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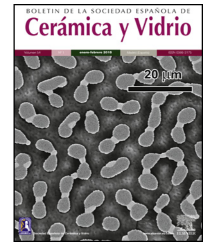

# Synthesis of pigments of $Fe_2O_3 \cdot SiO_2$ system, with Ca, Mg, or Co oxide additions

*Tsvetan Dimitrov*[a], *Stephan Kozhukharov*[b,*], *Nikolay Velinov*[c]

[a] *"Angel Kanchev" University of Ruse – Branch Razgrad, 47 "Aprilsko vastanie" blvd., 7200 Razgrad, Bulgaria*
[b] *University of Chemical Technology and Metallurgy, 8 "Klyment Okhridsky" blvd., 1756 Sofia, Bulgaria*
[c] *Institute of Catalysis, Bulgarian Academy of Sciences, Acad. "Gerorgy Bonchev" blvd., Block 11, 1113 Sofia, Bulgaria*

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ABSTRACT

The present research work is based on the comparative evaluation of the Ca, Mg, and Co dopant impact on the properties of new ceramic pigments from the system $Fe_2O_3 \cdot SiO_2$ obtained via classical ceramic technology. This approach enabled determination of the optimal temperature for the synthesis and the most appropriate mineralizer. The obtained specimens were submitted to systematical analysis, including X-ray Diffraction (XRD) spectroscopy, Electron Paramagnetic Resonance (EPR) analysis and Mössbauer spectroscopy for crystalline phase determination. The color characteristics are quantified by spectrophotometric measurements. The pigments particle size has been determined by Scanning Electron Microscopy (SEM), combined by Energy Dispersion X-ray spectroscopy (EDX). The obtained results enabled to determine the correlation between the calcination temperature and the phase compositions of the obtained pigments. In addition, some interesting magnetic properties were detected for the Co-doped composition.



## Síntesis de pigmentos del sistema $Fe_2O_3.SiO_2$ con adiciones de óxidos de Ca, Mg o Co

*Palabras clave:*
Pigmentos
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Resonancia electrónica paramagnética
Espectroscopia de Mössbauer
Microscopia electrónica de barrido
Dispersión energética de rayos X

RESUMEN

La investigación presente está basada en la evaluación comparativa del efecto de la adición de los óxidos de Ca, Mg, y Co sobre las propiedades de unos pigmentos cerámicos nuevos del sistema $Fe_2O_3.SiO_2$ obtenidos mediante la tecnología cerámica clásica. Ese método de investigación ha permitido la determinación de la temperatura de calcinación óptima y el mineralizador más apropiado. Las muestras obtenidas fueron sometidas al análisis sistemático, incluyendo espectroscopia de difracción de rayos X, análisis de la resonancia electrónica paramagnética (REP) y espectroscopia de Mössbauer para la determinación de las fases cristalinas constituyentes. Los parámetros colorimétricos han sido evaluados mediante medidas espectrofotométricas. El tamaño estimado de las partículas se ha

* *Corresponding author.*
E-mail address: stephko1980@abv.bg (S. Kozhukharov).
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determinado por microscopia electrónica de barrido (MEB) y su composición elemental se ha definido mediante la espectroscopia de dispersión energética de los rayos X (EDEX). Los resultados obtenidos han permitido la determinación la correlación entre la temperatura de calcinación y las composiciones cristalinas de los pigmentos obtenidos. En adición, se han registrado algunas propiedades magnéticas interesantes en el caso de la composición dopada por cobalto.



## Introduction

The ceramic pigments are important class materials which determine the color related characteristics, as well as other properties of the obtained ceramic products. Besides, the pigment addition enables enhancement of the resistance against atmospheric, thermal and chemical impact of the surrounding environments, especially the decomposing impact of silicate fusions (e.g. frits) and sun-light related UV-photochemical decomposition. These colored inorganic compounds should possess a high light refraction coefficient, and to be insoluble in water, organic solvents, ceramic slips, in order to form stable colloidal precursor systems with desirable color related characteristics [1].

The color possessed by a given pigment appears as a result of the selective light wave absorption by its crystalline lattice at defined wavelength. The color of given pigment is being determined by the presence of chromophores. They are composed by atoms or atomic groups capable to render colorization of the respective ceramic system containing them [2].

The color related characteristics are always derived by chemical compounds of d- or f-transition elements, such as vanadium, iron, cobalt, manganese, nickel, copper, chromium, praseodymium, etc.

Following their specific function, the pigments can be concerned as an entire class of materials. These compounds can be grouped by different indications. One of the most versatile and widely classifications used is drawn up by the Color Pigments Manufactures Association (CPMA) formerly the Dry Color Manufactures Association (DCMA) in the United States. This system provides a structural classification of pigments on the basis of the main substance crystalline lattice type. According to this classification, the pigments are divided into: spinel, garnet, zircon, olivine, baddeleyite, periclase, etc. [3,4].

Although the zircon-based pigments are relatively new class, they are already among the most perspective and widely used in the industrial practice, because of their remarkable thermal stability in glaze melts. The most distinguishable representatives of the Zr-based pigments are: vanadium zircon blue [5–8], praseodymium zircon yellow [5,9,10], iron-zircon pink [11–16], etc.

Other group of interesting high temperature resistant emerald-green pigments is developed on the basis of the mineral uvarovite. These pigments can be obtained from natural precursors at high temperatures (1200–1250 °C) at the presence of mineralizers (mainly borates and fluorides), and currently the processes involved in their synthesis are object of intensive scientific research activities [14–16].

The pigments based on spinel compounds also possess high color intensity, chemical and thermal stability. The structural and crystalline lattice similarity among various spinel based pigments enables isomorphic substitution with solid solution formation. Examples for stable pigments from this group are elaborated on the basis of $CaFe_2O_4$ [17], $MgFe_2O_4$ [18], $CoFe_2O_4$ [19–23], etc.

The aim of the present research work is to synthesize, and characterize doped ceramic pigments on the basis of $3MeO{\cdot}Fe_2O_3{\cdot}SiO_2$, where “Me” is Ca, Mg, or Co.

## Experimental

### *Sample preparation*

#### *Initial precursors*

Three compositions were investigated in the present research work: $3CaO{\cdot}Fe_2O_3{\cdot}3SiO_2$ (composition 1), $3MgO{\cdot}Fe_2O_3{\cdot}SiO_2$ (composition 2) and $3CoO{\cdot}Fe_2O_3{\cdot}SiO_2$ (composition 3). These compositions were selected on the basis of literature analysis, and preliminary experiments, as well as considering that the color should be originated from the following chromophores: $Ca_3Fe_2Si_3O_{12}$, $MgFe_2O_4$, and $CoFe_2O_4$. Following the literature, $H_3BO_3$ was added in quantities relevant to $2\%_{wt.}$ of the entire pigment composition, in order to act as a mineralizer [24–28]. The precursors used for pigment synthesis were, as follows: CaO, (Reachim) MgO, (Reachim) CoO (Sigma–Aldrich), $Fe_2O_3$ (Sigma–Aldrich), $SiO_2{\cdot}nH_2O$ and $H_3BO_3$ (Reachim). All these precursors were with analytical grade of purity.

The hydrated $SiO_2{\cdot}nH_2O$, used in the present case is much more reactive than the pure quartz sand and has particle size dimensions between 2 and 7 μm. Initially, after calcination in a platinum crucible, its composition was estimated to 76.3% of $SiO_2$ and 23.7% of $H_2O$ (i.e. 4:1), respectively.

#### *Pigment synthesis*

The necessary precursor quantities for 100 g precursor mixture were weighted by a balance with ±0.1 g of precision, and subsequently dry ball-milled in PULVERIZETE – 6 product of “FRITCH” (Germany).

The pigment synthesis was performed in a muffle furnace by heating speed – 300–400 °C/h at air atmosphere in covered crucibles and isothermal step continuation for 2 h at 800 °C, 900 °C, 1000 °C, 1100 °C and 1200 °C, respectively. The technological schedule scheme is represented in Fig. 1.