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Influence of Some Mineralizers in the Synthesis of Sphene-Pink Pigments

E. Cordoncillo, F. del Río, J. Carda, M. Llusar and P. Escribano*

Departmento de Química Inorgánica y Orgánica. Area de Química Inorgánica. Universitat Jaume I,
12080 Castellón, Spain

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Abstract

In this paper the sphene-pink pigment with and without different mineralizers has been synthesized in order to know the best additive and proportion in which it has to be added. Characterisation of samples by X-ray diffraction indicates that samples without mineralizers exhibit peaks of small intensities assigned to the sphene structure after firing at 1300°C/2 h. The addition of H_3BO_3 points out that the synthesis of the above compound takes place at lower temperatures and establishes the best proportion in which Cr_2O_3 could be added. In order to improve the synthesis of the sphene pigment, $LiBO_2$, Li_2CO_3 and H_3BO_3–Li_2CO_3 have been employed. Results obtained by X-ray diffraction and colour measurements show that $LiBO_2$ is the best additive tested for sphene-pink synthesis. The influence of quantities of $LiBO_2$ and Cr(VI), as well as B contents in the washing liquids have also been established.

1 Introduction

The presence of the Cr(III) ions in solids yield to various colorations: pink, red, reddish-brown or green. Polymorphic crystals show the influence of the structure in which the Cr(III) ion acts as chromophore.

Calcium tin silicate, $CaSnSiO_5$, shows a structure which consists of infinite chains of vertex-sharing SnO_6 octahedra linked by isolated SiO_4 tetrahedra. This lattice—also known as 'tin sphene'—has attracted some interest, both as a host lattice for the incorporation of colorant metal ions as transition metals, and also as a sealant for the inclusion of glaze-unstable coloured pigments.[1,2] Although the 'chrome tin pinks' pigments, DCMA 12-25-5,[3] have been studied for a long time, there are many problems associated to the stability and reproducibility of the final colour originated by the problems of the solid state reactions in the raw materials.

In solid-solid state reactions, the extent of product formation is influenced by the area of interfacial contact and the ease of diffusion through a product layer. The diffusion of reactants through a product layer depends on temperature, defect structure of product layer, grain boundary contacts, presence of impurities and effectiveness of phase boundary contacts.[4]

In many cases, and since solid state reactions take place with great difficulty, it is necessary to reach high temperatures and consequently loss of volatile compounds and deviations from the stoichiometry can be occur. In order to avoid these problems, it is necessary to add additives in small amounts for favouring the interdifusion processes. So, the effect of some substances in silicate systems is to provide a fluid phase through which reactions can proceed without the activation energy barrier present for the solid-state process.[5]

These additives are known as mineralizers and several actions, as far as we know, can be attributed:[6]

1. if they melt at temperatures below that at which the pigment is obtained, they could provide a liquid medium and increase the diffusion rate between the reactives, thereby speeding up the reaction;
2. its action, which can also act on the particle size, is very important since the sintering rate is roughly proportional to the inverse of the particle size and in controlling the final colour. It is a well-known fact that the percentage of light which is reflected by a material increases with decreasing particle size;

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*To whom correspondence should be addressed:
e-mail: escriban@qio.uji.es

3. if some ion of the additive can be able to replace some chromophore ion of the pigment, a reinforcement of colour can take place due to a modification of the crystalline field intensity.

It is very difficult to study the action of mineralizers because despite the phase diagrams being very useful in obtaining the range of temperature and composition over which certain phases or mixtures of phases under conditions of thermodynamic equilibrium, they do not show all the effects of small changes in composition.[7]

The aim of this paper is first to test the most appropiate quantity of Cr_2O_3 in the synthesis of sphene-pink pigment; once this has been established to study the influence of certain additives by controlling the synthesis temperature by means of X-ray diffraction and colour of the pigment by colorimetric measuments. The quantity of Cr(VI) and B in the washing liquids and the stability of the obtained pigment in some glazes have also been proved.

2 Experimental

The raw materials used were: SnO_2, Cr_2O_3, $CaCO_3$, SiO_2 (industrial quality) and as additives: H_3BO_3, Li_2CO_3 and $LiBO_2$ (CP grade).

On the basis of the stoichiometric composition of tin sphene, $CaSnSiO_5$, the samples were prepared by introducing the chromophore cation in the form of Cr_2O_3 and by substitution of four Cr(III) ions by three Sn(IV) ions in order to preserve the electroneutrality.

The samples prepared are shown in Table 1. The mixtures were refined and homogenized in acetone in a planetary ball mill. After being dried, the samples were fired in an electrical furnace GR/8C-S Nannetti model at a heating rate of 10°C/min at 800, 900, 1000, 1100, 1200 with soaking times of 2 and 6 h at each temperature and at 1300°C for 2 h. In order to improve the reactivity between solid phases, a continued grinding was done after each heat cycle.

Crystalline phase evolution of calcined powders was carried out with a SIEMENS D5000 diffractometer with Bragg–Brentano geometry using CuK_α radiation (40 kV, 20 mA, divergence slit = 1°, receiving slit = 1°, detector slit = 0·15°), a scintillation detector and a secondary graphite monochromator.

Table 1. Stoichiometry of samples without mineralizers

Sample	*Stoichiometry*
1	$CaSnSiO_5$
2	$CaCr_{0{\cdot}04}Sn_{0{\cdot}97}SiO_5$
3	$CaCr_{0{\cdot}16}Sn_{0{\cdot}88}SiO_5$
4	$CaCr_{0{\cdot}32}Sn_{0{\cdot}76}SiO_5$
5	$CaCr_{0{\cdot}48}Sn_{0{\cdot}64}SiO_5$

Intensities were collected by step-scanning from 20 to 50° (2Θ) with a step size of 0·050° (2Θ) and 1 s counting time each step. The goniometer was controlled by the Siemens DIFFRACT AT software, which makes the integration of the diffraction peaks.

Since the tin sphene was not observed in any compositions at the temperatures used in this study, H_3BO_3 was added as mineralizer to each sample (2% in weight, $1{\cdot}9\times10^{-2}$ g of B in the amount of sample prepared). The mixtures were submitted to the same thermal treatments. In Table 2, the samples studied are indicated.

The results obtained from XRD analysis indicated that the sample that developed better the tin sphene phase was sample 2A, but it was not obtained as a single phase after firing at 1300°C/2 h.

To improve the development of tin sphene, $LiBO_2$, Li_2CO_3 and Li_2CO_3–H_3BO_3 were added to the sample 2. The quantities of B and Li were calculated to be equal in all the additives tested ($1{\cdot}2\times10^{-2}$ g of Li and $1{\cdot}9\times10^{-2}$ g of B, calculated for a same quantity of sample 2). Table 3 shows the samples and amounts (in g) of mineralizers employed. In this table, sample prepared with H_3BO_3 has also been included for reference.

From XRD diffractograms of fired samples and CIELAB colour parameter measurements, the additive that showed more effectiveness in the development of the tin sphene was $LiBO_2$ (sample 2B). Because of that, in Table 4 we present the samples prepared by varying the quantity in g of that mineralizer. Sample 2B has been included in this table for reference.

Considering that the content of Cr(VI) ions is very important due to its high toxicity as carcinogen, the amount of Cr ions in washing liquids was

Table 2. Stoichiometry of samples with H_3BO_3 (2% in weight)

Sample	*Stoichiometry*
1A	$CaSnSiO_5$–2% H_3BO_3
2A	$CaCr_{0{\cdot}04}Sn_{0{\cdot}97}SiO_5$–2% H_3BO_3
3A	$CaCr_{0{\cdot}16}Sn_{0{\cdot}88}SiO_5$–2% H_3BO_3
4A	$CaCr_{0{\cdot}32}Sn_{0{\cdot}76}SiO_5$–2% H_3BO_3
5A	$CaCr_{0{\cdot}48}Sn_{0{\cdot}64}SiO_5$–2% H_3BO_3

Table 3. Composition of sample 2 with H_3BO_3, $LiBO_2$, $LiCO_3$ and H_3BO_3–Li_2CO_3 as additives

Sample/ precursor	*B (H_3BO_3)*	*Li, B ($LiBO_2$)*	*Li (Li_2CO_3)*	*Li, B (Li_2CO_3, H_3BO_3)*
2A	$1{\cdot}9\times10^{-2}$	—	—	—
2B	—	$1{\cdot}2\times10^{-2}$ $1{\cdot}9\times10^{-2}$	—	—
2C	—	—	$1{\cdot}2\times10^{-2}$	—
2D	—	—	—	$1{\cdot}2\times10^{-2}$ $1{\cdot}9\times10^{-2}$

Table 4. Compositions of samples with different amounts of $LiBO_2$

Sample	*Li, B ($LiBO_2$)*
2B	$1{\cdot}2\times10^{-2}$, $1{\cdot}9\times10^{-2}$
2B1	$0{\cdot}4\times10^{-2}$, $0{\cdot}6\times10^{-2}$
2B2	$0{\cdot}8\times10^{-2}$, $1{\cdot}2\times10^{-2}$
2B3	$1{\cdot}5\times10^{-2}$, $2{\cdot}3\times10^{-2}$

determined by atomic absorption, 0·3 g of sample was subjected to successive washings with hot 0·3 M HNO_3 until 50 ml of solution was obtained. The measurements were conducted in an atomic absorption spectrophotometer VARIAN model spectrAA 640.

The analysis of boron in water can also be very helpful from an environmental point of view and since this element is present in water due to industrial processes, particularly from the ceramic sector, the content of boron in the former washing liquids was analysed by the Azomethine-H method.[8]

Sample 2, with and without mineralizers fired at 1000°C/6 h, was tested as ceramic pigment in both transparent and opaque frits, taking into account that in the ceramic industry chrome-tin pinks work better in glazes with high content in calcium, low in boron and almost free from zinc and magnesium. Tin oxide improves the stability because as opacifier serves to retard dissolution of the pigment in the glaze.

Glazing essays were carried out on earthenware bodies previously fired at 1050°C. The washed pigment was added in an amount of 5% in weight to the frit. To that mixture, water was incorporated so that a density of about $1{\cdot}25\,g\,cc^{-1}$ can be obtained. Homogenization was accomplished in a planetary ball mill after 20 min. The glazes were fired at 1000°C and maintained at this temperature for 5 min.

CIELAB colour parameter measurements[9] in unglazed and glazed samples, were conducted with a colorimeter using a standard illuminant D, in order to differenciate the pigment in terms of colour. L* is the lightness axis [black (0) to white (100)], a* is the green (−) to red (+) axis, and b* is the blue (−) to yellow (+).

3 Results and Discussion

Figure 1 shows the spectra of 1, 2, 3, 4 and 5 samples fired at 1300°C/2 h. As it can be observed, peaks are assigned to SnO_2, SiO_2, $CaSiO_3$ and only peaks of small intensities that can be attributed to $CaSnSiO_5$ (JCPDS, 25-176) appear in the diffractograms.

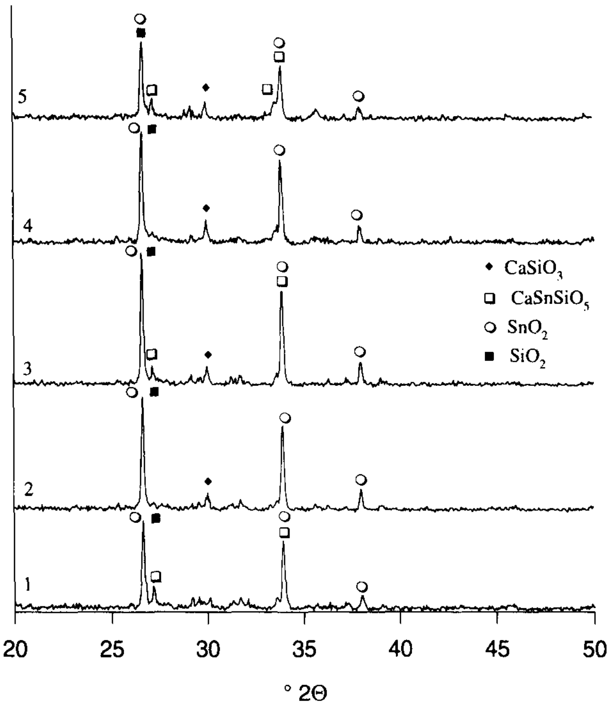

Fig. 1. XRD spectra of samples 1, 2, 3, 4 and 5 fired at 1300°C/2 h.

Because the sphene phase is not appreciably formed in the above samples, H_3BO_3 was added and the resulting mixtures were submitted to the same thermal treatments. After each firing, the samples were analyzed by XRD. The results indicated that in sample 2A calcined at 1100°C/2 h, $CaSnSiO_5$ peaks are detected, although of small intensities, and in 3A, 4A and 5A samples the sphene peaks are observed at 1100°C/6 h. The intensity of $CaSnSiO_5$ peaks increases when temperature increases. In Fig. 2, XRD spectra of samples fired at

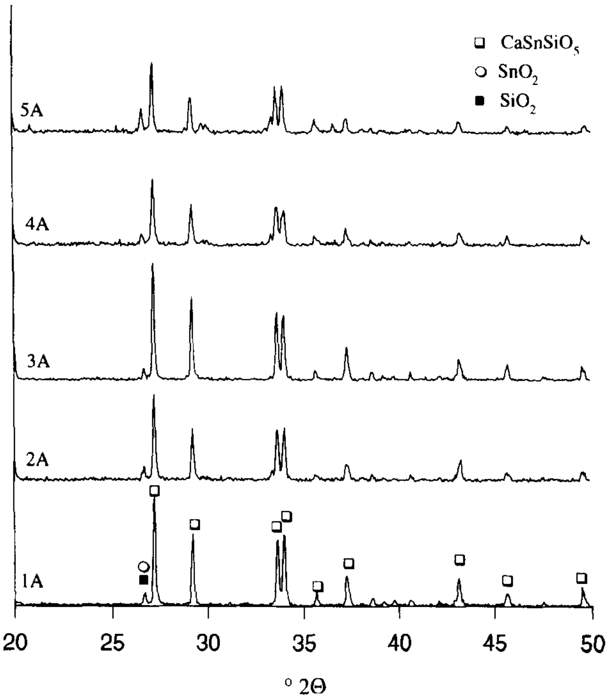

Fig. 2. XRD spectra of samples 1A, 2A, 3A, 4A and 5A fired at 1300°C/2 h.

1300°C/2 h are represented. From the figure, it can be inferred that the most intesive peaks are those of $CaSnSiO_5$. These results could be attributed to the fact that the B_2O_3, formed from H_3BO_3, has a melting point around 450°C. Boric oxide has a particularly useful effect in decreasing the time needed to achieve satisfactory melting and refining (removal of gas bubbles) and because of that, boron is a typical fluxing agent that increases fluidity by favouring the interdiffusion processes between ions.

From these results, and as 2A and 3A samples exhibit the same characteristics in the XRD spectra, in order to avoid a high content of chromium ions, sample 2 was chosen to test the effectiveness of some other additives: $LiBO_2$ (m.p., 845°C), Li_2CO_3 (m.p., 723°C), and H_3BO_3–Li_2CO_3. These mineralizers have been chosen due to their low melting points and because alkali metal oxides reduce the viscosity of a melt by introducing non-bridging oxygen ions in place of bridging oxygen ions which link adjacent SiO4 tetrahedra. Lithium oxide has a greater effect in reducing the viscosity of the melt than the other alkali oxides due to the fact that a Li(I) ion is a small cation of high field strength.[10] Also of interest is to check if lithium could be incorporated together with chromium in the sphene structure modifying the crystalline field intensity and in relation with that, the final colour.

In Table 5 the results of XRD are presented for samples 2A, 2B, 2C and 2D treated at different thermal treatments. The evolution of the sphene peak intensities was followed by I_E parameter,

$$I_E = \frac{i_E}{i_E + i_S}.100$$

where i_E and i_S are the XRD peak heights measured on the diffractogramme at $2\Theta = 27{\cdot}2$ that correponds to $CaSnSiO_5$ and 26·6 to SiO_2 and SnO_2.

From Table 5 it can be inferred that the additives containing Li and B develop $CaSnSiO_5$ after firing at 1000°C/2 h. The intensities of peaks increase with temperature. It was not observed a displacement in diffraction peaks with the addition of lithium. This is attributed to the fact that the size of chromium ions in the six cordination is 75·5 pm and lithium in the same environment is 90 pm. If these ions replace the tin (83 pm) in the structure, the shift to higher 2Θ produced by the chromium is compensated by the shift to lower $2\ \Theta$ originated by the lithium.

Since the colour of sample 2A after thermal treatment at 1300°C/2 h was very similar to 2B, 2C and 2D fired at 1000°C/6 h; L*a*b* parameters were obtained under these synthesis conditions and are shown in Table 6. An industrial pigment synthesized at 1250°C is included for reference together with sample 2 fired at 1300°C/2 h without mineralizer.

Table 5. Evolution of I_E parameter with temperature in sample 2 with the different additives employed

	900°C/ 6 h	*1000°C/ 2 h*	*1000°C/ 6 h*	*1300°C/ 2 h*
H_3BO_3 (2A)	—	—	—	84
$LiBO_2$ (2B)	—	55	57	76
$LiCO_3$ (2C)	—	—	31	40
H_3BO_3–Li_2CO_3 (2D)	—	17	44	67

Table 6. L*a*b* parameters for samples with the different mineralizers before glazing

	2	*2A*	*2B*	*2C*	*2D*	*Reference*
L*	63·70	47·90	55·60	67·20	59·20	58·00
a*	4·50	12·80	18·80	12·90	15·30	18·00
b*	0·05	3·47	2·20	4·10	1·80	3·00

It can be seen from Table 6 that L*a*b* parameters of sample 2B are very close to those of industrial pigment, and that the sample without mineralizer has a lower a* parameter than the others. The quality of powders as ceramic pigments was tested in opaque and transparent glazes. The samples were previously washed in hot 0·3 M HNO_3. The L*a*b* parameters for the transparent frit are given in Table 7.

The obtained data indicate that, after glazing, 2B and industrial pigments exhibit similar values for L* and a* parameters and the b* parameter for 2B indicates a higher blue content. The high a* parameter is in agreement with the modification of the field intensity by the incorporation of lithium in the structure.

From these results it can be inferred that $LiBO_2$ is the best additive to synthesize this pigment because it develops sphene at lower temperature and colorimetry parameters are very similar to those of the industrial pigment that we attribute to the action of Li_2O and B_2O_3.

In the case of the use of Li_2CO_3 as mineralizer, the CO_2 formed from this raw material can introduce some porosity and according to that when pores are present during the initial stages of sintering, grain growth could be inhibited.

Table 7. L*a*b* parameters for sample with the different mineralizers after glazing

	2	*2A*	*2B*	*2C*	*2D*	*Reference*
L*	53·00	37·00	45·20	51·10	50·50	44·00
a*	3·00	15·00	27·40	22·20	25·00	28·00
b*	5·00	4·00	2·20	1·70	5·00	10·00

Table 8. L*a*b* parameters for sample with different quantities of $LiBO_2$ before and after glazing

	2B (p)	*2B (g)*	*2B1 (p)*	*2B1 (g)*	*2B2 (p)*	*2B2 (g)*	*2B3 (p)*	*2B3 (g)*
L*	55·60	45·20	70·30	67·20	66·50	60·70	31·90	43·50
a*	18·80	27·40	9·80	11·00	12·60	18·60	18·50	27·50
b*	2·20	2·20	1·20	−1·00	−1·00	1·20	2·90	5·60

Once the best mineralizer established, and in order to determine the influence of Li and B content, some samples were prepared by varying the amount of $LiBO_2$. The mixtures studied are shown in Table 4. XRD results at 1000°C/6 h indicate that the intensity of sphene is higher in samples 2B and 2B3, as can be observed in Fig. 3.

The quality as ceramic pigments was achieved, after washing, by measurements of L*a*b* parameters in the powders (p symbol) and in a transparent glaze (g symbol). The values are included in Table 8.

The colorimetric results are in accordance with XRD above mentioned. The quantities of B and Li in samples 2B and 2B3 are the best to obtain the pigment at a lower temperature and L*a*b* parameters are very close to those of an industrial pigment.

The content in Cr ions and B (ppm) in the washing liquids in samples 2A, 2B and 2B3 fired at 1000°C can be seen in Table 9. We can observe that chromium is not detected in either sample and B content is lesser in pigments prepared with $LiBO_2$. We attributed this to a better sintering process that retain a more quantity of boron inside.

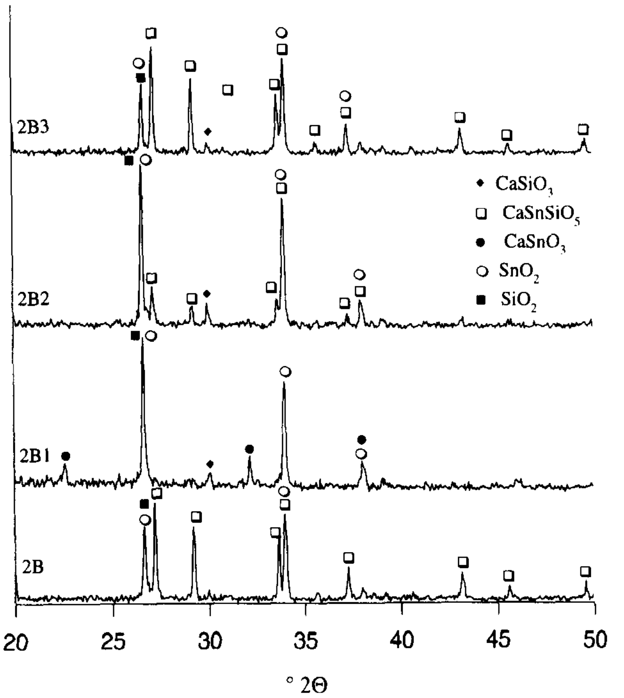

Fig. 3. XRD spectra of samples 2B, 2B1, 2B2 and 2B3 fired at 1000°C/6 h.

Table 9. Cr(VI) ions and B contents in the washing liquids

	2A	*2B*	*2B3*
Cr ions (ppm)	0·00	0·00	0·00
B (ppm)	12·10	6·07	6·40

4 Conclusions

From the experimental results discussed above the following facts can be pointed out:

1. It is not possible to obtain the sphene whithout mineralizers under our working conditions.
2. The addition of H_3BO_3 allows to synthesize the sphene pigment at 1300°C/2 h because the most intense peaks are assigned to $CaSnSiO_5$ in the XRD spectra and the presence of sphene is necessary for developing the pink colour.
3. From the results of XRD and L*a*b* parameters, it can be inferred that the presence of Li and B helps sphene formation at lower temperatures.
4. The best additive for the synthesis of sphene-pink pigment is $LiBO_2$ in the amounts corresponding to samples 2B and 2B3. The L*a*b* parameters of the obtained pigments are very close to those of an industrial pigment.
5. From an environmental point of view, the quantities of Cr ions and B in the washing liquids indicate that the best additive is $LiBO_2$ because the chromium content is negligible and the B amount is less in samples 2B and 2B3.

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References

1. Sanghani, D. V., Abrams, G. R. and Smith, P. J., A structural investigation of some tin-based coloured ceramic pigments. *Trans. J. Br. Ceram. Soc.*, 1981, **80**, 210–214.

2. Escribano, P., Guillem, C. and Alarcón, J., Cr–SnO_2–CaO–SiO_2 based ceramic pigments. *Ceramic Bulletin*, 1984, **63**(12), 1492–1494.
3. DCMA, *Clasification and Chemical Description of the Mixed Metal Oxide Inorganic Colored Pigments*, 2nd edn. Metal Oxides and Ceramic Colors Subcommittee, Dry Color Manufacturer's Assn., Washington, DC, 1982.
4. Wold, A., The preparation and characterization of materials. *J. of Chem. Ed.*, 1980, **57**(8), 531–536.
5. Kingery, W. D., Bowen, H. K. and Uhlmann, D. R., *Introduction to Ceramics*, 2nd edn. John Wiley and Sons, New York, 1976, p. 314.
6. Olazcuaga, R., El Kira, A., Maestro, P., Tastu, R. and Le Flem, G., Sur de nouveaux pigments rouges de type perosvkite stables à haute température. *Revue de Chimie minérale*, 1984, **21**, 221–228.
7. Kingery, W. D., Bowen, H. K. and Uhlmann, D.R., *Introduction to Ceramics*, 2nd edn. John Wiley and Sons, New York, 1976, p. 496.
8. López, F. J., Giminez, E. and Hernández, F., Analytical study on the determination of boron in environmental water samples. *J. Anal. Chem.*, 1993, **346**, 984–987.
9. Commission Internationale del' Eclariage, *Recommendations on Uniform Color Spaces, Color Difference Equations, Psychometrics Color Terms*. Supplement no. 10 of CIE Publications no. 15 (E1-1.31) (1971). Bureu Central de la CIE, Paris, 1978.
10. McMillan, P. W., *Glass–Ceramics*, 2nd edn. Academic Press, London, 1979, p. 92.