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Published by
IATED Academy
iated.org

EDULEARN20 Proceedings
12th International Conference on Education and New Learning Technologies
July 6th-7th, 2020

Edited by
L. Gómez Chova, A. López Martínez, I. Candel Torres
IATED Academy

ISBN: 978-84-09-17979-4
ISSN: 2340-1117
V-1216-2020

Book cover designed by
J.L. Bernat

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A WAY TO UNDERSTAND THE SOLID-STATE CHEMISTRY FOR HIGH LEVEL EDUCATION STUDENTS: THE CASE OF A CERAMIC PIGMENT

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Abstract

The design of undergraduate laboratory sessions that provide meaningful research-based experiences enhances undergraduate curricula and prepares future graduate students for research careers. Solid State Chemistry has attracted the attention of many fields due to its wealthy chemistry as well as the versatility of its applications. Among the wide fields in this area, the study of an inorganic ceramic pigment has been selected in this experience.

A ceramic pigment can be defined as a colored inorganic solid, black, white or fluorescent, normally insoluble and practically unaffected neither chemically or physically by the vehicle or substrate in which it is incorporated. From a structural point of view, a ceramic pigment is formed by a host network where the chromophore component, usually transition ions, generates the color without producing a change in the structure. A suitable host network must have, in addition to a high chemical resistance against oxidation and reduction and a high melting point, energy differences between favorable bands to allow the chromophore to produce colors in the region of the visible spectrum.

A teaching strategy has been proposed for undergraduate chemistry students, introducing them to the solid-solid reaction by the synthesis of a pink ceramic pigment based on chromium doped ZnAl_2O_4 with spinel structure. The as-prepared pigment has been characterized by two different techniques, such as X-Ray Diffraction and UV-Vis spectroscopy, commonly used in Solid-State Chemistry. In this way, students will have a first approach to the basic concepts of the Solid-State Chemistry through simple laboratory sessions.

Due to the simplicity and easy strategy used in this study, the students will be able to participate actively, fulfilling the pedagogical character demanded by a Problem Based Learning.

Keywords: Solid-State Chemistry, Inorganic Pigment, Chromophore, Problem-Based Learning.

1 INTRODUCTION

Nowadays, students are demanded to work in different environments where higher-level thinking skills are required. Hence, problem-based learning (PBL) has been a longstanding educational approach that allows them to acquire new concepts to solve problems critically and work more independently [1,2].

The ceramic tiles sector, highly related to the Solid-State Chemistry, is an industrial field that includes both the production of ceramic tiles and the supply of the raw materials for their production. Among all of its subsectors, special attention must be put on the production of ceramic pigments.

Based on these two premises, Master's students with additional specialization in "Advanced Materials" are asked to study a ceramic pigment using the PBL tool, in order to approach to the Solid-State Chemistry in a practical way, and to understand some advanced concepts that they learn in their theory lessons, including the basics of a pigment and its possible applications.

1.1 Theory

1.1.1 Understanding the Solid-Solid Reactions

A solid-state reaction occurs between two or more solid substances which produce another solid without using solvents to solubilize reactants (also known as a dry reaction). This process is one of the most important ones in the ceramic industry for the preparation of solids, both in powder and in bulk form.

In these reactions, the extent of product formation is influenced by the area of interfacial contact and the diffusion through a product layer. The driving force of the reaction is the diffusion process which depends on the temperature, existence of possible structural defects, presence of impurities and effectiveness of phase boundary contacts.

This method holds many obvious advantages such as simple operation, energy-conserving, cost-saving and no solvents, which is very suitable for mass production. However, since solid-state reactions take place with great difficulty, it is necessary to reach high temperatures and consequently, some losses of volatile compounds and deviations from the nominal stoichiometry can occur. To solve these problems, it is necessary to add some additives, known as mineralizers, in small amounts that favor the diffusion processes. As a result, a fluid phase is generated and the reactions proceed without the high activation energy barrier required for the solid-state processes [3].

1.1.2 Understanding the Inorganic Pigments

A pigment can be defined as a colored organic or inorganic solid normally insoluble and practically unaffected neither chemically or physically by the vehicle or substrate in which it is incorporated. Inorganic pigments are an integral part of many decorative and protective coatings. They are also used for mass coloration of materials such as glaze, ceramics and porcelain enamels. To be considered as a good ceramic pigment, it must satisfy some basic requirements: having a stable crystalline structure at high temperatures, being insoluble in a glass matrix, having a uniform color, and no modifying the properties of the material (hardness, resistance to abrasion and the attack by acids or bases).

Inorganic pigments are mainly based on transition metal ions (known as chromophores) which are incorporated into the crystalline structures of oxides. Cr(III) is one of the most common dopant ions due to its broad optical and technological properties as a consequence of its electronic structure. Moreover, the host matrix influences the strength of the crystal field surrounding the Cr(III) ions, leading to a large chromatic variety from green to red-pink colors upon low and high crystal field conditions, respectively [4].

The spinel-type family of compounds, AB_2O_4 , has a host matrix that allows obtaining a great variety of colors depending on the chromophores and, as a result, it is probably the most used pigment structure. In particular, the $ZnAl_2O_4$ spinel (gahnite) presents a good optical quality provided by the very small size of spinel nanocrystals formed during the thermal treatment. In fact, the $Zn(Al,Cr)_2O_4$ system yields a pink pigment. It is important to note that students are familiarized with the crystallochemistry concepts required to understand and describe these inorganic structures (atomic positions, coordination polyhedra, unit cell parameters...). Thus, this experience enables them to link these concepts with the Solid-State Chemistry and evaluate how these factors may influence the final properties of the materials.

1.1.3 Understanding the Color

The human eye can perceive millions of colors. Indeed, everyone can see the color in different ways. Therefore, how can we evaluate, in a precise way, the color of an object using a consistent model and standard? This is why the CIE $L^*a^*b^*$ color space was developed. This color space is widely used because it correlates numerical color values with human visual perception. Researchers and manufacturers use it to evaluate color attributes, identify inconsistencies, and express precisely their results in numerical terms. In this color space, L^* indicates luminosity, and starts at 0 in the center, a^* is the red/green coordinate (+a indicates red, -a indicates green) and b^* is the yellow/blue coordinate (+b indicates yellow, -b indicates blue), Figure 1.

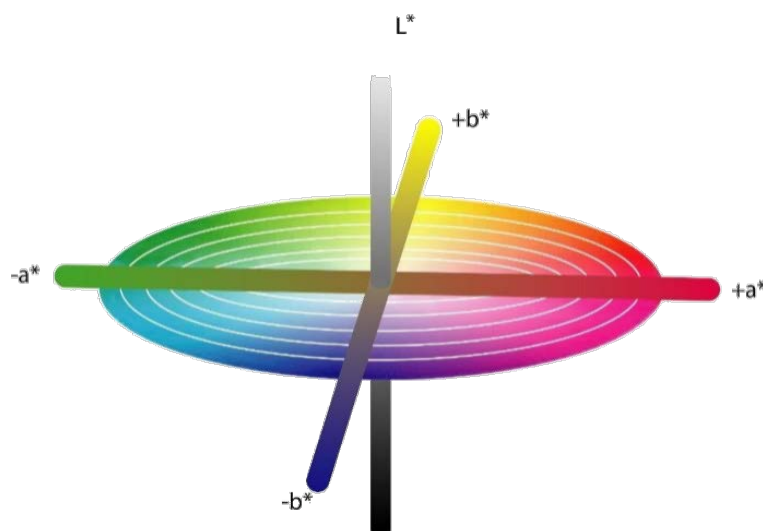


Figure 1. Representation of the CIE $L^*a^*b^*$ color space.

1.1.4 Understanding the X-Ray Diffraction

After the synthesis of the pigment, students face the main characterization technique used nowadays in the Solid-State Chemistry and crystallography, the X-Ray Diffraction (XRD). This technique is based on the interaction of the X-rays with a crystalline sample.

The equipment is mainly composed of an X-ray tube, a sample holder and a detector. The X-rays are produced when the accelerated electrons collide with a metallic target. A crystal can be schematized as a structure composed of semi-transparent mirrors arranged in parallel layers, called crystal planes, and spaced by distances (d) of the same order of the wavelength of the incident radiation applied in the sample (λ). The λ of the X-ray commonly used is the characteristic radiation K_α emitted by the Cu, $\lambda=1.5418$ Å. Some of the X-rays are reflected in the plane with the angle of reflection equal to the incidence angle. These reflections can be combined constructively or destructively, depending on the interplanar distance (d). The condition for constructive interference to occur is:

$$n \lambda = 2d \sin\theta \quad (1)$$

This fundamental relation regulating the XRD is known as the Bragg's law, where the path difference between two waves undergoing constructive interference is given by $2d \sin\theta$. θ is the scattering angle, n is the reflection order (an integer number), λ is the wavelength of the X-rays, and d is the interplanar distance. When the Bragg's Law is satisfied, the reflected beams are in phase and interfere constructively. These interferences can be represented in a diffractogram.

For a crystalline inorganic material, its diffractogram is like its fingerprint and can help us to identify what crystalline phase is that of our material. In order to do that, we can check the existing databases, where different XRD cards can be found according to the JCPDS-ICDD notation (Journal Committee Powder Diffraction Standard-International Centre of Diffraction Data). Furthermore, XRD is easy, fast and reasonably cheap, making it one of the most characterization techniques used in worldwide inorganic laboratories [5–7].

2 METHODOLOGY

2.1 Time Distribution

Seven work sessions (4 h/session) were used to complete the proposed project. The first one was used to weigh, grind and fire the powders obtained. The following two sessions were employed to perform the characterization of the pigments, XRD and UV-Vis spectroscopy were used for this propose. Finally, in a period of four sessions, students made a complete report of the results with exhaustive bibliographic research, helped by their teachers.

2.2 Synthesis of the Pigments

In this section, students learn the basics of solid-state reaction, the difficulties and the reason for the use of mineralizers. The method used to prepare all the samples was the ceramic method. The amount of raw materials was calculated for obtaining 10 g of the final product. Based on the stoichiometric composition of $\text{ZnAl}_{2-x}\text{Cr}_x\text{O}_4$ (being $x = 0$ and 0.4), the samples were prepared by partial substitution of the Al(III) ions by Cr(III) to preserve the electroneutrality. The raw materials used were: ZnO, Al_2O_3 , Cr_2O_3 , H_3BO_3 , and LiF. All the reagents were industrial grade. For comparison purposes, the mineralizers H_3BO_3 or LiF were also added to each sample (2% in weight) [3].

The mixtures were refined and homogenized with acetone in a planetary ball mill. After being dried, the samples were fired in an electrical furnace at a heating rate of $10^\circ\text{C}/\text{min}$ at 1000 and 1200°C for 2 h. The synthesis process is depicted in Figure 2.

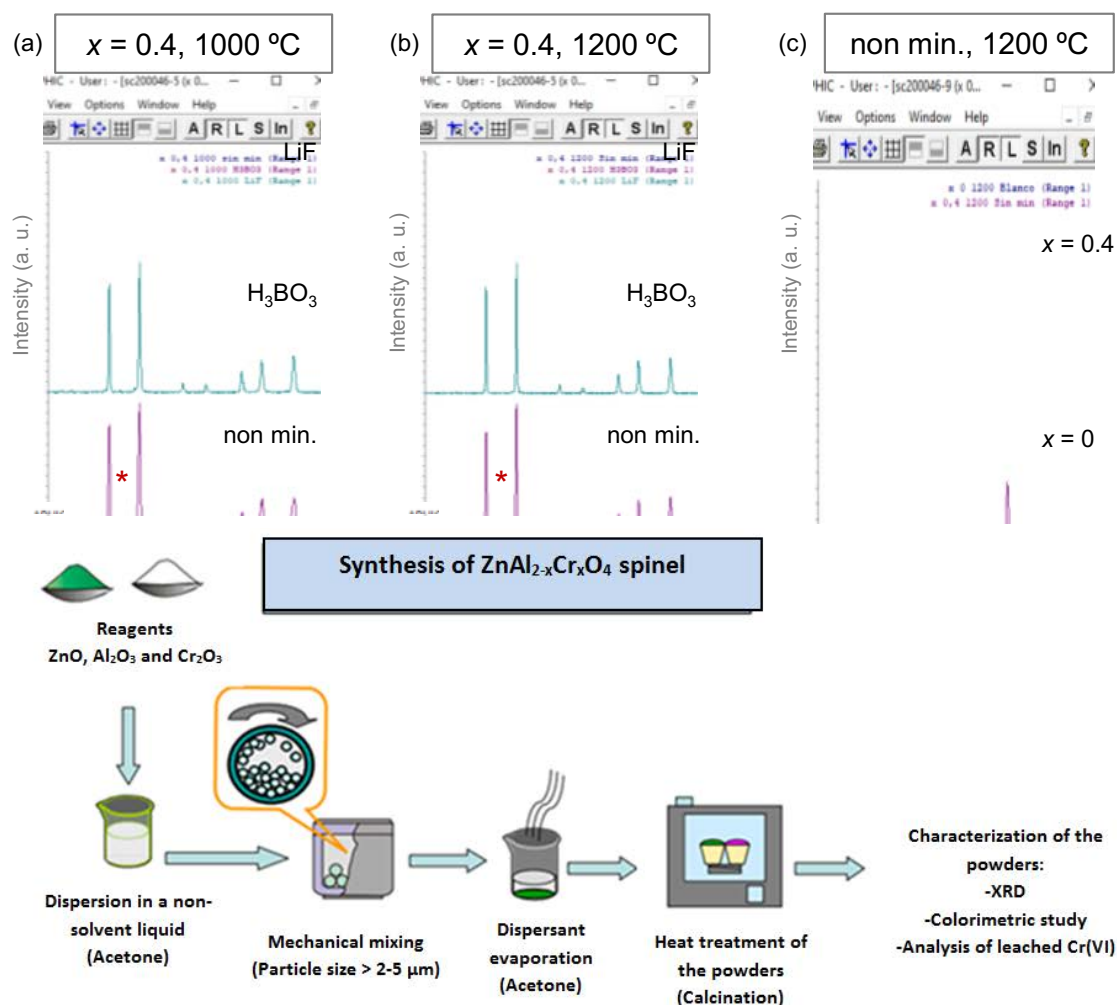


Figure 2. Scheme of the synthesis procedure.

2.3 Experimental Analysis

Powder X-ray diffraction (XRD) measurements were performed using a Bruker D4-Endeavor X-ray diffractometer with $\text{CuK}\alpha$ radiation. All data were collected between $20 \leq \theta \leq 70$ at room temperature. The CIE $L^*a^*b^*$ coordinates were measured using a Minolta CR310 colorimeter with a beam diameter of 8 mm. The study of Cr(VI) content in the washing liquids of the samples was performed with a CARY 500 SCAN VARIAN spectrophotometer at 540 nm.

3 RESULTS

Following a pedagogical approach, students ask themselves some questions to understand the results obtained after the characterization of the different samples.

3.1 X-Ray Diffraction

Figure 3(a,b) shows the diffractograms of samples doped with Cr(III) fired at 1000 °C (a) and 1200 °C (b) using different mineralizers (LiF and H₃BO₃) or without them (non min.). All the main peaks observed were assigned to the zinc aluminate structure (JCPDS-ICDD 82–1043). However, for samples without mineralizer, some peaks corresponding to secondary phases were also observed (red stars in Figure 3). Figure 3(c) highlights the effect of the dopant when it is introduced into the host lattice at 1200 °C.

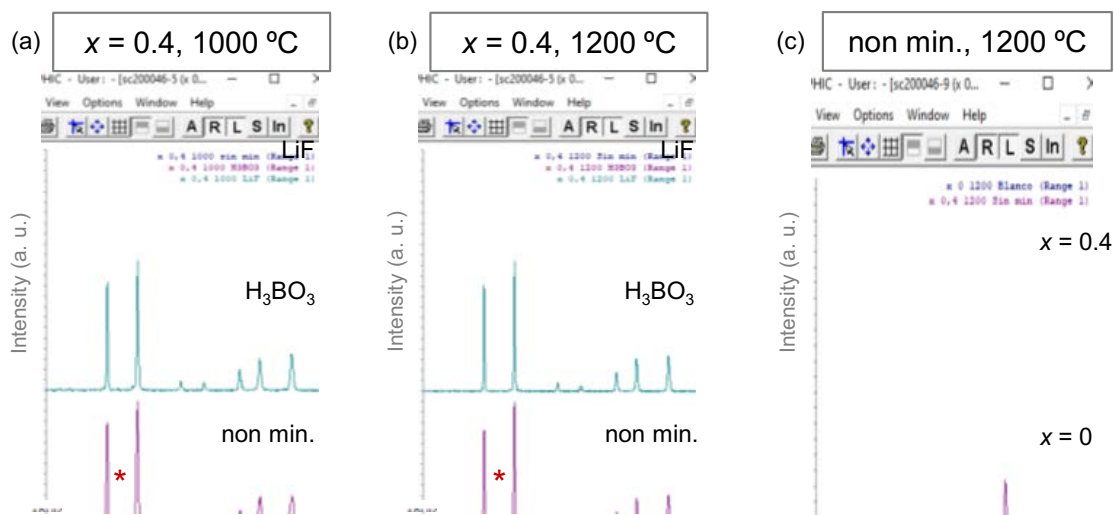


Figure 3. XRD patterns for the powder samples with $x = 0.4$ at (a) 1000 °C and (b) 1200 °C. (c) Effect of the dopant when it is introduced into the host lattice for samples fired at 1200 °C without using mineralizers. The red stars correspond to secondary phases.

In order to understand the most important results observed in these XRD analyses, the students could raise the following questions:

- Question 1: What is the difference between the diffractograms of samples fired at 1000 and 1200 °C?
 - ✓ Answer 1: As can be easily seen, the peaks corresponding to the samples fired at 1200 °C are narrower than the ones corresponding to those fired at 1000 °C. Furthermore, the background noise at 1200 °C is very low in comparison to the one at 1000 °C.
- Question 2: How do mineralizers affect the samples?
 - ✓ Answer 2: Samples without mineralizers present some peaks associated with the presence of secondary phases, highlighted with red stars in Figure 3(a, b). However, the use of mineralizers leads to the formation of pure single phases since the reactivity is higher.
- Question 3: According to Figure 3(c), what is the effect of Cr(III) when it is introduced into the host lattice?
 - ✓ Answer 3: The effect of Cr(III) in the structure can be described considering the Bragg's Law, previously explained. Cr(III) has a higher ionic radius than Al(III). As a consequence, when we partially substitute Al(III) ions by Cr(III), the interatomic distances are increased, and so does the interplanar distance (d). Therefore, a shift of the peaks towards the left (smaller 2θ angles) occurs, as can be seen in Figure 3(c).

3.2 Colorimetric parameters







In Table 1 we can see the results of the colorimetric characterization of the powders: those using different mineralizers and the sample without it; all of them fired at different temperatures (1000 °C and 1200 °C). To choose the best pigment, we analyze the value of a^* and b^* : since we want to obtain a pink color, the best mineralizer is the one that has higher a^* and b^* parameters.

Given it, the best powder is the one obtained using LiF with $x = 0.4$ and fired at 1200 °C. On the other hand, all the values of L^* are between 77 and 81 with the lowest values corresponding to LiF.

Once the colorimetric parameters were obtained, the students could ask the following questions:

- *Question 1: Why are different tonalities of colors obtained?*
 - ✓ *Answer 1:* The variety of colors can be well explained considering the different values of L^* , a^* , and b^* . As can be seen in Table 1, the presence of mineralizers allows obtaining more intense colorations because they contribute to a higher reactivity, as it has been previously explained in the XRD section (Figure 3). The table also shows that either in the absence of mineralizer or at lower firing temperatures, grey tones are obtained.
- *Question 2: Why the color of the sample obtained using LiF and fired at 1200 °C is more intense than the others?*
 - ✓ *Answer 2:* When using LiF as a mineralizer, the most intense and pink color is obtained due to the highest value of the parameters a^* and b^* , corresponding to the pink tone in the CIEL*a*b* color space. This result highlights the effect of mineralizers and firing conditions on the reactivity and, as a result, on the color of the powders.

Table 1. Colorimetric parameters and color pigment obtained for the different Cr(III)-doped samples.

Sample	Nominal Composition	Mineralizer	Firing Temperature (°C)	Color	L^*	a^*	b^*
1	$ZnAl_{1.6}Cr_{0.4}O_4$	-	1000		78.8	5.7	4.9
			1200		81.0	8.46	6.5
2	$ZnAl_{1.6}Cr_{0.4}O_4$	H_3BO_3	1000		80.85	6.8	7.0
			1200		81.0	10.1	9.7
3	$ZnAl_{1.6}Cr_{0.4}O_4$	LiF	1000		77.5	9.2	8.3
			1200		79.1	12.4	10.1

3.3 Leaching

During the thermal treatment of the pigment, it is possible that some trivalent chromium does not react totally and, therefore, is not introduced in the spinel structure and might be oxidized to Cr(VI).

In this part of the project, the students learn the importance of taking into account all the hazardous components during the synthesis of chemical products. Some chromium species, especially Cr(VI), are carcinogenic and, thereby, mandatory to eliminate in industrial production to safeguard the employer's health [8,9]. Many clinical reports have studied the mechanisms of chromium toxicity. Indeed, according to Dayan A. D. *et al.* [10], it has been found that Cr(VI) is the ion responsible for most of the toxic actions, while the underlying molecular damage might be attributed to its intracellular reduction to the even more highly reactive and short-lived chemical species Cr(III) and Cr(V).

In this case, the students made an acid leaching using 3 M HNO₃ so as to wash out the possible Cr(VI) present in the as-synthesized pigment. To assess the quantity of Cr(VI) leached, absorbance measurements of the washing waters were performed irradiating with a wavelength of 540 nm, which corresponds to the maximum peak of absorption of Cr(VI) species. The experiment was based on the Beer-Lambert's law, which linearly correlates the absorbance of sample (*A*) with its molar absorption coefficient (ϵ), molar concentration (*c*) and the optical path length (*l*):

$$A = \epsilon c l \quad (2)$$

Therefore, having previously prepared a calibration curve, students were able to calculate the Cr(VI) content in the different samples. For the samples without mineralizer, the analyses indicated that there was only small segregation of Cr(VI), approximately 0.3 ppm, but below the permitted limits of the European legislation [3]. With the increment of the firing temperature, even lower concentrations of Cr(VI) were obtained. Furthermore, samples prepared with the addition of a mineralizer had negligible concentrations of Cr(VI), thus corroborating the formation of a solid solution with all chromium ions introduced in the structure. *As a conclusion, following a question-answer pedagogical approach again, the students were able to relate these results with all the previous characterizations:*

- *Question 1: What is the oxidation state of chromium found in the washing waters?*
 - ✓ *Answer 1:* In our study, the chromium incorporated in the structure is Cr(III), while the chromium not incorporated in the crystal structure is Cr(VI).
- *Question 2: How can we relate the presence of Cr(VI) in the washing waters with the resulting color of the pigment?*
 - ✓ *Answer 2:* The red color is attributed to the presence of Cr(III) inside the crystal. Thereby, when the pigment is redder (higher values of the parameter *a**), less Cr(VI) is leached out of the sample.

Therefore, through this experience, the students have been able to understand the basics concepts of the Solid-State Chemistry by putting the acquired knowledge into practice. Moreover, they have been able to establish a plausible relation between the synthesis, structure, and properties (mainly the color) of the ceramic pigments based on the Zn(Al,Cr)₂O₄ system.

4 CONCLUSIONS

One of the aims of the present work was to make science more attractive, close and enjoyable to undergraduate students. In particular, in this work, the synthesis of an inorganic pigment has been proposed as a simple but, at the same time, an effective way to understand the basic concepts of Solid-State Chemistry. In the present work, students used different mineralizers (LiF and H₃BO₃) to increase the reactivity of the compounds. As a result, they concluded that LiF turned out to be the best mineralizer, which allowed improving the inter-diffusion of the chromophore cation and increasing the chromatic coordinates, which lead to the obtention of a more pink-colored pigment. Moreover, students could see that the reactivity of the material is higher when the temperature is increased from 1000 to 1200 °C, as it is proved in the XRD patterns.

Finally, it is worthy of praise to notice that through this experience, students had the opportunity to learn the importance of Solid-State Chemistry and Materials Science in their daily life. Besides, they have achieved a better comprehension of the solid-state reaction and the most common characterization techniques used in this field of science.

ACKNOWLEDGMENTS

We would like to thank the “Máster en Química Aplicada y Farmacológica” of the Universitat Jaume I of Castellón. We are really grateful to Lisa Giambellini, student of “Design e comunicazione visiva” at the Politecnico di Torino (Italy) for her design “Representation of the CIE L*a*b* color space”. We think that her contribution helps to have a clearer vision of the color theory. P. S.-G. also thanks the Spanish Ministerio de Ciencia, Innovación y Universidades for an FPU predoctoral contract.

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