SYNTHESIS OF CERAMIC PIGMENTS WITH SPHENE STRUCTURE BY LYOPHILISATION

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1. INTRODUCTION

A wide variety of ceramic pigments in many shades and with quite satisfactory properties is available. At the present time, there is practically no red pigment that displays good characteristics. The only one that could be really considered red is cadmium sulphoselenide and this has a thermal stability that does not exceed 1000°C, i.e., very low for use in the ceramic field. Nowadays sphene is one of most important chromium-doped pigments used in the ceramic industry, because it is the only alternative for replacing pigments with high cadmium content that display intense shades of red.

The pigment $CaSnSiO_5$:Cr_2O_3, known as tin-chromium carmine sphene has its origin in the natural mineral $CaTiSiO_5$, known as titanite. This belongs to the class of silicates and the monoclinic crystallographic system. Its structure is formed by tetrahedral groups of SiO_4 linked to the octahedral groups of TiO_6 with shared oxygens and calcium forming polyhedrons of hepta-coordination with oxygen, CaO_7. In this compound both the Ti and the Ca can be replaced with other elements.[1]. The sphene used for pigment production is that of Sn, better known as malayaite $CaSnSiO_5$. This has a pink-violet colour when it forms solid dissolutions with chromium. In the case of sphene the chromophore element is Cr(III) which provides the pink colour. Some authors have long considered that chromium-doped malayaite is a solid solution pigment that contains cations of Cr(III)[2,3] in octahedral coordination, whereas the latest studies present more probabilities in favour of Cr(IV) and its situation in tetrahedral silicon positions. These cations replace Sn(IV) in hexa-coordination and in isolated octahedral coordination and, in addition, a little amount of these replaces Si(IV) in the malayaite matrix.[4,5]

Nowadays the synthesis of this pigment based on conventional ceramic technology is still considered more appropriate, in which chromium forms a solid solution with tin. This procedure requires high calcination temperatures and the addition the use of fluxes [6] that have negative effects on the environment.[7].

The search for and the development of new synthesis techniques have been driven by the strong demand for new materials with optimised properties and appropriate profitability for the multiple applications that they require. In this sense, the object of the present study has been the synthesis of ceramic pigments with a sphene structure from precursors prepared by means of freeze-drying or lyophilisation. These materials have been developed through heat treatments with infrared radiation in an electric kiln at different temperatures, avoiding the addition of fluxes and their environmental aggressiveness. The pigments obtained have been applied in glazes for the evaluation of their physico-chemical stability and degree of colour development. A comparison has been made between the optical properties displayed by a commercial pigment and the developed materials.

2. METHODOLOGY AND EXPERIMENTAL DEVELOPMENT

The synthesis has been performed by applying a drying technique that has been used for many years for eliminating water and stabilising many pharmaceutical products. It is applied successfully in the food industry; however it has hardly been used in the preparation of ceramic pigments until now. Brief studies exist on the decomposition of precursors prepared by means of this method[8]. With the lyophilisation method products of very high quality are obtained, in comparison with other common drying methods. The main advantage is the obtainment of an end product with good homogenisation and high purity. The procedure enables keeping the homogeneity and stoichiometry of a multicomponent solution when the dry end product is obtained (freeze-dried). The process consists of eliminating the solvent of a solution by sublimation. Sublimation is favoured thermodynamically as opposed to fusion, and the evaporation occurs under partial steam pressure and temperature conditions below the solvent triple point. In this synthesis route soluble salts have been used as precursors. Chlorides and nitrates have been used, which are frequently recommended by the literature. The raw materials used together with their purity are detailed in the table 1.

Precursor	Supplier	Purity (%)
$Ca(NO_3)_2.9H_2O$	Merck	98
Tetraetoxysilane (TEOS) $C_8H_{20}O_4Si$	Aldrich	98
$SnCl_4.5H_2O$	Panreac	98
$Cr(NO_3)_3.9\ H_2O$	Panreac	98
Nitric acid, HNO_3	Panreac	65
Ethanol	Panreac	98

Table 1. The reagents used in the synthesis

After a literature study the chemical compositions indicated in table 2 have been chosen.

Reference	Chemical compositions
L1	$CaCr_{0.018}Sn_{0.982}SiO_5$
L2	$CaCr_{0.036}Sn_{0.964}SiO_5$
L3	$CaCr_{0.054}Sn_{0.946}SiO_5$

Table 2. Chemical compositions of the prepared samples

The starting precursors have been dissolved in the minimum amount of distilled water, followed by heating of the solution to 70ºC with continuous stirring. The silicon alkoxide has been dissolved in a proportion of TEOS: water equal to 1:2 (v/v) and the relation TEOS: ethanol has been 1:4 (v/v), with the minimum amount of nitric acid catalyst, concentration 0.1M. After the homogenisation, drops of the solution have been frozen by adding liquid nitrogen. The frozen particles have then been dried through a lyophilisation system under pressure of approximately 1-10 Pa. This yielded the sublimation of the solvent from the matrix of the frozen sample and the obtainment of a dry end product in powder. Finally, this has been milled and prepared for calcination.

To obtain the materials we applied heat treatment in an electric kiln with a heating rate of 10ºC/min up to the peak firing temperatures (500, 700, 900, 1100, 1200, 1300ºC) with a 2 hour soak at these peak temperatures, followed by free cooling.

Glazing trials were performed with the obtained materials with a view to evaluating the stability and colour development in a glassy matrix. Glazes without ZnO have been chosen, because this adversely affects tin colours. The pigments have been taken in a proportion with the frit of 5:95 by weight. The slips have been applied directly on a white body ceramic biscuit and subjected to a single-firing thermal cycle of 1080ºC. The pigmenting strength has been evaluated before and after the application in the glaze.

3. RESULTS OBTAINED AND DISCUSSION

The materials obtained have been characterised through structural and microstructural analysis, and measurements of the optical properties.

The analysis performed by X-ray diffraction of the crystalline phases in the synthesised samples shows the development of the desired malayaite phase above 700ºC. Next to this, peaks are detected of SnO_2 cassiterite, which have still not reacted completely, as well as a light presence of calcium silicate $CaSiO_3$. At temperatures of 1300ºC, a notable increase is observed in the proportion and crystallinity of the malayaite phase, accompanied by the phases mentioned.

The microstructural study has been conducted by scanning electron microscopy (SEM). The results show a homogeneous distribution of the particles in which it can be observed how the precursors have reacted among these. The grains have an average size of approximately 1 μm and a high degree of agglomeration is detected, which evidences a process of maximum sintering. The energy-dispersive X-ray analysis shows the compositional homogeneity with values similar to the theoretical ones.

The colours developed through these compositions have been analysed by means of CIE-L*a*b* colorimetry, determining their chromatic coordinates. A comparative study has been performed between the chromatic coordinates of the pigments obtained and an example of an industrially synthesised sphene, before applying it as a pigment onto a glaze (table 3) and after (table 4) introducing it into this glaze.

Sample reference	L1	L2	L3	Commercial pigment
CIE L*	39.80	38.11	40.21	53.87
a*	15.54	17.26	15.34	20.59
b*	3.52	3.41	3.74	2.18

*Table 3. CIE-L*a*b* chromatic coordinates of pigments synthesised at 1300ºC/2h*

The pigmenting stability of these synthesised materials has also been verified when using them in glazes. All the glazed pieces have pink shades and good physico-chemical stability, without the addition of mineralisers. On the other hand the commercial pigment contains fluxes that stabilise the colour. The chemical composition of the sphene that develops a more intense pink coloration (greater value of the a* coordinate) after introduction in the glaze, corresponds to the composition doped with 1.8 mol% chromium.

Sample reference	L1	L2	L3	Commercial pigment
CIE L*	61.59	65.83	61.24	50. 25
a*	32.90	31.49	31.35	26.26
b*	6.12	9.83	12.18	6.35

*Table 4. CIE-L*a*b* chromatic coordinates of the pigments applied in glazes*

4. CONCLUSIONS

Pink ceramic pigments with a sphene structure have been obtained, through precursors produced by lyophilisation, without the addition of fluxes.

The microstructural analysis of the materials prepared indicates mean particle sizes of approximately 1 μm, sufficient for direct application in the glaze.

The glazing trials with the obtained pigments show that they all develop intense and stable shades of pink in the glazes used. The best chromatic capacity after incorporation in the glaze is exhibited by the L1 sample, doped with 1.8 mol% chromium.

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