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Preparation of ceramic pigments by sol-gel and combustion methods

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Ceramic pigments are extensively used in the decoration of ceramic wares. These pigments need to be stable (homogeneity, colour intensity, crystallinity) at high temperatures in a glaze. Malayaite ceramic pigments ($CaSnSiO_5$) in this research study have been prepared in two ways: by means of a sol-gel method and a combustion method. The starting substances in the sol-gel method was TEOS, $Ca(NO_3)_26H_2O$, $SnCl_4$ and $Ni(NO_3)_26H_2O$ whereas in the combustion reaction the same substances with the addition of CH_4N_2O (urea) were used. In order to elucidate the structural evolution of these pigments with heat-treatment, infrared spectroscopy, X-ray diffraction and scanning electron microscopy were used.

Key Words: Combustion, Sol-Gel, Ceramic Pigments.

Introduction

Malayaite is a structure type sphene [1]. Its structural formula is $CaO.SnO_2.SiO_2$ where the chromophore element is nickel which gives it a purple color. Ceramic pigments are usually produced by classical synthesis procedures, but these techniques require mechanical mixing, high temperatures and long soaking times. Additionally, the size distribution of the powder, affecting the color a intensity-chemical homogeneity- which affects, color quality- is difficult to control. Recently investigations in this field have been aimed at new processes which will promote a classical production process and enable the synthesis of pigments at lower temperatures.

The aim of this study is the synthesis and characterization of tin and calcium silicate doped with nickel, sphene network, by means of different means of synthesis such as sol-gel and combustion methods [1].

Combustion synthesis is a novel powder processing technique that can produce ceramic pigments. This method is a low temperature synthesis technique that offers a unique synthesis route via a highly exothermic redox reaction between metal nitrates and an organic fuel to produce ceramic pigments [2]. This process is characterized by a high temperature, rapid heating rate and a short reaction time. Some other advantages of combustion synthesis are; use of relatively simple equipment, formation of high-purity products, stabilization of metastable phases and formation of virtually any size and shape products [3].

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Experimental

For the synthesis of malayaite by a sol-gel procedure, TEOS (tetraethylorthosilicate), calcium nitrate hexahydrate, $SnCl_4$, citric acid, water and ethanol were used as starting materials. We have used a parent solvent (EtOH) for the TEOS precursor and citric acid as the catalyst because this combination resulted in the best quality TEOS hydrolysis [4]. The solutions were prepared with the molar ratio for the hydrolysis of TEOS which takes place in two steps. A mixture of TEOS, ethanol and water in molar ratios of 1 : 3 : 1 was stirred for one hour at room temperature [5]. After this step calcium nitrate hexahydrate and $SnCl_4$ solutions were added. The final solution (pH = 2-3) was stirred for one hour and kept at 120 °C [6, 7]. The samples were heat treated at a temperature range of 200-1200 °C in an electrical oven for four hours in order to complete the calcinations. The calcinated samples were identified by X-ray diffraction, FTIR, SEM, EDX and color analysis.

A solution combustion process was employed to synthesize various shades of ceramic pigments. It was performed by rapidly heating an aqueous solution containing a stoichiometric quantity of corresponding metal nitrates and urea at 400 °C. This process lasted for about 5 minutes and resulted in voluminous powder.

The stoichiometric composition of metal nitrates and fuel was calculated based on the total oxidizing and reducing valency of the oxidizer and the fuel, which serves as a numerical coefficient for a stoichiometric balance such that the equivalence ratio is unity, i.e. O : F = 1.0 [8, 9, 10] and energy released is at a maximum. According to the concept used in propellant chemistry, the elements H, C, or any other metal are considered as reducing elements with corresponding valences +1, +4 (or the valency of the metal ion in that compound), respectively. The element oxygen is considered as an oxidizing element with valency -2. The valency of nitrogen is considered to be zero. Accordingly, the valences of $M(NO_3)_2$ and CH_4N_2O become -10 and +6 respectively. Therefore, the molar ratio of $M(NO_3)_2$: CH_4N_2O.

Combustion Method:

The redox mixture containing metal nitrates and CH_4N_2O when rapidly heated at 400°C ignites and yields voluminous powder. However, both $SnCl_4$ and TEOS do not have an exothermic reaction with urea; only metal nitrates have exothermic reactions with it. For this reason, ammonium nitrate was used as the oxidizer. Formation of transition metal ion doped $CaSnSiO_5$ ceramic pigments may be represented by the following reaction:

$$[M(NO_3)_2 6H_2O + SnCl_4 + M(NO_3)_2 6H_2O] + TEOS + CH_4N_2O + NH_4NO_3 \rightarrow CaSnSiO_5 + \text{gaseous product} \quad (1)$$

Sol-gel Method:

Ceramic Pigments were prepared from hydrolysis and condensation of TEOS by a sol-gel method [11]:

$$Si(OC_2H_5)_4 + 4\,H_2O \xrightarrow{\text{Hydrolysis}} \text{--K-----}\ Si(OH)_4 + 4C_2H_5OH \quad (2)$$

K is a catalyst (citric acid)

$$Si(OH)_4 + Si(OH)_4 \xrightarrow{\text{Condensation}} \text{----------} \equiv Si\text{-}O\text{-}Si + 4H_2O \equiv \quad (3)$$

$$Si(OH)_4 + Si(OC_2H_5)_4 \text{ ----------} \equiv Si\text{-}O\text{-}Si + 4C_2H_5OH \equiv \quad (4)$$

$$Ca(NO_3)_2 \xrightarrow{H_2O} Ca^{2+}_{(aq)} + 2NO_3^{-}{}_{(aq)} \quad (5)$$

$$SnCl_4 \xrightarrow{H_2O} Sn^{4+}_{(aq)} + 4Cl^{-}{}_{(aq)} \quad (6)$$

The stability of pigments in the glaze and color intensity was increased by combustion method. The CIE - L^* a^* b^* colorimetric method recommended by the Commission Internationale de I'Eclairage (CIE) was followed. In this method, L^* is the lightness axis [black (0), white (100)], b^* is the blue (-), yellow (+), axis, a^* is the green (-), red (+) axis and ΔE is the hue variation. $\Delta E^2 = (L^*)^2 + (a^*)^2 + (b^*)^2$ [12].

Results and Discussion

X-ray diffraction patterns from powder produced by the combustion method and sol-gel method (1000 °C) are shown in Figs. 1 and 2. The malayaite phase is obtained for samples prepared around 1000 °C. All precursor components have been converted to malayaite in the basic phase at 1000 °C.

In the combustion method, the intensities and sharpness of the reflections in the spectrum increase. This can be interpreted as an increase of sample crystallinity since the peak intensity is proportional to the crystallite size (Table 1) [13]. Two SEM images corresponding to the glazed pigment samples of the sol-gel and combustion methods are shown in Figs. 3 and 4, respectively. The increased crystallinity from the combustion method inhibits its dissolution, whereas the pigments produced by the sol-gel method are better dissolved in a glaze. EDX measurements given in Table 2 also supports this observation.

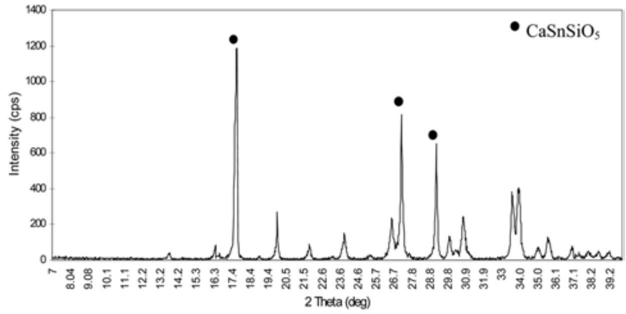

Fig. 1. X-ray diffraction pattern of powders produced by the combustion method.

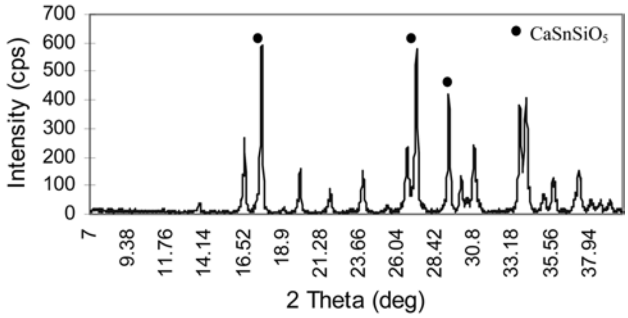

Fig. 2. X-ray diffraction pattern of powders produced by the sol-gel method.

Table 1. Peak intensity of pigments

Temperature (°C)	Combustion Method Peak Intensity (cps)	Sol-Gel Method Peak Intensity (cps)
1000	1186	592

Figs. 5 and 6 show IR spectra of the samples. Significant differences were eminent between the pigments synthesized by the sol-gel and combustion methods. The absorption bands at around 1100cm^{-1} attributed to stretching modes of Si-O-Si are prominent. The bands at 563-905-907-940 cm^{-1} can be associated to vibrations of the Sn-O in the malayaite structure (Table 3) [14, 15].

With the combustion method, as can be seen in Table 4 there is an increase in the pale warm brown range. The choromphore element is Ni.

Conclusions

The solution combustion process has been successfully extended to prepare various shades of ceramic pigments. The exothermic nature of the redox reaction between

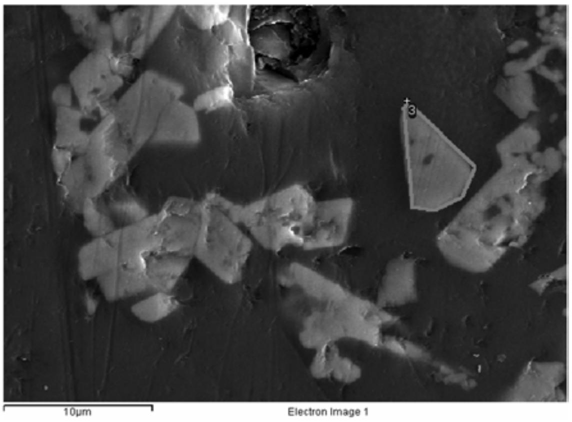

Fig. 3. SEM image of a pigment within a transparent glaze by the combustion method.

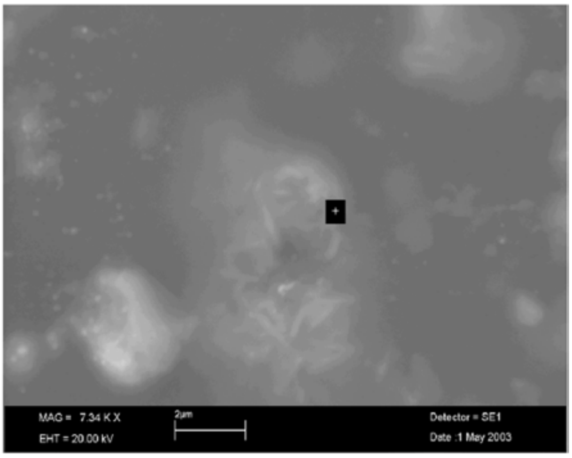

Fig. 4. SEM image of a pigment withina transparent glaze by the sol-gel method.

Table 2. EDX point analysis of pigments

Element	Combustion Method	Sol-Gel Method	Formula
Al	0.85	2.44	Al_2O_3
Si	14.08	16.12	SiO_2
Ca	12.48	7.99	CaO
Sn	37.00	24.08	SnO_2
O	32.34	49.37	
Totals	100.00	100.00	

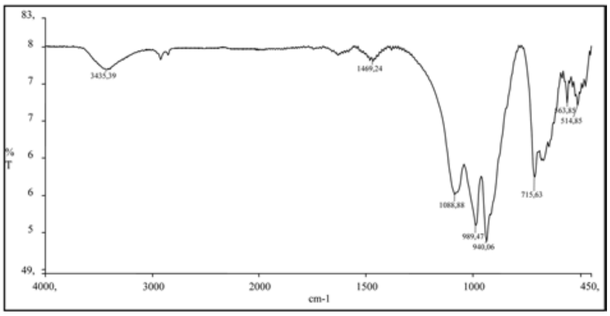

Fig. 5. IR spectra of the malayaite pigment obtained by the sol-gel method.

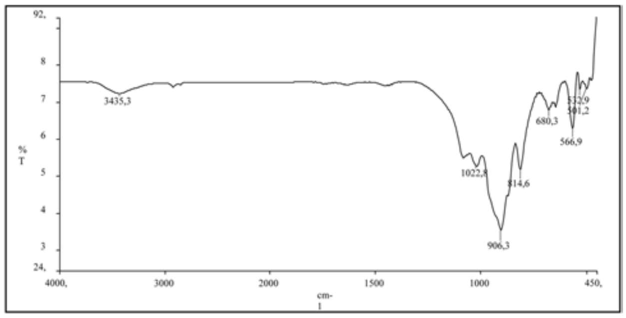

Fig. 6. IR spectra of the malayaite pigment obtained by the combustion method.

Table 3. Major Infrared absorption bands for malayaite at 293 K [15]

Frequence (cm^{-1})	Width (cm^{-1})	Intensity
90		Very Weak
145		Very Weak
220	17	Strong
239	13	Strong
258	17	Strong
279	13	Weak
316	29	Strong
340	27	Weak
362	30	Weak
424	10	Strong
471	24	Strong
500	19	Strong
533	9	Weak
563	27	Very Strong
817		Very Strong
879		Weak
907		Very Strong
941		Very Strong

Table 4. CIE L^* a^* b^* color coordinates of pigments

Samples	Temperature 1000(°C)	Color Values		
		L*	a*	b*
Malayaite(Ni) Combustion	1	74,30	11,06	10,78
	2	75,67	10,75	10,32
	3	74,82	11,16	10,66
Malayaite(Ni) Sol-gel	1	68,76	12,08	13,45
	2	69,87	11,89	12,48
	3	68,94	12,06	13,04

metal nitrates/hydrazide provides the heat required for the synthesis of ceramic pigments. The solution combustion process is simple, fast and energetically attractive. It has all the advantages of wet chemical methods such as homogeneity, purity and molecular level doping of transition metal ions in the crystal structure. Additionally, the amount of Sn is minimized in the Ni-doped malayaite and dissolution is inhibited in the glaze. Hence these facts can be considered as improvement in terms of environmental concerns.

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