

Physics and heritage / Physique et patrimoine

## Physical colors in cultural heritage: Surface plasmons in glass

Jacques Lafait\*, Serge Berthier, Christine Andraud, Vincent Reillon, Julie Boulenguez

*Institut des nanosciences de Paris, UMR 7588 CNRS – Université Pierre-et-Marie-Curie, Paris 6, Campus Boucicaut, 140, rue de Lourmel, 75015 Paris, France*

### Abstract

Gold ruby glass and lustre ceramics are the almost unique examples of physical colors in the cultural heritage. The main physical effect at the origin of their color is the excitation of surface plasmon modes in metal nanoparticles. Moreover, in lustre, interference effects due a multilayer structure add a bright iridescence. The principle of plasmons is recalled in detail and applied to Gold ruby glass. The case of luster ceramics is treated in more detail due to the complexity of the effects involved: plasmon, scattering, interference between specular reflected light beams and also between scattered beams. **To cite this article: J. Lafait et al., C. R. Physique 10 (2009).**

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### Résumé

**Couleurs physiques et patrimoine culturel : Plasmons de surface dans les verres.** Le verre rubis et les céramiques lustrées sont pratiquement les seuls exemples de couleurs physiques dans le patrimoine culturel. L'effet physique principal à l'origine de leur couleur est l'excitation de modes de plasmons de surface dans des nanoparticules métalliques. Dans les lustres, les interférences dues à une structure multicouche complexe viennent ajouter un brillant effet d'iridescence. Nous rappelons en détail le principe des plasmons et l'illustrons par le verre rubis. Les céramiques lustrées sont étudiées plus en détail du fait de la complexité des phénomènes impliqués : plasmon, diffusion, interférence entre faisceaux lumineux réfléchis spéculairement, mais aussi entre faisceaux diffusés. **Pour citer cet article : J. Lafait et al., C. R. Physique 10 (2009).**

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**Mots-clés :** Couleur physique ; Plasmon de surface ; Interférence ; Diffusion ; Verre rubis ; Céramique lustrée ; Patrimoine culturel

### 1. Introduction

At the very beginning of the 19th century, Wolfgang Goethe, in his book *Theory of Colors* (1810) [1], put the physiological point of view as an essential element of the perception of color. He also proposed to distinguish between three ways of producing color which can be schematized as: a purely physiological way, a chemical one and a physical one. The two last ways were also, respectively, called: matter (or material)-color and light-color. Matter-color is the color created by color pigments or molecules dispersed in a binding agent. Light color is the “color without color”, produced only by the interaction of light with a structure a priori colorless. It is the color created by refraction and

\* Corresponding author.

*E-mail address:* [jacques.lafait@insp.jussieu.fr](mailto:jacques.lafait@insp.jussieu.fr) (J. Lafait).

dispersion (prism, water droplets, rainbow) [2], or by interference and diffraction in thin films, gratings, and more generally in photonic crystals [3]. These structures, presenting a periodicity of the size of the wavelength of the visible light, “play” with that light and produce colors associated with prized effects like iridescence, opal, nacre, or more commonly mate, gloss, saturation, etc. These effects are particularly striking in nature and more specifically in the living world (butterflies, beetles, etc.) [4], due to the very brilliant colors that they produce by an additive contribution of light beams. On the other hand, colors realized with pigments result from a subtractive process based on the absorption of pigments and therefore can never reach the brightness of structural colors [5]. The origin of structural colors and of most of these effects has only very recently been understood and analyzed, thanks notably to electron microscopy. It has allowed one to reveal the intimate nature of the structures, their multiscale organization and the role played by disorder as part of the robustness of their optical properties. It has been also the case for an other type of effect which can be positioned between chemical and physical effects or, in other words, between pigmentary and structural origins: the color due to surface plasmon excitation in metal colloids. It is the aim of this article to give the latest physical interpretation of the color of special glass from cultural heritage, Gold ruby glass and luster ceramics, within this analysis. As will be seen further, as early as the Roman times, complex structures using this phenomenon were empirically produced to realize new colors or new visual effects related to color. In a first part of this article, we will recall some fundamental results about surface plasmons and their characteristic properties in glass. In two last parts, we will analyze their use in Gold ruby glass and in luster ceramics.

## 2. Surface plasmons in metal colloids

A plasmon is a quantum object associated with longitudinal waves propagating in bulk matter through the collective oscillation of large numbers of electric charges [6]. It occurs obviously in gaseous charged plasmas, but also in solids containing enough free charges, like metals with a high density of conduction electrons: noble metals (gold, silver, copper) and simple metals (alkali metals and aluminum). This oscillation of charges has essentially a longitudinal character. It can therefore be excited in the bulk only by longitudinal waves, like electron waves, and not by light which is a transverse wave. Nevertheless, if the isotropy of the medium is broken, there exists a subset of these *eigenmodes* of free electrons which can couple with light. For instance at the plane interface between a dielectric and the conducting medium (in some specific conditions), or at the surface of a metal nanograin embedded in a dielectric (in any condition). In these configurations, the quantum character of the excitation is relaxed and one gets a polariton type excitation called a surface plasmon polariton which can be accessed optically over a large frequency range and is typically evidenced by a resonant absorption of the material under the correct coupling conditions. If this absorption occurs in the visible part of the light spectrum, it results a specific color.

This question has already been addressed at the end of the 19th century, from the point of view of scattering of electromagnetic radiation by spherical particles. Ludvig Lorenz solved the problem as early as 1889 by a mathematical derivation of fundamental principles of physics. His results, published only in Danish in 1890, were ignored by his contemporaries. Lord Rayleigh derived almost the same results in 1899 from Maxwell electrodynamics, in the case of spheres of size small compared to the wavelength. It is eventually Gustav Mie, apparently ignoring the Lorenz’s calculation, who gave in 1908 [7] a comprehensive solution of the problem applied to metal colloids, within the framework of the Maxwell equations. Due to the antecedents mentioned above and others, its theory is often called Lorenz–Mie theory or Lorenz–Mie–Debye theory. A modern formulation of the Mie solution to the scattering problem on a sphere has been given by J.A. Stratton in 1941 [8]. The first term of the Mie expansion of the intensity  $I_{scatt}$  scattered by a sphere versus the radius  $r$  of the sphere is analogous to the Lorenz expression and is proportional to

$$I_{scatt} \propto (2\pi/\lambda)^4 r^6 ((\epsilon_i - \epsilon_m)/(\epsilon_i + 2\epsilon_m))^2 \quad (1)$$

where  $\epsilon_i$  and  $\epsilon_m$  are the complex dielectric functions of, respectively, the inclusion (metal sphere) and the matrix (in general a dielectric), and  $\lambda$  the wavelength in the matrix. We recall that the complex dielectric function  $\epsilon = \epsilon_1 + i\epsilon_2$  is the square of the complex optical index  $\tilde{n} = n + ik$ . All these quantities depend on the frequency (i.e. the wavelength), that we omit for simplicity in the equations.

Within our modern interpretation in terms of modes, when the incident electromagnetic wave couples with the surface plasmon mode in the metal sphere, the intensity scattered by the sphere diverges. It occurs at the frequency where the following condition is fulfilled:

$$\epsilon_i = -2\epsilon_m \tag{2}$$

First remark: this condition needs a component with a negative dielectric function. It cannot be fulfilled by two dielectrics with real positive dielectric functions, at least in general in the visible spectrum. It can, however, be achieved with noble metals (see further). Second remark: the first term of the Mie expansion, that we envisage here, can be associated with the electric dipole contribution of the response of the sphere to the electromagnetic wave. The terms of higher order in  $r$  correspond successively to the magnetic dipole, the electric quadrupole, the magnetic quadrupole, etc. They do not diverge at the surface plasmon frequency, but produce an oscillatory response as a function of the frequency (or of the size  $r$ ) [9].

It is this approximation of the dipolar response or, in other words, the quasi-static approximation, which has been historically used first to derive the optical response of a real medium, like a metal colloid, containing a large number (but a not too high volume fraction) of metal grains (dielectric function  $\epsilon_i$ ) of size small compared to the wavelength, embedded in a dielectric (dielectric function  $\epsilon_m$ ). The realistic assumption in this approach is that this medium does not produce any measurable scattering and can be therefore treated as a homogeneous effective medium characterized by an effective dielectric function which can be calculated knowing the dielectric function of the constituents and the morphological parameters of the heterogeneous medium. Let us very briefly recall this classical (even if not totally rigorous) derivation [12]. The metal volume fraction  $p$  is the relevant morphological parameter, as soon as the size of the particles is small:

$$p = v_i / (v_i + v_m) \tag{3}$$

where  $v_i$  and  $v_m$  are the volumes respectively occupied by the metal inclusions and the matrix.

If the multipolar interactions between inclusions (mentioned above) can be neglected, i.e. if  $p$  is small, the electric field  $\mathbf{E}_e$  inside the effective medium is the volume average of the fields  $\mathbf{E}_i$  and  $\mathbf{E}_m$  inside respectively the inclusions and the matrix.

$$\mathbf{E}_e = p\mathbf{E}_i + (1 - p)\mathbf{E}_m \tag{4}$$

The electric displacement  $\mathbf{D}$  must follow the same rule

$$\mathbf{D}_e = p\mathbf{D}_i + (1 - p)\mathbf{D}_m \tag{5}$$

and it follows

$$\epsilon_e \mathbf{E}_e = p\epsilon_i \mathbf{E}_i + (1 - p)\epsilon_m \mathbf{E}_m \tag{6}$$

The expression of the field inside a spherical inclusion  $\mathbf{E}_i$  as a function of the uniform external field (in the matrix)  $\mathbf{E}_m$  can be derived from an easy electrostatic calculation

$$\mathbf{E}_i = \frac{3\epsilon_m}{\epsilon_i + 2\epsilon_m} \mathbf{E}_m \tag{7}$$

The effective dielectric function  $\epsilon_e$  can be calculated from the three Eqs. (4), (6) and (7) for spheres:

$$\epsilon_e = \epsilon_m \frac{\epsilon_i(1 + 2p) + 2\epsilon_m(1 - p)}{\epsilon_i(1 - p) + \epsilon_m(2 + p)} \tag{8}$$

This is the well-known Maxwell Garnett formula, published by James Clerk Maxwell Garnett in 1904 [10]. Its extension to spheroids has been given by Cohen–Cody–Couts–Abeles in 1973 [11]. Both are valid for small inclusions at very low concentration. They present a pole leading to a strong absorption for a frequency which now (as compared to formula (2)) also depends on the metal volume fraction  $p$ :

$$\epsilon_i = -\epsilon_m \frac{2 + p}{1 - p} \tag{9}$$

for spheres, and in addition, of a depolarization factor  $A$  in the case of spheroids. These conditions are formally analogous to the excitation of a surface plasmon polariton, as described at the beginning of this section. It leads to a divergence of the effective dielectric function of the medium if the dielectric function of the metal is purely real and negative or to a strong maximum if it has a small imaginary part.

One can now briefly analyze the influence of the different parameters, identified above, on the resonance frequency and consequently on the color. For this, it is necessary to recall the general expression of the dielectric function of metals [13]:

$$\epsilon_m = \epsilon_m^{ib} + \epsilon_m^c \quad (10)$$

a sum of an interband (*ib*) contribution of bound electrons of the valence bands and an interband or conduction (*c*) contribution of nearly free electrons of the conduction band. The interband contribution is associated with the allowed transitions of bound electrons between two energy levels. For the noble metals that we consider here, the first interband transitions are transitions between the top of the *d* bands and the first empty levels of the hybridized *s-p* conduction band. It is associated to this energy  $E_{ib}$  an absorption threshold called interband edge, beyond which other transitions (and thus absorptions) may occur. In terms of wavelength, these absorptions occur below  $\lambda_{ib}$  ( $E_{ib} = \hbar\omega_{ib} = hc/\lambda_{ib}$ ) and are directly related to the color of the metal. The high reflectivity of metals beyond  $\lambda_{ib}$  is achieved by the conduction contribution to the dielectric function, which is well accounted for by the Drude formula:

$$\epsilon_m^c = 1 - \frac{\omega_p^2}{\omega(\omega + i\gamma)} \quad (11)$$

where  $\omega_p$  is the plasma frequency<sup>1</sup> of the bulk metal.  $\gamma$  is a relaxation parameter accounting for collisions between electrons in the conduction electron cloud (electron–electron interactions) and interactions of these electrons with the metal network (electron–phonon interactions) and with defects in that network. The intrinsic color of bulk metals results from their reflectance as calculated from that dielectric function following:

$$R = \left( \frac{\tilde{n} - 1}{\tilde{n} + 1} \right)^2 \quad (12)$$

We recall that  $\epsilon = \tilde{n}^2$ . The reflectance of the three metals is represented in Fig. 1. Silver, which reflects all the wavelengths beyond 318 nm ( $E_{ib} = 3.9$  eV) looks colorless. Gold which reflects all the wavelengths beyond 496 nm ( $E_{ib} = 2.5$  eV) looks yellow, while Copper which reflects all the wavelengths beyond 590 nm ( $E_{ib} = 2.1$  eV) looks red or reddish.

Note that far enough beyond  $\lambda_{ib}$  (or below  $E_{ib}$ ), the tail of the interband contribution can be assimilated to a constant,  $P - 1$ , independent of the frequency in a relatively large domain, simplifying thus the expression of the metal dielectric function

$$\epsilon_m = P - \frac{\omega_p^2}{\omega(\omega + i\gamma)} \quad (13)$$

Let us now go back to the color of these metals when they are put under the form of nanoparticles dispersed in a dielectric matrix. The surface plasmon–polariton resonance occurs at the frequency  $\omega_{sp}$  given by Eq. (9) in the case of spherical metal inclusions. By using the Drude formulation (Eq. (13)) for the metal dielectric function and neglecting the relaxation term  $\gamma$ , one gets, for spherical particles:

$$\omega_{sp} = \frac{\omega_p}{\sqrt{P + \frac{2+p}{1-p}\epsilon_m}} \quad (14)$$

The principal parameters governing the optical behavior of the colloid clearly show from Eqs. (8) and (14): (i) the nature of the metal (*via*  $\omega_p$  and  $P$ , and possibly  $\gamma$ ); (ii) the metal volume fraction (*via*  $p$ ); (iii) the shape of the metal particles, that we will not envisage here.

For a given metal, the main dependence is on the metal volume fraction. It is summarized for Ag, Au and Cu in the following three figures (Figs. 2, 3, 4), where the calculation of the transmittance of a 1 mm thick glass slab containing spherical metal nanoparticles with variable concentration has been performed with the exact value (after formula (10)) of the dielectric function of the metals. It clearly shows up that the dip, characteristic of the surface plasmon–polariton occurs around 410 nm for Ag, 520 nm for Au and 570 nm for Cu. It is, however, less and less easy to define precisely

<sup>1</sup> We will make an abusive but common use of the word *frequency* for the *angular frequency*  $\omega_p$  (instead of  $\nu = \hbar\omega$ ).

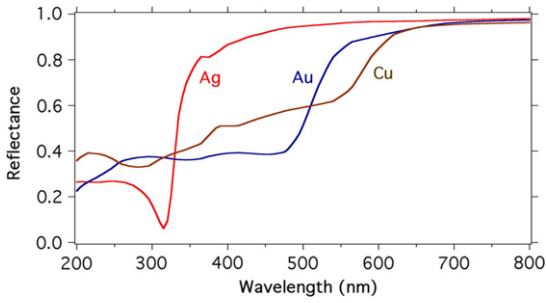


Fig. 1. Spectral reflectance under normal incidence of bulk Ag, Au and Cu.

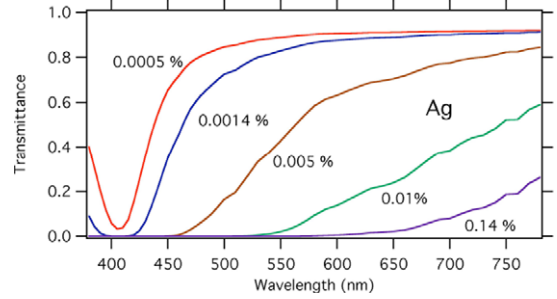


Fig. 2. Spectral transmittance of a 1 mm thick glass slab containing Ag nanoparticles of variable volume fraction.

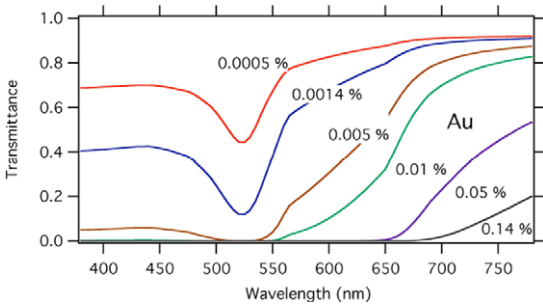


Fig. 3. Spectral transmittance of a 1 mm thick glass slab containing Au nanoparticles of variable volume fraction.

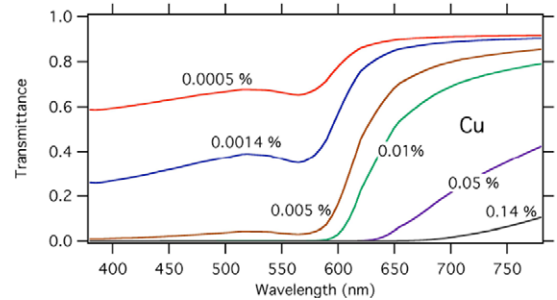


Fig. 4. Spectral transmittance of a 1 mm thick glass slab containing Cu nanoparticles of variable volume fraction.

from Ag to Cu because of the closer and closer vicinity of the interband transition edge (respectively 318 nm, 496 nm and 590 nm) which makes the right slope of the dip run weaker and weaker. Nevertheless, a common behavior is observed at increasing (but relatively low) metal fraction: the broadening of the dip and the global decrease of the transmittance. The corresponding evolution of the color observed in transmission is represented in Fig. 5 in the CIE 1931 color space. At very low metal fractions (few ppm), the hue is not far from white ( $x = y = z = 1/3$  in the  $x, y, z$  color space). At increasing metal fraction, the color evolution of Ag colloids follows an upper circle portion through the yellow and then the orange and tends eventually towards a saturated red, but with an extremely low brightness, i.e. a very dark color. The color of the Au and Cu colloids follows a lower circle portion with the same qualitative behavior, crossing the orange and the red before saturating with very low brightness. For the three metals, the optimum in saturation and brightness is obtained for metal fractions  $p$  around  $5 \times 10^{-5}$ , giving a yellow–orange color for Ag and deep reds for Au and Cu. Complementary calculations with much higher metal fractions (0.1 to 0.3), but also much thinner slabs, show that a shift of a few tens of nanometers towards the red can be obtained with a much increased absorption. However, these values of the morphological parameters do not correspond to those of the colored glass of the cultural heritage that we will describe in this article.

We have to eventually mention the dependence on the shape of the particles, even if not met in the cultural heritage materials. It is in fact the only dependence, allowing us to cover the whole visible color spectrum. By varying the axis-ratio of oblate to prolate spheroids from 0.14 to 3.2 one can effectively shift the surface plasmon–polariton resonance of Silver colloids [14] from 360 nm to 670 nm. The influence of the size of the particles is, for its part, very weak, as long as  $r$  remains small compared to the wavelength. It takes place *via* the relaxation term  $\gamma$  in the Drude formulation (formulae (11) or (13)), by adding to this term a contribution inversely proportional to the size of the particle. Its only influence is on the amplitude of the resonance which is damped at increasing particle size.

### 3. Gold ruby glass

To our knowledge, the first historical trace of the use of the surface plasmon effect in human activity is, at the 4th century, the production of what will be called later the *Gold ruby glass*. Its very first origin remains rather mysterious.

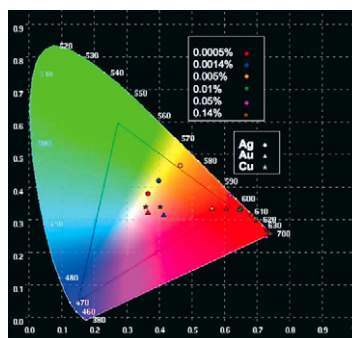


Fig. 5. Hue of a 1 mm thick glass slab with Ag or Au or Cu nanoparticles with different volume fractions ( $x$ ,  $y$  coordinates in the CIE 1931 color space).



Fig. 6. Lycurgus cup (4th century), ruby-red when illuminate from inside, by transmission. ©British Museum.



Fig. 7. Lycurgus cup (4th century), green when illuminate from outside, by reflection. ©British Museum.

Some make it date back up to the 7th century BC where Assyrian tablets of clay would mention a recipe allowing to produce an *artificial coral*. The oldest known object, kept in the British Museum, is the Lycurgus cup which dates back to the 4th century. It is the proof of the skill and the high technical level of the Roman in the work of glass and in the precipitation of noble metal particles in molten glass, even if this technicity was empirical and often accidental. The exact composition of the metal particles has been established only in the late 1980s [15]. The nanoparticles (50–100 nm in diameter) are composed of an Ag–Au alloy (mass ratio 7/3) containing a small amount of Cu in addition. In transmission (illumination from inside), the cup shows a beautiful deep ruby-red (see Fig. 6), while in reflection (illumination from outside) it looks green (see Fig. 7). These observations (red color) are in agreement with the predictions of the calculations presented above in transmission. Similar calculations in reflexion, not shown here, predict a green color. The recipe would have been lost during almost thirteen centuries and, in spite of the efforts of the Venetians to find its secret, it is in Bohemia that it would coming from a family of glass-masters of Brandenburg. He described that recipe in the book *Ars Vetraria Experimentalis* edited in 1679. Some bulk gold (silver is neither present in this recipe nor in the earlier one) is dissolved in *Aqua Regia* (nitric and hydrochloric acid mixture) then this solution is included in the doughy glass. Some tin is sometimes added in small quantities. The paternity of this rediscovery is disputed because it is mentioned that, at the same time, other Gold ruby glass were produced by Andreas Cassius, doubtless from similar techniques. The Cassius purple is met in numerous stained glasses and sacred vases of that time.

It is in any case in the middle of the 19th century in England, that the production of Gold ruby glass, from the same recipes, reached its peak with creations intended for lighting (glass chandeliers) and for the *art of the table*. The color comes then in a variety of less saturated tints, close to pale pink, called *cranberry*, very appreciated at that time. They were obtained by decreasing the gold concentration, as predicted by our simulations (see Fig. 5). The rich American tourists liked these tints to which they gave the name of their favorite fruit. These objects of Victorian time are very popular nowadays among the collectors and are produced in small quantities as copies for tourist purposes in Italy



Fig. 8. Small dish from Irak (9th century) probably from Samarra.



Fig. 9. Dish from Deruta (Italy, 15th century) decorated with a hunting scene.

and in New Zealand. The Gold ruby glass is also still used punctually in luxury bottling, for example by Guerlain or Christian Dior for their perfumes. For practical reasons and also for saving money, it is often now a thin glass layer which is colored and then stacked on the colorless glass constituting the bulk. The tints ranging from ruby-red to pink are thus obtained at a lower cost by using semi-conductors like CdSe or ZnS or Sn doped CdS (originally yellow).

The analysis of these glass reveals a composite structure composed of inclusions of gold and sometimes copper, with a size of few nanometers to a hundred nanometers, dispersed in the glass matrix in very low concentration, approximately 10 ppm for the *Gold ruby* and even less for the *cranberry* [16]. These values are in agreement with the results of our simulations (Figs. 3 and 5). Johann Kunckel's recipe shows that it is the reduction of gold chloride (produced from metal dissolved in *Aqua Regia*) in the molten glass that makes the precipitation of metal nanoparticles. This process is facilitated by the addition of tin, which reinforces the reducing character of the environment. The formation of the metal nanoparticles directly from the metal, as the legend about it, seems hardly feasible.

#### 4. Luster ceramics

To complete this short panorama of colors made from metal colloids, it is necessary to mention the luster. This technique is not so old as the Gold ruby glass, while very similar, because produced on the glaze of a ceramic, which is glass. It adds the coherent effect of an interference layer and the scattering by a rough interface to the effect of surface plasmons evoked in Section 2. It is thus the realization of a very special and striking optical effect related to color, from a material with a complex structure produced by an empirical and traditional way. It is an effect of iridescence similar to that observed on the wings of the Morpho butterfly, but with a spectral range of colors enormously wider and of an exceptional luminosity. It is coupled with another color effect, more attenuated, observable out of the specular direction, on the scattered light flux. Its color also depends on the angle of illumination. Moreover, on the contrary of Gold ruby glass, the metal nanoparticles do not contain any gold, but only silver and copper.

There are traces of this effect for the first time in the 9th century on Iraqi pottery in Samarra (Fig. 8), the capital of the Kingdom of the Abbasids at the time [17]. The technique develops in Iraq and Syria until the 11th century, then invades the entire Middle East in the 13th and 14th centuries [18]. It systematizes and reorients between the 13th and the 15th centuries, when reaching Spain [19]. It reaches its peak in Italy in the 15th and 16th centuries, in Umbria in the cities of Deruta and Gubbio (Fig. 9) [20]. A superb illustrated survey of these luster ceramics can be found in [21]. In short, the technique consists in depositing with a brush on top of the glaze layer of a ceramic, an overlayer of a silver (and/or copper) salt and appealing together under a reducing atmosphere at about 700 to 750 °C (low fire) [22]. Metal ions penetrate into the glaze where they precipitate and produce a composite layer of about 700 nm thick composed of metallic grains of varying size from 10 to 50 nm with a gradient of size and concentration (see Fig. 10) [23]. The whole can be modeled as a multilayer composed of a top layer of glass, with a rough interface with air, over a nanocermet layer (Ag and/or Cu grains in a glass matrix, with gradient of size and concentration) put on the ceramic scattering substrate (see Fig. 11) [24]. This produces two types of color effects, independent of one another, observed respectively around the specular direction of reflection (see Fig. 12) and beyond, in the cone of scattering (see Fig. 13) [25]. The specular color being specifically of structural origin, all hues can be obtained. And,

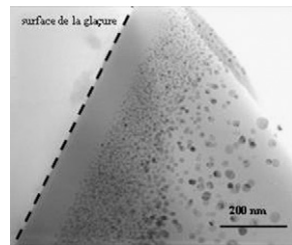


Fig. 10. Transmission Electron Micrography of a cross section of a luster ceramic showing its multilayer structure.

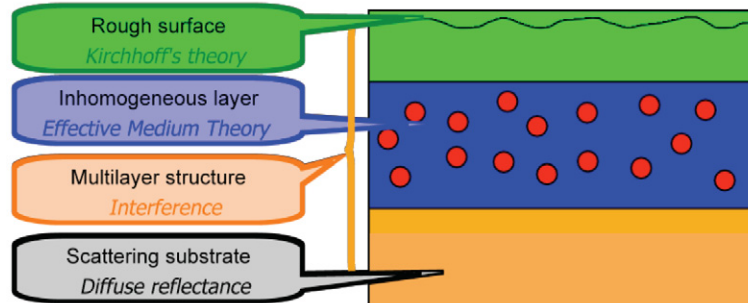


Fig. 11. Schematization of the multilayer structure of the cross section; optical effects and modeling of these properties in each layer.

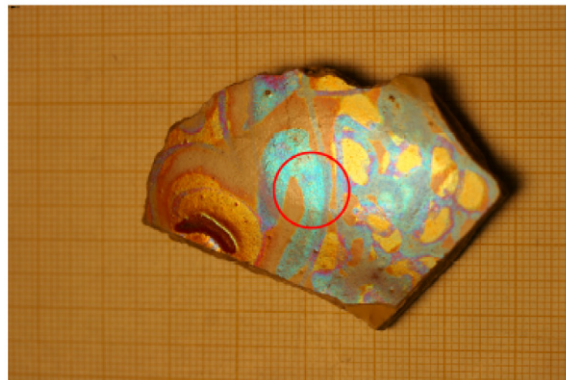


Fig. 12. Colors reflected by a luster ceramic illuminated at an angle of  $45^\circ$ , in the specular direction.

because of the multilayer structure, an exceptional brightness can be achieved, hence the brilliant metallic aspect of the iridescent colors in the specular direction (Fig. 12). These properties are illustrated in Fig. 15, which shows all the colors seen in specular on approximately 200 luster ceramics samples from all origins. The color obtained in the cone of scattering in turn is specifically due to the absorption of a plasmon-type and thus depends directly on the metal used (Ag or Cu or both). It is therefore, as we saw in Section 2, much more dull (lower brightness), although it may reach high levels of saturation (Fig. 13). These properties are collected in Fig. 16 for the 200 samples studied. They confirm the narrowness of the palette that is thus obtained and can be compared with colors of noble metal colloids shown in Fig. 5.

A sophisticated optical modeling, involving for the first time interference between scattered fluxes, allowed one to accurately account for the optical properties measured on these samples [26,27]. The main parameters governing these properties are:

- In the specular direction (green zone in Fig. 14): interference (number of layers, optical index and thickness of each layer);



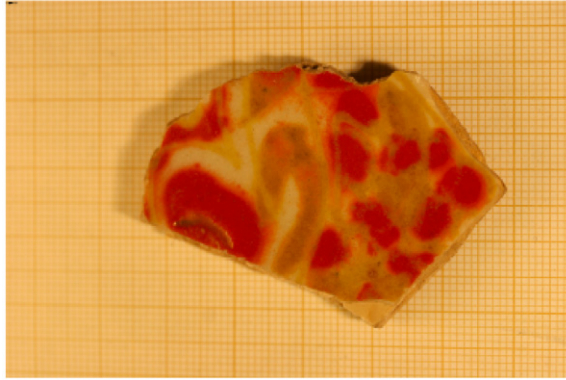


Fig. 13. Colors reflected by a luster ceramic illuminated at an angle of  $45^\circ$ , in the cone of scattering.

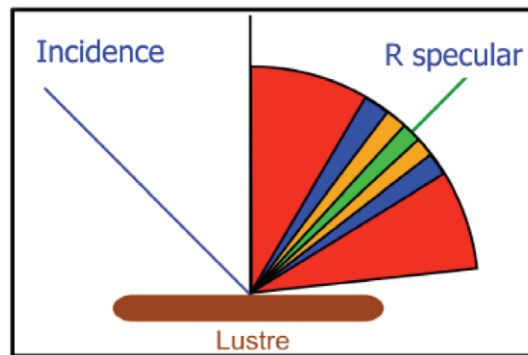


Fig. 14. Schematization of the beams reflected by a luster ceramic illuminated at an angle of  $45^\circ$ . In the cone of scattering, red zone. In the specular direction, green zone. The orange and blue cones, around the specular direction, schematize the transition between a dominant coherent component in the reflected beam (able to produce interference) and a dominant scattered incoherent component. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

- In the scattering cone (red zone in Fig. 14): plasmon absorption (kind of metal used, metal volume fraction, particle size, kind of matrix);
- In the intermediate cone close to the specular direction (orange zone in Fig. 14), there is observed a transition between a dominant coherent component in the reflected beam (able to produce interference) and a scattered incoherent component;
- In the intermediate cone close to the scattering cone (blue zone in Fig. 14), it is observed a transition between a coherent component in the reflected beam (able to produce interference) and a dominant scattered incoherent component.

This, of course, refers to the parameters of the potter, the cooking parameters (temperature, reducing atmosphere, duration of reduction).

## 5. Conclusion

We have insisted in detail on the description of the surface plasmon phenomenon which is the key phenomenon explaining the color of Gold ruby glass. It is clear that it is a resonant absorption phenomenon which therefore acts by a subtractive effect in the production of color. The color obtained by reflection is thus not very bright. On the other hand, the color obtained by transmission (which is not the exact complementary of the color by reflection, due to the absorption) can be bright enough, especially in the case of not too saturated hues. It is the case of the stained glass of the 17th century and more recently of the *cranberry* glass.

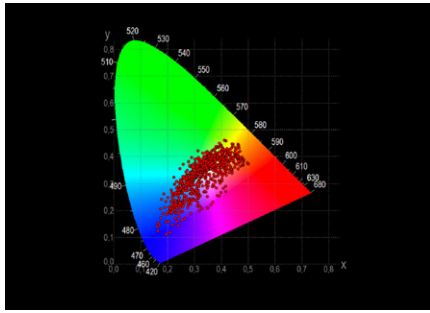


Fig. 15. Palette of the hues measured on 200 luster samples of all origins, in the specular direction, for four different directions of illumination ( $20^\circ$ ,  $30^\circ$ ,  $45^\circ$  and  $60^\circ$ ).

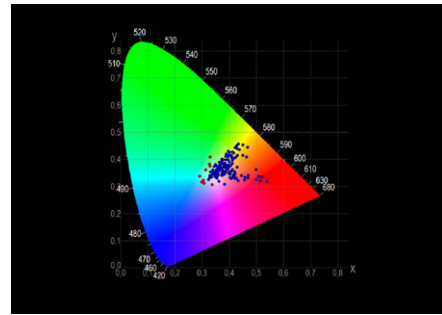


Fig. 16. Palette of the hues measured on 200 luster samples of all origins, in the cone of scattering, for four different directions of illumination ( $20^\circ$ ,  $30^\circ$ ,  $45^\circ$  and  $60^\circ$ ).

The surface plasmons do not play such a key role in the color and the visual effects of the luster ceramics. They fix the optical index of the medium (at a given depth in the layer), but the main visual effect is the bright iridescence of the luster, with such a large palette of hues. It is due to interference and manifests by a change of the color by varying the angle of illumination or observation. Besides this effect, other more dull colors can be observed out of the specular direction of reflection, in the cone of the scattered light, more directly related with plasmons. This effect has been totally understood and modeled only very recently [27]. Moreover, it has been demonstrated that the transition between the bright iridescent color in the specular direction and the color in the cone of scattering can be explained by interference between scattered light beams. It is a very unusual explanation, even if the effect is not so rare in the living world, for instance in butterfly wings.

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