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Synthesis of Beige Pigment on the Basis of (Fe, Zn, Cr, Al) Spinel

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Abstract*— The beige pigment based on (Fe, Zn, Cr, Al) Spinel structures were successfully synthesized by solid reaction of oxides. At first a reference beige pigment CBD3002 from Qumisar company has been analysed by XRF, XRD, SEM and LPSA. Then according to these results, various formulations have been prepared and calcined at different conditions. The obtained pigments have been analysed by XRD, SEM/EDS, LPSA and CIE-Lab. The prepared pigments as well as the reference pigments, have been added to the glaze. Then, after glaze firing, their colors have been measured in CIE-Lab system. The results showed that color quality of the optimized pigment (i.e. ZnO/Cr_2O_3=4.16, Fe_2O_3/Cr_2O_3=1.50 and Cal at 1200°C) prepared it in this work was better than the reference one. Adding more than 3Wt.% of the pigments in the glaze does not induce significant changes in color. The prepared pigment showed good thermal and chemical stability.

***Index Terms*— Beige, Synthesis, Spinel, Ceramic pigment**

I. INTRODUCTION

Ceramic materials with spinel structure have been studied for decades, due to its wide applicability as ceramic pigments, magnetic devices, semiconductors, refractories and others. In order to obtain powder ceramics with high quality, there are important factors synthesis method determines not only stoichiometric and morphologic control but also physical and chemical properties [1-2]. Color is an optical property that takes to countless applications. For ceramic tiles, pigments give a stable coloration to a glaze, through a simple mechanical dispersion in the middle to be colored [3-4]. The spinel pigments belong to the group of mixed metal oxides pigments. Mixed metal oxide pigments can be considered as a subcategory of complex inorganic colour pigments. The name, mixed metal oxides, does not represent the reality, as these pigments are not mixtures, but solid solutions or compounds consisting of two or more metal oxides. Each pigment has a defined crystal structure which is determined by the host lattice. Other oxides interdiffuse at high temperature into the host lattice structure by forming either a solid-state solution or a new compound [5]. Structurally, mixed metal oxide pigments belong to one of fourteen structure types [6-7] the most common are rutile and spinel ones. Pigments with the spinel structure are widely used in ceramic and plastic industries. They cover a wide range of colours and many of them are thermally stable up to 1400°C. They are resistant to molten glass [8]. Another advantage is their mutually complete miscibility, allowing the user a choice of creating many intermediate colours [9-10].

A high temperature process is almost always used for the preparation of inorganic pigments. This method is based on a reaction of solid phases [11]. Oxides, hydroxides and other inorganic compounds are usually used as raw materials. The reaction is performed at high temperature, up to 1300°C, an agent of mineralization is usually present. Next method, which is very often used for preparation of inorganic pigments, is based on milling activation. Some spinel compounds that are not used as pigments were also prepared by this ceramic technique [12].The third method of preparation of pigments is the polymeric precursor method (Pechini) [13].The most brown/beige pigments used in ceramic industry are the basis of Iron, Zinc and Chrome oxides. The spinel structure $RO.R_2O_3$, is formed by association of a trivalent cations (Cr^{3+}, Al^{3+}, Fe^{3+}) with a bivalent cations (Zn^{2+}, Fe^{2+}). Such a ceramic pigment is able to develop stable color in relation to temperature and chemicaly agents, resisting to the aggressive attacks, specially by glaze material during its melting, in other words, the pigment should be insoluble in glazes (substrate) [14]. The main aim of the research was to propose, verify and analyze the conditions of synthesis of spinel pigment on basis of (Fe, Zn, Cr, Al).

II. EXPERIMENTAL PROCEDURE

The starting materials were high purity powders which commercially available; Fe_2O_3 (~ 99.9%), ZnO (~ 99.8 %), Cr_2O_3 (~ 99.8 %), Al_2O_3 (~ 99.5 %) also, $ZrSiO_4$ and SiO_2 according to XRF results added to raw materials as shown in "Table. 1" the formulation of mixtures. The pigment was synthesized by solid reaction after sintering at 1200 °C in Electrical kiln (Extion-1500-221) for 50 min as shown in "Fig. 1" the preparation route of it. Then, the best prepared pigment (i.e. ZnO/Cr_2O_3=4.16, Fe_2O_3/ Cr_2O_3=1.50) as well as the reference pigment about 1, 3 and 5 Wt.%, have been added to the glaze (ferrit~90 Wt.%, Clay ~10 Wt.% and TTP ~ 3 Wt.% which TTP was as a binder). The prepared pigments were studied by X-ray diffraction analyses. X-ray analyses were measured by equipment diffractometer PW1800 (PHILIPS Company), by CuKα radiation. X-ray diffraction (XRD) was employed to identify the phase formed. The particle morphology and size were directly imaged, using scanning electron microscopy VEGA// TESCAN-15.00 kV) which is equipped with an energy dispersive X-ray analyzer (SEM/EDS) and the particle size distribution was determined by using a laser particle size analyzer (LPSA-Hydro 2000MU –Malvern).

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L*a*b* color parameters and diffuse reflectance of fired pigments were measured by the Gretac Macbeth Color-eye spectrophotometer TL84, from 360–760 nm range, using the D65 illumination.

Table 1. The formulation of mixtures

Oxide Wt.%	A_1	A_2	A_3	A_4
ZnO	50	50	50	50
Cr_2O_3	12	10	12	12
Fe_2O_3	18	20	20	18
Al_2O_3	15	20	18	9.3
$ZrSiO_4$	5	-	-	3.8
SiO_2	-	-	-	6.9

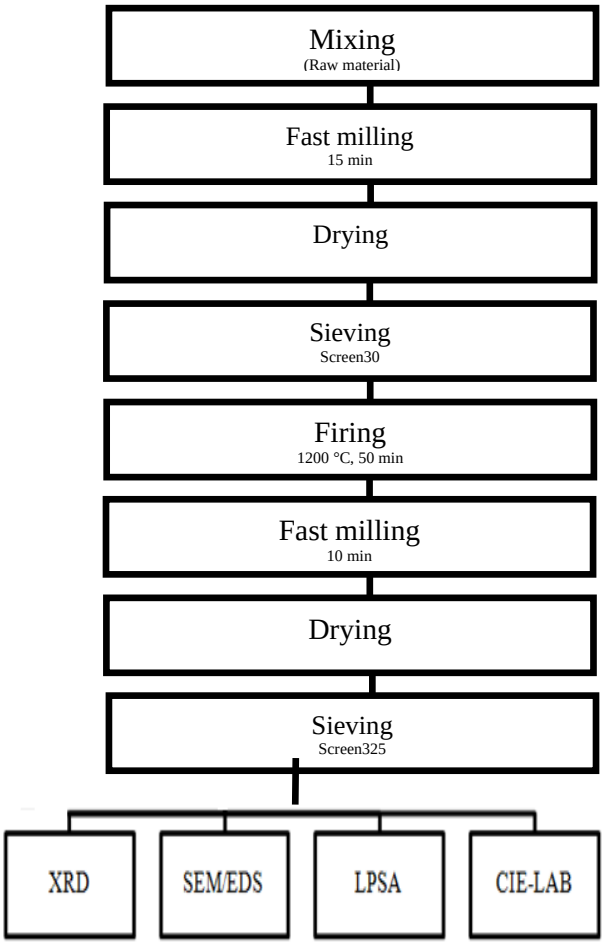

Fig. 1. The preparation route of pigment

III. RESULTS & DISCUSSION

"Fig. 2" which shows the X-ray diffraction patterns of CBD3002 and A_4 sample. It is observed, that the main spinel phases are (Zn, Fe) (Cr, Al)$_2$O$_4$, which could be matched with JCPDS file number 00-009-0353 from Fd3m space group and other lateral phases which are similar to prepared pigment. These results are in good accordance with SEM/EDS observations which are shown in "Fig.3 and 4". The average grain sizes were determined from the XRD pattern according to the Scherrer's equation [15].

$$D = k\lambda/(B\cos\theta) \qquad (1)$$

Where;

D is the size of powder, λ is the X-ray wavelength, B is the FWHM of diffraction peak, θ is the diffraction angle and k is a constant equal to 0.89. The average particle size of the sample A_4 was smaller than the reference one. The average particle size estimated from SEM is similar to the results of the average particle size computed by XRD data and LPSA which are shown in "Fig. 5".

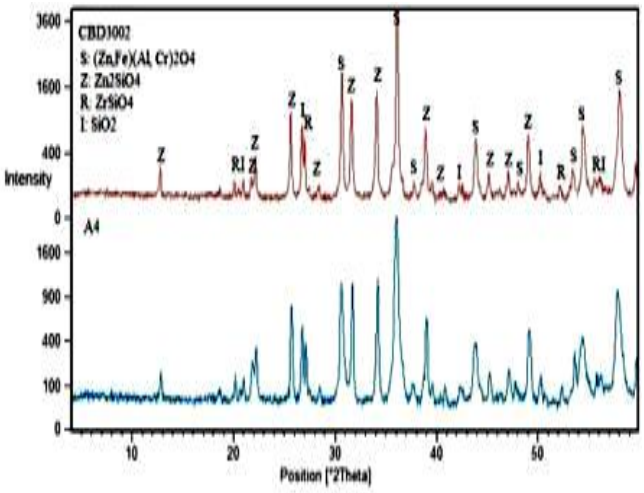

Fig.2 Comparing X-ray diffraction patterns between CBD 3002 and the sample of A_4

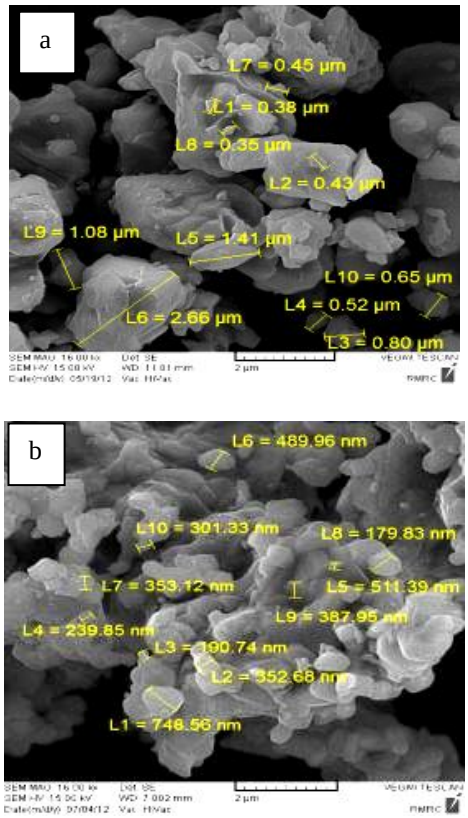

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Fig.3 Comparing SEM morphology a) CBD3002 and b) A_4

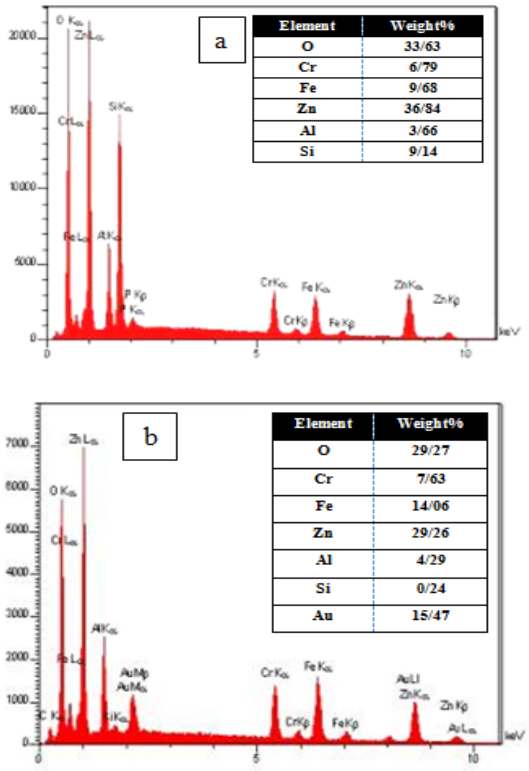

Fig.4 Microchemical analysis by energy dispersive X-ray analysis (EDS) a) CBD3002 and b) A_4

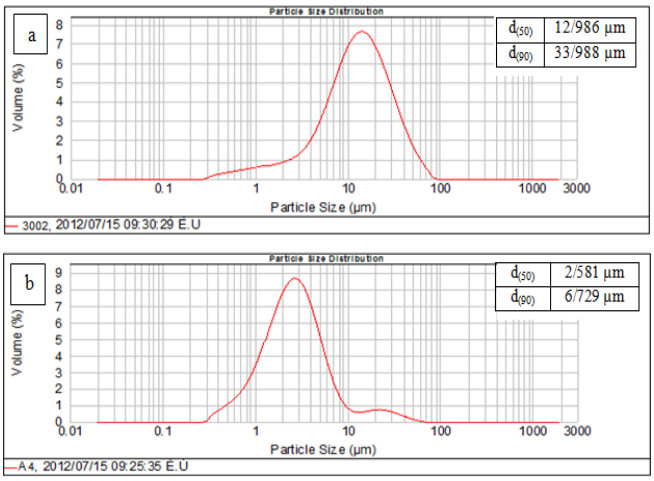

Fig 5. Comparing particle size distribution curve a) CBD3002 and b) A_4

The particle sizes and particle size distributions can markedly affect the colour properties of inorganic pigments. That is why the prepared sample were tested from this point of view. The main aim was to decrease the particle sizes and monitor the influence of particle sizes on the colour properties of the pigment. The CIE-L*a*b* colorimetric method was used, as recommended by the Commission Internationale de l'Eclairage (CIE) [16]. 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 DE is the hue variation. "Fig. 6" shows the curves of diffuse reflectance, which are in agreement to XRD results. After calcination at 1200 °C, the material is crystalline and presents a characteris- tic band around 590-640 nm, with a beige color.

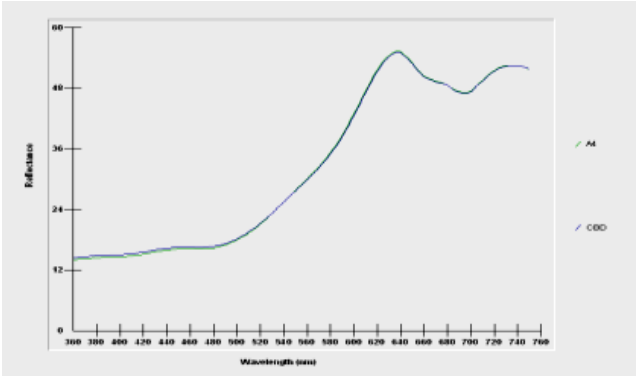

Fig.6 Comparing the diffuse reflectance of CBD and A_4

"Table.2" presents the colorimetric coordinates (L*, a*, b*), the tonality variation (ΔE). Based on the values of ΔE^*_{CIE}, we can say that the pigment prepared from sample A_4 is colorfully comparable with the reference one and the difference between them is <1.

Table.2 the colorimetric coordinates (L*, a*, b*), the tonality variation (ΔE)

Name	Illuminant	L*	a*	b*	C*	h°	ΔE*
A_4	D65	61.57	18.74	24.88	31.14	53.01	------
	A	65.14	21.60	30.56	37.42	54.75	
	TL84	63.85	17.82	28.89	33.94	58.33	
CBD 3002	D65	61.53	18.56	24.06	30.39	52.34	0.839
	A	65.04	21.40	29.67	36.59	54.20	0.912
	TL84	63.76	17.66	27.99	33.10	57.74	0.915

However, application tests must be done in order to evaluate pigment stability during glazing. We have done this test in different glazes such as floor tile glaze, wall tile glaze and lead-rich glaze. The best prepared pigment (i.e. ZnO/Cr_2O_3=4.16, Fe_2O_3/ Cr_2O_3=1.50) as well as the reference one about 1, 3 and 5 Wt.%, have been added to the glaze (ferrit~90 Wt.%, Clay ~10 Wt.% and TTP ~ 3 Wt.%). According to results the prepared pigment showed good thermal and chemical stability similar to reference one and adding more than 3Wt.% of the pigments in the glaze does not induce significant changes in color. The curves of diffuse reflectance and CIE-L*a*b* colorimetric method are shown in "Figs. 7" and "Table. 3".

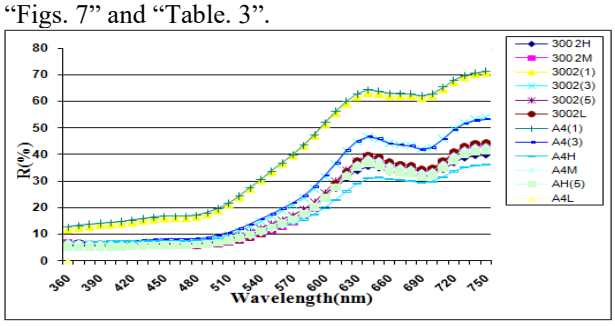

Fig.7 Comparing the diffuse reflectance of CBD and A_4 in different glaze by adding 1, 3, 5 Wt.%

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Table. 3 Comparing the colorimetric coordinates (L*, a*, b*) CBD and A_4 adding 1, 3, 5 Wt.% in glazes

Sample (1 Wt.%)	**L***	**a***	**b***
CBD3002	66.12	19.00	31.07
A_4	66.26	19.57	31.47
Sample (3Wt.%)	L*	a*	b*
CBD3002	51.29	24.73	31.96
A_4	52.10	23.69	30.49
Sample (5Wt.%)	L*	a*	b*
CBD3002	46.96	23.35	29.09
A_4	45.29	23.07	28.53

IV. CONCLUSION

The beige pigment based on (Fe, Zn, Cr, Al) Spinel structures were successfully synthesized by solid reaction of oxides. The purity of raw materials and calcination temperatures have a strong influence on the crystal structure, percent spinel phase and the particle size of the pigments. Adding 3 Wt.% of prepared pigment showed good thermal and chemical stability. The colorfully comparable with the reference one ($\Delta E^* < 1$). Finally, presented SEM, X-ray analyses and LPSA showed advantageous microstructures, with the appropriate pores/materials ratio and good candidates for application in the chemical industry as catalysts and colour pigments and we can suggest this prepared pigment for wall tile glazes.

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