photocurrent (Iph) when the pigment-modified working electrodes (WE) are exposed to light with $hv > E_g$ (Table 3). This is a typical behavior for n-type semiconductors, due to minority carrier (h⁺) mediated oxidation processes taking place at the pigment surface (Figure 6)^{31,61,62}. The absorption of a suprabandgap photon causes in fact the excitation of one electron (e) from the valence band (VB) to the conduction band (CB) of the semiconductor. This process leaves behind a positively charged hole (h⁺) in the VB, resulting in a displacement from equilibrium of the concentration of each charge carrier (e⁻ and h⁺). In an n-type semiconductor, the amount of photo-generated e⁻ does not alter significantly the total concentration of majority carriers in the CB, while the amount of photo-generated h⁺ strongly increases the total concentration of minority carriers in the VB. For this reason, the quasi-fermi level defined for e⁻ in this non-equilibrium condition $({}_{n}E_{F}^{*})$ remains approximately the same as the general E_F observed for the semiconductor in the dark. On the contrary, ${}_{p}E_{F}^{*}$ (quasi-fermi level for h⁺ upon light exposure) drastically increases in energy compared to preillumination E_F. This translates into a higher minority carrierrelated reactivity of the pigments upon light exposure. The presence of band bending at the pigment/electrolyte interface promotes the charge separation upon illumination, preventing the recombination of electron-hole pairs due to the existing electric field at the surface. N-type semiconductors most of the time present an upward band bending due to the accumulation of positive charges at the interface (mostly due to the transfer of eto the solution during the equilibration of the respective Fermi levels in the dark)³¹. In this case, the electric field at the surface forces the free holes formed upon illumination towards the external solution, while the photo-generated electrons are pushed away from the surface. This leads to minority carrier (h⁺) mediated oxidation processes taking place at the pigment surface upon illumination (Figure 6)^{31,61,62}, translating into an overall positive current in the cell.



CB = conduction band;

VB = valence band;

E_F = Fermi level of semiconductor;

E_{F sol} = Fermi level of electrolyte (in aqueous environment = reduction potential of water, H₂O red);

nE_F* = Quasi Fermi level for e⁻ upon illumination;

_pE_F* = Quasi Fermi level for h⁺ upon illumination;

 $H_2OOx = oxidation potential of water;$

 Φ Ox = surface self-oxidation potential of the semiconductor;

E_g = band gap size;

X₀ = thickness of the surface space-charge layer.

Figure 6. Mechanism responsible for the anodic photocurrent observed on LAY, LTAY and CdS-modified WE upon illumination with Vis light. a) Energy levels alignment before illumination in an aqueous solution; b) effect of the absorption of light with different wavelengths.

Table 3. I_{ph} values measured for LAY, LTAY and CdS-modified electrodes in different light conditions and electrolytes at the OCP.

	NaCl 1 mM			Ionic Liquid				
	LOD ^[a]	LAY	LTAY	CdS	LOD ^[a]	LAY	LTAY	CdS
I _{ph} (nA) RED Laser	0.2	<lod< td=""><td><lod< td=""><td>4±3</td><td>3.8</td><td><lod< td=""><td><lod< td=""><td><lod< td=""></lod<></td></lod<></td></lod<></td></lod<></td></lod<>	<lod< td=""><td>4±3</td><td>3.8</td><td><lod< td=""><td><lod< td=""><td><lod< td=""></lod<></td></lod<></td></lod<></td></lod<>	4±3	3.8	<lod< td=""><td><lod< td=""><td><lod< td=""></lod<></td></lod<></td></lod<>	<lod< td=""><td><lod< td=""></lod<></td></lod<>	<lod< td=""></lod<>
I _{ph} (nA) GREEN Laser	0.2	1.6±0.3	3.6±0.5	34±8	5.1	<lod< td=""><td><lod< td=""><td>28±9</td></lod<></td></lod<>	<lod< td=""><td>28±9</td></lod<>	28±9
I _{ph} (nA) BLUE Laser	0.8	6.6±0.8	19±5	233±41	3.0	5.5±1.4	18±3	203±68

^[a] LOD= $3*\sigma_{blank}$, where LOD=limit of detection and σ_{blank} =standard deviation of the blank.

Comparable results are obtained in an aqueous electrolyte (1mM NaCl) and in an ionic liquid with a large potential stability window ([BMIM][BF₄]). This confirms that the anodic photocurrent observed is the result of the h⁺-mediated self-oxidation of the pigment grains, and not of water oxidation. The significantly lower I_{ph} observed for LAY ad LTAY in both media, however, confirms the extreme stability of these pigments compared to CdS. A small photocurrent, in fact, is the direct result of a much lower tendency of the pigments to be oxidized when exposed to light with hv $\geq E_g^{31}$. The dependency of the I_{ph} magnitude on the energy of the incident light is in agreement with

the experimental size of the band gap and the absorption properties for all the pigments (Figure 5 and Table 2). In fact, the anodic I_{ph} was higher in all samples when illuminated with a blue laser (3.06 eV), and progressively lower with a green (2.33 eV) and a red (1.89 eV) laser (Table 3).

When an increasing positive over-potential (compared to the OCP) is applied to the WE, a clear increase in the relative anodic I_{ph} is observed for both pyroantimonate pigments (Figure 7, Figure S8).



Figure 7. I_{ph} (Blue and Green laser) dependency on the potential applied at the WE. Scan rate = 0.5 mV/s in 1 mM NaCl.

A poor p-type conductivity in the pyrochlore phases is most likely responsible for the experimental results obtained. As observed in the computed band structures (Figure 8), in fact, a clear difference in the degree of dispersion of the upper lying valence bands exists between these phases and CdS. In the pyrochlore pigments, these energy levels originate essentially from the same states, i.e. the p-states from the octahedral O atoms surrounding the Sb atoms. The very flat nature of these bands, as often observed for metal oxides presenting cornersharing octahedral structures⁶³, translates into high h⁺ effective masses. An accurate calculation of these effective masses requires taking into account various factors, such as the multiplicity of concerned extrema in the Brillouin zone and possible temperature effects⁶⁴. In the present case, however, the band structures are relatively simple, with a single band at the valence band maximum (VBM) for all the phases except CdS, where degenerate bands are present. It is thus possible to have a good idea of the differences in effective mass among the compounds we study by considering the effective mass corresponding to the VBM along a high symmetry line. In the case of CdS, there are two effective masses because of the degeneracy at the CBM, resulting in what are dubbed as light and heavy holes. Mobility in that case will obey to the average of these effective masses. The results are presented in Table 4. Since the carrier mobility depends directly on the inverse of the carrier effective mass, this material property results into a low minority carrier mobility for all the pyrochlore phases. Mobility which is likely to be further hindered by the presence of grain boundaries in the pigment powders^{65,66}. Since conductivity depends both on mobility and

charge carrier concentration, the combination between low h⁺ mobility and low optical absorption coefficients explains the extreme stability of LAY and LTAY pigments. In fact, this means not only that less e⁻/h⁺ pairs are formed upon light exposure in LAY and LTAY compared to CdS, but also that the photo-generated holes struggle to reach the surface and react before a recombination takes place. For this reason, when an external potential is applied driving the positive charges towards the surface of the pigment grains³¹, a significant increase in I_{nh} is observed. The similar lightfastness observed for LAY and LTAY can therefore be ascribed to the analogous effect of Sn and Na substitutions on the band structure of the pigments. These substitutions, in fact, affect mainly the position of the upper valence band energy levels, but only weakly their nature and dispersion. This translates into h⁺ mobilities which remain low and are not significantly affected by the nature of the substituent cation. The only difference observed in the valence band structures of Na- and Sn-substituted phases is the larger density of states near the valence band maximum for the latter (Figure 8 and Figure S9). This means that more electrons are potentially available for excitation near the band maximum, which explains the small experimental differences previously encountered: namely the slightly higher near-edge optical absorption (Figure 5), the slightly larger photocurrent at the OCP (Table 3) and the consequently smaller relative I_{ph} increase with the applied potential for LTAY (Figure 7).

For CdS, on the contrary, all the lighter photo-generated h⁺ are most likely capable of reaching the surface of the grains without the need for an external electric field. Hence the high I_{ph} at the OCP, in agreement with the documented instability for this pigment in paintings^{31,34}, and the lack of a significant dependency on the potential applied at the WE. The slightly higher increase in Iph observed under green laser illumination compared to blue laser illumination for CdS is related to the fact that green light is absorbed less efficiently by the semiconductor. The e⁻/h⁺ pairs are therefore formed deeper in the semiconductor. Here the separation of the photo-generated free charges is less efficient, due to the lower influence of the electric field present only in the superficial space-charge layer, and therefore the recombination is more probable (Figure 6 b)⁶⁷. When a positive over-potential is applied at the WE, however, the thickness of the space-charge layer is increased⁶⁸. This makes the separation of the e^{-}/h^{+} pairs generated by the absorption of green light more efficient, leading to the relative I_{ph} increase observed experimentally.



Figure 8. Band character with respect to the atomic species present in the compounds considered. a) $Na_{0.5}Pb_{1.5}Sb_2O_{6.75}$ and b) $NaPbSb_2O_{6.5}$ (Blue=Sb, Green=Pb, Red=O; Na relative contribution is negligible). c) $Pb_2SNSbO_{6.5}$ (Blue=Sb, Green=Pb, Red=O; Sn contribution does not differ significantly from Sb). d) CdS (Green=S, Red=Cd).

Table 4. Hole effective masses (in units of m_e) for all the phases considered.

Phase	VBM	Effective m _h
Pb ₂ SnSbO _{6.5}	along the K- Γ line	1.89
Na _{0.5} Pb _{1.5} Sb ₂ O _{6.75}	at L	2.68
NaPbSb ₂ O _{6.5}	at L	1.32
CdS	at Γ	$0.64^{[a]}$

^[a]harmonic average of 0.40 (light hole) and 1.63 (heavy hole)

Conclusion

The multi-faceted analytical and computational approach employed in this study allowed to unravel the material properties behind the stability of lead pyroantimonate yellow pigments.

First, meaningful insights were obtained on the intrinsic instability of stoichiometric $Pb_2Sb_2O_7$ in the cubic pyrochlore structure. This confirms that the latter formula, extensively employed to describe the pyrochlore pigment commonly known as Naples Yellow, is not correct. Since accurately understanding the material composition is the first fundamental step for conservation, this information is crucial.

The presence of a diverse range of substitutions in the lattice of both natural and synthetic lead pyroantimonates supports our findings. As shown in the present work, in fact, substitutions taking place both at the A and B sites of this pyrochlore lead to

similar changes in its stoichiometry and electronic properties, ultimately stabilizing the pigment in a cubic structure. While substitutions at the octahedral sites are well documented, however, the effects of A-site substitutions are not yet studied in the literature. For the first time, our study demonstrates that the partial substitution of Pb²⁺ by Na⁺ in the A sites of the pyrochlore allows to stabilize the cubic lead antimonate mixed oxide. No evidence of the presence of Na in paintings and historical samples of Naples yellow is reported in literature, however this element is too light to be detected with the non-invasive p-XRF instruments often used to perform the analysis. As a next step, the laboratory analysis of paint microsamples is being planned in order to prove the presence of Na in historical Naples Yellow samples. Being able to confirm the link between the historical synthesis processes and the presence of different substituents in the pigment structure could represent an extremely useful tool for the attribution and authentication of historical paintings.

Furthermore, this study unraveled fundamental information on the optoelectronic properties of lead pyroantimonates. The experimental and computational results, in fact, confirmed the hypothesis of a semiconducting nature for this class of pigments. However, the absorption of visible light by these semiconductors does not trigger self-corrosion mechanisms or catalytic degradation of the organic binding medium in contact with them. This behavior is the result of a combination of poor light absorption properties and low minority carrier (h⁺) mobility, preventing potential h⁺-mediated (self-)oxidation reactions from taking place at the surface of the pigment grains. This confirms that the extreme stability of this family of yellow pigments is the result of intrinsic material properties, hence not depending on the medium in which the pigment is embedded (e.g. insulating glassy matrix in glass objects rather than siccative oil in easel paintings). This is in agreement with the information available in literature about the extreme stability of this family of pigments in different media.

The results of this work represent a fundamental step towards a better understanding of the complex material properties and photochemistry of artists' pigments and of pyrochlore mixed oxides in general. Given the extraordinarily wide range of fields in which these mixed oxides find application, a better understanding of the effect of lattice substitutions on their optoelectronic properties is of capital importance.

In addition, the methodology described in this study can potentially be used to probe the material properties of any semiconducting pigment in powder form, with applications also beyond the field of conservation science and cultural heritage.

ASSOCIATED CONTENT

Supporting Information.

PDF file containing the following supplementary Figures and Tables:

Fig. S1. SEM imaging of LAY and LTAY.

Table S1. SEM-EDX elemental characterization of LAY and LTAY.

Fig. S2. Stability triangle and formation energies as a function of Pb, Sb and O chemical potentials for different LAY phases.

Fig. S3. High resolution STEM-HAADF Z-contrast image of the two pyrochlore phases in the LAY sample.

Fig. S4. Computed band structure for $Pb_2Sb_2O_7$ in a pyrochlore structure.

Fig. S5. Computed crystalline structures for all the pyrochlore phases considered.

Fig. S6. Tauc plots with calculated band gap sizes for LAY, LTAY and CdS.

Fig. S7. Computed band character for Na_{0.5}Pb_{1.5}Sb₂O_{6.75}.

Fig. S8. Linear sweep voltammetry under light chopped illumination conditions for LAY, LTAY and CdS.

Fig. S9. Computed total density of states near the valence band maximum for the pyrochlore phases considered.

This material is available free of charge via the Internet at http://pubs.acs.org.

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Author Contributions

K.D.W. and A.M. conceived and designed the experiments. The synthesis of the samples was performed by C.P.. Data acquisition/analysis was performed by: A.M. and K.D.W. (Photoelectrochemistry, DR-UV-Vis); D.K. and J.V. (STEM-EDS, STEM-HAADF); L.R. and A.M. (μ -RS); G.N. and A.M. (SEM-EDX); S.D.M., G.N. and K.J. (XRPD). R.S. performed the computational study. D.L., B.P. and K.D.W. coordinated the project. The manuscript was written by A.M. in collaboration with R.S., revised by S.D.M., D.K., K.J., D.L., B.P., C.P., K.D.W. and with input from all other authors. All authors contributed to the manuscript. All authors have given approval to the final version of the manuscript.

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ABBREVIATIONS

LAY, Lead antimonate yellow; LTAY, Lead tin antimonate yellow (Pb₂SnSbO_{6.5}); LAY1, Na_{0.5}Pb_{1.5}Sb₂O_{6.75} in a pyrochlore structure; LAY2, NaPbSb₂O_{6.5} in a pyrochlore structure; [BMIM][BF4], 1butyl-3-methylimidazolium tetrafluoroborate; SEM-EDX, Scanning Electron Microscope with Energy Dispersive X-Ray detector; p-XRF, portable X-Ray Fluorescence spectroscopy; XRPD, X-Ray powder diffraction; μ -RS, micro Raman spectroscopy; STEM-HAADF, Scanning Transmission Electron Microscopy with High Angle Annular Dark Field detector; STEM-EDS, Scanning Transmission Electron Microscopy with Energy Dispersive X-ray detector; ICA, Independent component analysis; DR-UV-Vis, diffuse reflectance UV-Vis spectroscopy; OCP, open circuit potential; WE, working electrode; CB, conduction band; VB, valence band; LOD, limit of detection; VBM, valence band maximum.

REFERENCES

(1) Dik, J.; Hermens, E.; Peschar, R.; Schenk, H. Early Production

Recipes for Lead Antimonate Yellow in Italian Art. Archaeometry **2005**, 47 (3), 593–607. https://doi.org/10.1111/j.1475-4754.2005.00221.x.

- (2) Wainwright, I. N. M. R.; Taylor, J. M.; Harley, R. D. Lead Antimonate Yellow. In Artists' pigments: a handbook of their history and characteristics; Feller, R. L., Ed.; National Gallery of Art: Washington DC, 1986; pp 219–254.
- (3) Dik, J.; Peschar, R.; Schenk, H. The Introduction of Lead Antimonate Yellow in the 18th Century. Zeitschrift für Kunsttechnologie und Konserv. 2006, 20, 138–146.
- (4) Agresti, G.; Baraldi, P.; Pelosi, C.; Santamaria, U. Yellow Pigments Based on Lead, Tin, and Antimony: Ancient Recipes, Synthesis, Characterization, and Hue Choice in Artworks. *Color Res. Appl.* 2016, 41 (3), 226–231. https://doi.org/10.1002/col.22026.
- (5) Eastaugh, N.; Walsh, V.; Chaplin, T.; Ruth, S. Pigment Compendium: A Dictionary and Optical Microscopy of Historical Pigments; Butterworth-Heinemann: London, 2008.
- (6) Chiarantini, L.; Gallo, F.; Rimondi, V.; Benvenuti, M.; Costagliola, P.; Dini, A. Early Renaissance Production Recipes for Naples Yellow Pigment: A Mineralogical and Lead Isotope Study of Italian Majolica from Montelupo (Florence). Archaeometry 2015, 57 (5), 879–896. https://doi.org/10.1111/arcm.12146.
- (7) Kirmizi, B.; Göktürk, E. H.; Colomban, P. Colouring Agents in the Pottery Glazes of Western Anatolia: New Evidence for the Use of Naples Yellow Pigment Variations During The Late Byzantine Period. *Archaeometry* 2015, 57 (3), 476–496. https://doi.org/10.1111/arcm.12101.
- (8) Seccaroni, C. Giallorino. Storia Dei Pigmenti Gialli Di Natura Sintetica; De Luca Editore, Ed.; Rome, 2006.
- (9) Pelosi, C.; Agresti, G.; Santamaria, U.; Mattei, E. Artificial Yellow Pigments: Production and Characterization through Spectroscopic Method of Analysis. *ePreserv. Sci.* 2010, 7, 108– 115.
- (10) Santamaria, U.; Agresti, G.; Pelosi, C. Memory and Matter of Cultural Heritage: Lead, Tin and Antimony Based Yellow Pigments. In *Fatto d'Archimia*; Kroustallis, S., del Egido, M., Eds.; Ministerio de Educatión, Cultura y Deporte: Madrid, 2012; pp 145–156.
- (11) Zecchin, L. Il Ricettario Darduin. Un Codice Vetrario Del Seicento Trascritto e Commentato.; Arsenale: Venezia, 1984.
- (12) Zecchin, L. Vetro e Vetrai Di Murano. Studi Di Storia Del Vetro. Vol.1; Arsenale: Venezia, 1987.
- (13) Zecchin, L. Vetro e Vetrai Di Murano. Studi Di Storia Del Vetro. Vol. 2.; Arsenale: Venezia, 1989.
- (14) Zecchin, L. Vetro e Vetrai Di Murano. Studi Di Storia Del Vetro. Vol. 3.; Arsenale: Venezia, 1990.
- (15) Rico, L. Pigmenti Del XVI Secolo Tra Venezia e La Spagna. Tiziano, l'Escorial e Il Commercio Con Venezia. *Kermes* 2000, 37, 58–71.
- (16) Moretti, C.; Salerno, C. S.; Tommasi Ferroni, S. Ricette Vetrarie Muranesi. Gaspare Brunuoro e Il Manoscritto Di Danzica; Nardini Editore, Ed.; Firenze, 2004.
- (17) Janssens, K. H. A. Modern Methods for Analysing Archaeological and Historical Glass. Vol.1; John Wiley & Sons: Chichester, 2013.
- (18) Ferrer, P.; Ruiz-Moreno, S.; López-Gil, A.; Chillón, M. C.; Sandalinas, C. New Results in the Characterization by Raman Spectroscopy of Yellow Pigments Used in Ceramic Artworks of the 16th and 17th Centuries. *J. Raman Spectrosc.* **2012**, *43* (11), 1805–1810.
- (19) Kock, L. D.; De Waal, D. Raman Analysis of Ancient Pigments on a Tile from the Citadel of Algiers. *Spectrochim. Acta A* 2008, 71, 1348–1354.
- (20) Bensi, P.; Montiani Bensi, M. R. Osservazioni Tecniche e Iconografiche Sui Colori Gialli Nella Pittura Del XVI e XVII Sec. In Scritti ed immagini in onore di Corrado Maltese; Marconi, S., Dalai, M., Eds.; Quasar: Rome, 1999; pp 167–175.
- (21) Montanari, R.; Alberghina, M. F.; Casanova Municchia, A.; Massa, E.; Pelagotti, A.; Pelosi, C.; Schiavone, S.; Sodo, A. A Polychrome Mukozuke (1624–1644) Porcelain Offers a New Hypothesis on the Introduction of European Enameling

Technology in Japan. J. Cult. Herit. 2018, 32, 232-237.

- (22) Montanari, R.; Murakami, N.; Alberghina, M. F.; Pelosi, C.; Schiavone, S. The Origin of Overglaze-Blue Enameling in Japan: New Discoveries and a Reassessment. J. Cult. Herit. 2019, 37, 94–102.
- (23) Rosi, F.; Manuali, V.; Grygar, T.; Bezdicka, P.; Brunetti, B. G.; Sgamellotti, A.; Burgio, L.; Seccaroni, C.; Miliani, C. Raman Scattering Features of Lead Pyroantimonate Compounds: Implication for the Non-Invasive Identification of Yellow Pigments on Ancient Ceramics. Part II. in Situ Characterisation of Renaissance Plates by Portable Micro-Raman and XRF Studies. J. Raman Spectrosc. 2011, 42 (3), 407–414. https://doi.org/10.1002/jrs.2699.
- (24) Buzzegoli, E.; Cardaropoli, R.; Kunzelman, D.; Moioli, P.; Montalbano, L.; Piccolo, M.; Seccaroni, C. Valerio Mariani Da Pesaro, Il Trattato "Della Miniatura": Primi Raffronti Con Le Analisi e Le Opere. OPD Restauro. Riv. dell'Opificio delle Pietre Dure e Lab. di Restauro di Firenze 2000, 12, 248–256.
- (25) Berrie, B. H. Mining for Color: New Blues, Yellows, and Translucent Paint. *Early Sci. Med.* 2015, 20, 308–334. https://doi.org/10.1163/15733823-02046p02.
- (26) Roy, A.; Berrie, B. H. A New Lead-Based Yellow in the Seventeenth Century. *Stud. Conserv.* 1998, 43 (sup1), 160–165. https://doi.org/10.1179/sic.1998.43.Supplement-1.160.
- (27) Sandalinas, C.; Ruiz-moreno, S. Lead-Tin-Antimony Yellow: Historical Manufacture, Molecular Characterization and Identification in Seventeenth-Century Italian Paintings. *Stud. Conserv.* 2004, 49 (1), 41–52.
- (28) Subramanian, M. A.; Aravamudan, G.; Subba Rao, G. V. Oxide Pyrochlores - A Review. *Prog. Solid State Chem.* **1983**, *15* (2), 55–143. https://doi.org/10.1016/0079-6786(83)90001-8.
- (29) Atencio, D.; Gieré, R.; Andrade, M. B.; Christy, A. G.; Kartashov, P. M. The Pyrochlore Supergroup of Minerals: Nomenclature. *Can. Mineral.* **2010**, *48* (3), 673–678. https://doi.org/10.3749/canmin.48.3.673.
- (30) Anaf, W.; Schalm, O.; Janssens, K.; De Wael, K. Understanding the (in)Stability of Semiconductor Pigments by a Thermodynamic Approach. *Dye. Pigment.* 2015, *113*, 409–415. https://doi.org/10.1016/j.dyepig.2014.09.015.
- (31) Anaf, W.; Trashin, S.; Schalm, O.; Van Dorp, D.; Janssens, K.; De Wael, K. Electrochemical Photodegradation Study of Semiconductor Pigments: Influence of Environmental Parameters. Anal. Chem. 2014, 86 (19), 9742–9748. https://doi.org/10.1021/ac502303z.
- (32) Ayalew, E.; Janssens, K.; De Wael, K. Unraveling the Reactivity of Minium toward Bicarbonate and the Role of Lead Oxides Therein. Anal. Chem. 2016, 88 (3), 1564–1569. https://doi.org/10.1021/acs.analchem.5b02503.
- (33) Rahemi, V.; Sarmadian, N.; Anaf, W.; Janssens, K.; Lamoen, D.; Partoens, B.; De Wael, K. Unique Optoelectronic Structure and Photoreduction Properties of Sulfur-Doped Lead Chromates Explaining Their Instability in Paintings. *Anal. Chem.* 2017, 89 (6), 3326–3334. https://doi.org/10.1021/acs.analchem.6b03803.
- (34) Monico, L.; Chieli, A.; De Meyer, S.; Cotte, M.; de Nolf, W.; Falkenberg, G.; Janssens, K.; Romani, A.; Miliani, C. Role of the Relative Humidity and the Cd/Zn Stoichiometry in the Photooxidation Process of Cadmium Yellows (CdS/Cd1–xZnxS) in Oil Paintings. *Chem. - A Eur. J.* 2018, 24 (45), 11584–11593. https://doi.org/10.1002/chem.201801503.
- (35) Vanmeert, F.; Vandersnickt, G.; Janssens, K. Plumbonacrite Identified by X-Ray Powder Diffraction Tomography as a Missing Link during Degradation of Red Lead in a van Gogh Painting. Angew. Chemie - Int. Ed. 2015, 54 (12), 3607–3610. https://doi.org/10.1002/anie.201411691.
- (36) Burchard, V. G.; Rudorff, W. Zur Frage Nach Der Existenz Eines Kubischen Pyrochlors Pb2Sb207. Z. anorg. allg. Chem 1978, 447, 149–152.
- (37) Brisse, F.; Stewart, D. J.; Seidl, V.; Knop, O. Pyrochlores . VIII . Studies of Some 2-5 Pyrochlores and Related Compounds and Minerals. *Can. J. Chem.* **1972**, *5*, 3648–3666.
- (38) Cloutis, E.; Norman, L.; Cuddy, M.; Mann, P. Spectral Reflectance (350-2500 Nm) Properties of Historic Artists' Pigments. II. Red-Orange-Yellow Chromates, Jarosites,

Organics, Lead(-Tin) Oxides, Sulphides, Nitrites and Antimonates. *J. Near Infrared Spectrosc.* **2016**, *24* (2), 119–140. https://doi.org/10.1255/jnirs.1207.

- (39) Allen, J. P.; Scanlon, D. O.; Watson, G. W. Comparison of the Defective Pyrochlore and Ilmenite Polymorphs of AgSbO 3 Using GGA and Hybrid DFT. *Phys. Rev. B Condens. Matter Mater. Phys.* 2011, 83 (3), 1–8. https://doi.org/10.1103/PhysRevB.83.035207.
- (40) Mizoguchi, H.; Woodward, P. M. Electronic Structure Studies of Main Group Oxides Possessing Edge-Sharing Octahedra. Implications for the Design of Transparent Conducting Oxides. *Chem. Mater.* 2004, 16 (2), 5233–5248. https://doi.org/10.1021/cm049249w.
- (41) Mizoguchi, H.; Eng, H. W.; Woodward, P. M. Probing the Electronic Structures of Ternary Perovskite and Pyrochlore Oxides Containing Sn4+ or Sb5+. *Inorg. Chem.* 2004, 43 (5), 1667–1680. https://doi.org/10.1021/ic034551c.
- (42) Shi, J.; Ma, L.; Wu, P.; Zhou, Z.; Guo, P.; Shen, S.; Jing, D.; Guo, L. A Novel Sn 2 Sb 2 O 7 Nanophotocatalyst for Visible-Light-Driven H 2 Evolution. 2012, 5 (8), 576–583. https://doi.org/10.1007/s12274-012-0243-0.
- (43) Agresti, G. I Gialli Di Piombo, Stagno, Antimonio: Colore e Materia Dell'opera d'arte; PhD thesis, University of Tuscia: Viterbo, 2017.
- (44) Capobianco, G.; Pelosi, C.; Agresti, G.; Bonifazi, G.; Santamaria, U.; Serranti, S. X-Ray Fluorescence Investigation on Yellow Pigments Based on Lead, Tin and Antimony through the Comparison between Laboratory and Portable Instruments. J. Cult. Herit. 2017. https://doi.org/10.1016/j.culher.2017.09.002.
- (45) Picolpasso, C. The Three Books of the Potter's Art, facsimil.; Victoria & Albert Museum: London, 1976.
- (46) Hradil, D.; Grygar, T.; Hradilová, J.; Bezdička, P.; Grunwaldová, V.; Fogaš, I.; Miliani, C. Microanalytical Identification of Pb-Sb-Sn Yellow Pigment in Historical European Paintings and Its Differentiation from Lead Tin and Naples Yellows. J. Cult. Herit. 2007, 8 (4), 377–386. https://doi.org/10.1016/j.culher.2007.07.001.
- (47) Cascales, C.; Alonso, J. A.; Rasines, I. The New Pyrochlores Pb2
 (MSb) O6.5 (M = Ti, Zr, Sn, Hf). J. Mater. Sci. Lett. 1986, 5, 675–677. https://doi.org/10.1007/BF01731548.
- (48) De Nolf, W.; Vanmeert, F.; Janssens, K. XRDUA: Crystalline Phase Distribution Maps by Two-Dimensional Scanning and Tomographic (Micro) X-Ray Powder Diffraction. J. Appl. Crystallogr. 2014, 47 (3), 1107–1117. https://doi.org/10.1107/S1600576714008218.
- (49) Jutten, C.; Herault, J. Blind Separation of Sources, Part I: An Adaptive Algorithm Based on Neuromimetic Architecture. *Signal Processing* **1991**, 24 (1), 1–10. https://doi.org/10.1016/0165-1684(91)90079-X.
- (50) Sangiorgi, N.; Aversa, L.; Tatti, R.; Verucchi, R.; Sanson, A. Spectrophotometric Method for Optical Band Gap and Electronic Transitions Determination of Semiconductor Materials. *Opt. Mater.* (*Amst*). **2017**, *64*, 18–25. https://doi.org/10.1016/j.optmat.2016.11.014.
- (51) Zhang, Y.; Yin, J.; Parida, M. R.; Ahmed, G. H.; Pan, J.; Bakr, O. M.; Brédas, J. L.; Mohammed, O. F. Direct-Indirect Nature of the Bandgap in Lead-Free Perovskite Nanocrystals. J. Phys. Chem. Lett. 2017, 8 (14), 3173–3177. https://doi.org/10.1021/acs.jpclett.7b01381.
- (52) Kresse, G.; Furthmüller, J. Efficient Iterative Schemes for Ab Initio Total-Energy Calculations Using a Plane-Wave Basis Set. *Phys. Rev. B - Condens. Matter Mater. Phys.* **1996**, *54* (16), 11169–11186. https://doi.org/10.1103/PhysRevB.54.11169.
- (53) Kresse, G.; Joubert, D. Kresse, Joubert Unknown From Ultrasoft Pseudopotentials to the Projector Augmented-Wave Method. **1999**, *59* (3), 11–19.
- (54) Perdew, J. P.; Burke, K.; Ernzerhof, M. Generalized Gradient Approximation Made Simple. *Phys. Rev. Lett.* **1996**, 77 (18), 3865–3868. https://doi.org/10.1103/PhysRevLett.77.3865.
- (55) Heyd, J.; Scuseria, G. E.; Ernzerhof, M. Hybrid Functionals Based on a Screened Coulomb Potential. J. Chem. Phys. 2003, 118 (18), 8207–8215. https://doi.org/10.1063/1.1564060.
- (56) Van De Walle, C. G.; Laks, D. B.; Neumark, G. F.; Pantelides, S.

T. First-Principles Calculations of Solubilities and Doping Limits: Li, Na, and N in ZnSe. *Phys. Rev. B* **1993**, *47* (15), 9425–9434. https://doi.org/10.1103/PhysRevB.47.9425.

- (57) Rosi, F.; Manuali, V.; Miliani, C.; Brunetti, B. G.; Sgamellotti, A.; Grygar, T.; Hradil, D. Raman Scattering Features of Lead Pyroantimonate Compounds. Part I: XRD and Raman Characterization of Pb2Sb2O7 Doped with Tin and Zinc. J. Raman Spectrosc. 2009, 40 (1), 107–111. https://doi.org/10.1002/jrs.2092.
- (58) Shannon, R. D. Revised Effective Ionic Radii and Systematic Studies of Interatomic Distances in Halides and Chalcogenides. *Acta Cryst.* **1976**, *A32*, 751–767.
- (59) Hålenius, U.; Bosi, F. Oxyplumboroméite, Pb2Sb2O7, a New Mineral Species of the Pyrochlore Supergroup from Harstigen Mine, Värmland, Sweden. *Mineral. Mag.* 2013, 77, 2931–2939.
- (60) Cartechini, L.; Rosi, F.; Miliani, C.; D'Acapito, F.; Brunetti, B. G.; Sgamellotti, A. Modified Naples Yellow in Renaissance Majolica: Study of Pb–Sb–Zn and Pb–Sb–Fe Ternary Pyroantimonates by X-Ray Absorption Spectroscopy. *Journal of Analytical Atomic Spectrometry*. 2011, p 2500. https://doi.org/10.1039/c1ja10190k.
- (61) Davidson, R. S.; Willsher, C. J. Mercury(II) Sulphide: A Photo-Stable Semiconductor. *Nature* 1979, 278, 238.
- (62) Zhang, Z.; Yuan, Y.; Fang, Y.; Liang, L.; Ding, H.; Shi, G.; Jin,L. Photoelectrochemical Oxidation Behavior of Methanol on

- (63) Hosono, H.; Ueda, K. Transparent Conductive Oxides. In Springer Handbook of Electronic and Photonic Materials; Kasap, S., Capper, P., Eds.; Springer International, 2017; pp 1391–1404. https://doi.org/10.1007/978-3-319-48933-9.
- (64) Setyawan, W.; Gaume, R. M.; Lam, S.; Feigelson, R. S.; Curtarolo, S. High-Throughput Combinatorial Database of Electronic Band Structures for Inorganic Scintillator Materials. ACS Comb. Sci. 2011, 13, 382–390.
- (65) Seto, J. Y. W. The Electrical Properties of Polycrystalline Silicon Films. J. Appl. Phys. 1975, 46 (12), 5247–5254. https://doi.org/10.1063/1.321593.
- (66) Broniatowski, A. Electronic States at Grain Boundaries in Semiconductors. In *Polycrystalline Semiconductors*; Harbeke, G., Ed.; Springer: Heidelberg, 1985; pp 95–117.
- (67) Anaf, W.; Schalm, O.; Janssens, K.; De Wael, K. Understanding the (in)Stability of Semiconductor Pigments by a Thermodynamic Approach. *Dye. Pigment.* 2015, *113*, 409–415. https://doi.org/10.1016/j.dyepig.2014.09.015.
- (68) Pavlov, D. Semiconductor Mechanism of the Processes during Electrochemical Oxidation of PbO to PbO2. J. Electroanal. Chem. 1981, 118 (C), 167–185. https://doi.org/10.1016/S0022-0728(81)80539-6.



For Table of Contents Only

Supporting Information

Unraveling the role of lattice substitutions on the stabilization of the intrinsically unstable Pb₂Sb₂O₇ pyrochlore: explaining the lightfastness of lead pyroantimonate artists' pigments

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Figure S1. SEM backscattered electron image (BEI) of the powder samples: a) LTAY, 10⁴x; b) LAY, 10⁴x.

LAY	Na	Pb	Sb	Na + Pb
Average (wt%)	3.0±1.6	49.9±4.9	42.8±4.7	45.8±5.6
Average (mol)	0.13±0.07	0.24 ± 0.02	0.35±0.04	0.37±0.07
mol/mol _{Sb}	0.37±0.18	0.69±0.08	-	1.06±0.15
LTAY	Pb	Sn	Sb	Sn + Sb
LTAY Average (wt%)	Pb 61.3±1.4	Sn 17.8±2.3	Sb 20.6±1.2	Sn + Sb 38.4±1.4
LTAY Average (wt%) Average (mol)	Pb 61.3±1.4 0.30±0.01	Sn 17.8±2.3 0.15±0.02	Sb 20.6±1.2 0.17±0.01	Sn + Sb 38.4±1.4 0.32±0.01

Table S1. SEM-EDX	results for	the LAY a	nd LTAY	sample.
				-



c)

Compound (*)	a (Å)	E _g (eV)	E _f (eV)
Pb ₂ Sb ₂ O _{6.5}	10.8706 (PBE)	Metal	-0.1844
$Na_{0.5}Pb_{1.5}Sb_2O_7$	10.7194 (PBE)	Metal	0.4834
$Na_{0.5}Pb_{1.5}Sb_2O_{6.5}$	10.7194 (PBE)	Metal	-0.3303
$Na_{0.5}Pb_{1.5}Sb_2O_{6.75}$	10.5041 (HSE)	0.5557 (opt) 0.4152 (fund)	-1.4431
NaPbSb ₂ O ₇	10.5647 (PBE)	Metal	0.8858
NaPbSb ₂ O _{6.5}	10.3996 (HSE)	2.2759 (opt) 1.9582 (fund)	-1.6232
$Na_{1.5}Pb_{0.5}Sb_2O_7$	10.4731 (PBE)	Metal	2.9092
$Na_{1.5}Pb_{0.5}Sb_2O_{6.5}$	10.4731 (PBE)	Metal	2.3627
$Na_{1.5}Pb_{0.5}Sb_2O_{6.25}$	10.3344 (HSE)	2.2325 (opt) 2.0898 (fund)	0.2633

b)

Compound	⊿H _f (eV)	Source
PbO ₂	-2.8447	NIST
PbO	-2.2740	NIST
Sb ₂ O ₃	-7.3559	Wikipedia
Na ₂ O	-4.3115	Aspiala et al.
NaCl	-4.2610	NIST

°) FOR DOINLA WITH $\Delta \mu_{N_2} = -3.32$.eV	I
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(*) Na₂Sb₂O₆ exists in the pyrochlore structure with a lattice constant a=10.2 Å (www.aflowlib.org)

Figure S2. a) Stability triangle for the phases involved in this study. The light blue-gray area indicates the chemical potential ranges for which Pb₂Sb₂O₇ is thermodynamically stable against precipitation of the competing oxides in the triangle. In these areas Na_{0.5}Pb_{1.5}Sb₂O_{6.5} and NaPbSb₂O_{6.5} will have a lower formation energy than Pb₂Sb₂O₇ in sufficiently Na-poor conditions that nor Na₂O or NaCl precipitate. The interval of Na chemical potentials for which this occurs at the vertices of the blue-gray area are indicated in the figure (all energies in eV). b) Experimental enthalpies of formation used in the calculations. c) Calculated formation energies, lattice parameters and band gaps for chemical potentials corresponding to point "A" in figure (A), as an example.



Figure S3. High resolution STEM-HAADF Z-contrast image of the two pyrochlore phases in the LAY sample: a) Na_{0.5}Pb_{1.5}Sb₂O_{6.5} along [141] zone axis and b) NaPbSb₂O_{6.5} along [011] zone axis. The atomic columns showing darker contrast are assigned to be Na rich (Pb deficient). As expected, the density of these darker columns is higher in NaPbSb₂O_{6.5}.



Figure S4. Computed band structure for Pb₂Sb₂O₇ in a pyrochlore structure. The presence of highly localized states at the Fermi level suggests an intrinsic structural instability for this compound.



Figure S5. Computed crystalline structure for a) $Pb_2Sb_2O_7$, b) $Pb_2SbSnO_{6.5}$, c) $Na_{0.5}Pb_{1.5}Sb_2O_{6.75}$, d) $NaPbSb_2O_{6.5}$. The spheres represent single atoms in the structure: grey = Pb, brown = Sb, purple = Sn, yellow = Na and red = O.



Figure S6. Tauc plots with calculated band gap sizes for the indirect semiconductors LAY and LTAY (a) and for the direct semiconductor CdS (b). Green = LTAY, Black = LAY, Red = CdS.



Figure S7. Computed band character for Na_{0.5}Pb_{1.5}Sb₂O_{6.75} with respect to a) angular momentum and b) atomic species. Na relative contribution to the band character is negligible and therefore it is not shown in (b).



Figure S8. Linear sweep voltammetry under light chopped illumination conditions. Scan rate = 0.5 mV/s; electrolyte = 1mM NaCl. Results with blue and green laser for the pigments in analysis.



Figure S9. Computed total density of states near the valence band maximum for the pyrochlore phases considered.