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OBTAINING AND CHARACTERISATION OF THERMORESISTIVE PIGMENTS

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ABSTRACT

The paper describes the obtaining and chemical and physico-structural characterisation of a green thermoresistive pigment. The pigment is made of ZnO dopped with Sb, Bi, Cr, Co and Fe oxides and it is used at mosaics and stained glass. The procedure is based on a sequential coprecipitation "layer on layer" process in aqueous solution, followed by drying and calcinations at controlled temperature conditions, then grinding in a colloidal mill and mixed with glass powder forming the "frit pigment". This by vitrification and frosting colours superficial the glass.

The powder was analysed by SEM-EDX and DSC.

KEYWORD: chemical doped zinc oxide, thermoresistive pigment, mosaic, stained glass, SEM-EDX, TG/DTA.

1. Introduction

Zinc oxide based pigments are mainly white or grey. They have the disadvantage that is thermoluminiscent and they are degradated under the influence of light radiation.

The obtaining of different colours with high melting temperatures and photo-chemical resistant, from dopped zinc oxide is made on two ways: physical dopation in coloidal mills or chemical dopation by precipitation in aqueous or organic solutions [1-4] The sequential coprecipitation processes are new and allows the obtaining of powder hard fusible and photoresistant. By mixing with glass powder are obtained the frit pigments, which can be applied on the glass surface by vitrification or frosting [5]. In the paper is presented the obtaining procedure and the characterisation of the pigments by SEM-EDX and TG/DTA, for the evaluation of the structure, chemical composition and thermal stability.

2. Experimental Part

2.1. Obtaining of the pigment

The obtaining technology of pale green is based on three coprecipitation processes, as micro-eterogen system, hard soluble, based on oxyhydroxides of Zn, Bi or Sb and different cations of transitional metals, which after filtration, purification and washing are dried and calcinated.

For obtaining the pigment it is used distiled water mixed with $ZnCl_2$, $MnCl_2 \cdot 4H_2O$, $CoCl_2 \cdot 6H_2O$ şi $CrCl_3 \cdot 6H_2O$. After the total solubilisation the dispersion is filtered and mixed with a solution of NH_4OH 10N, till pH of 8.0...8.5. The system obtained is stabilised for 20...30 mins at 50°C, in order for the crystals to grow. After that is mixed with a solution of $SbCl_3$ and $BiCl_3$ with a few drops of HCl. The pH shouldn't be lower than 7.5. The pH can be adjusted with a solution of NH_4OH 10%.

2.2. SEM-EDX

The researches have been carried out with a SEM VEGA II LSH scanning electronic microscope manufactured by the TESCAN Co., the Czech Republic, coupled with an EDX QUANTAX QX2 detector manufactured by the BRUKER / ROENTEC Co., Germany.

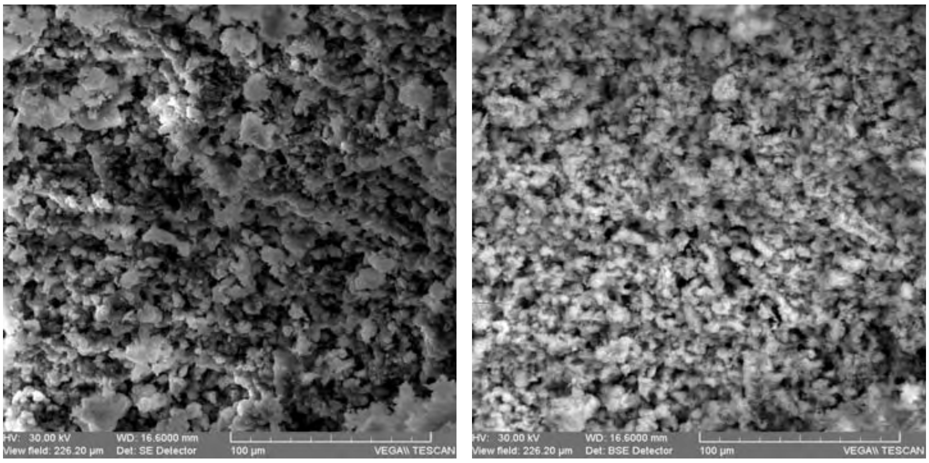
2.3. TG/DTA

In the thermal, it analysis was used a Thermobalance Linseis STA PT1600, which allows fast heating and cooling rates as well as a highly precise temperature control.

The temperature range was from 20 to 1000°C. The device is fully controlled by computer.

3. Results and discussions

In the figure 1 are presented the SEM images of the pigment at 1000X with secondary electrons detector (SE) and back scattered electrons detector (BSE).



a *b*

Fig.1. *SEM image of the pigment: a – 1000X SE, b – 1000X BSE*

As it can be seen on Fig 1. the grains are uniform distributed with vitroceramic morphology, with the internal phase – grains of doped ZnO and external phase (dispersive medium) – Sb and Bi oxides. The figure 2 represents the EDX spectra of the pigment, followed by the table 1 with the elemental composition.

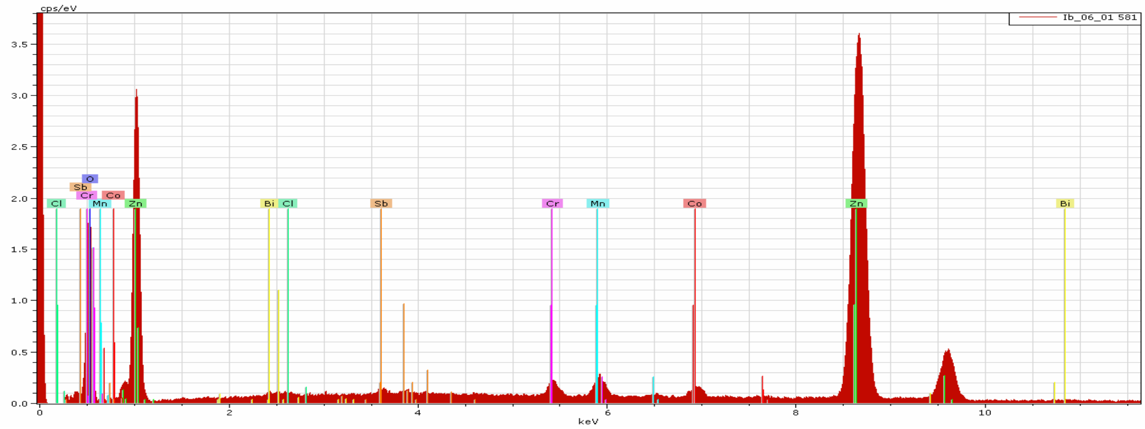


Fig. 2. *EDX Spectra of the pigment*

Table 1. *The Composition of the pigment according to the EDX Spectra from Fig. 2*

Element	Weight, %	Atoms, %	Error, %
Zinc	64.58572	37.09885	1.849272
Manganese	1.11221	0.760413	0.079453
Chromium	1.415505	1.022532	0.091944
Cobalt	1.201922	0.76604	0.068493
Antimony	1.396885	0.430925	0.084291
Bismuth	5.004422	0.899464	0.212932
Chlorine	0.259606	0.275043	0.043605
Oxygen	25.02373	58.74673	7.219001

The elemental composition determined by Xray dispersion proves the presence of the elements used in synthesis at the suggested concentration for obtaining a vitro-ceramic material. Figures 3, 4 and 5, according to the thermal analysis, presents the TG, DTG and respectively DTA curves of the pigment.

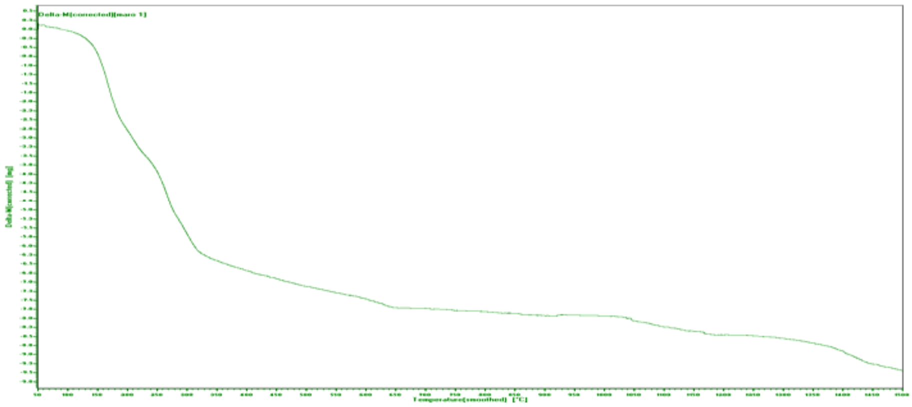


Fig. 3. *TG courve of the pigment*

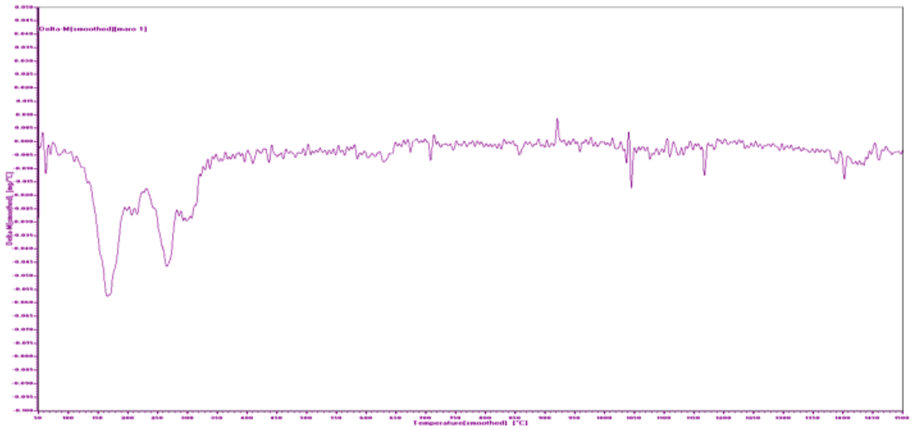


Fig. 4. *DTG courve of the pigment*

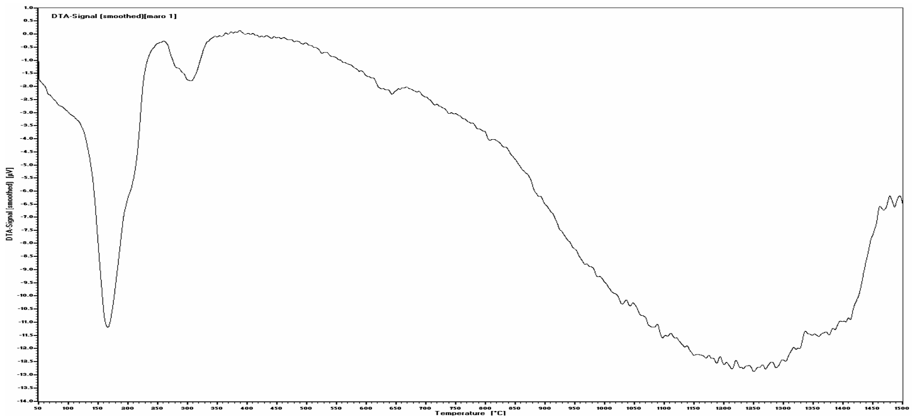


Fig. 5. *DTA courve of the pigment*

The thermal analysis data evidentiates the temperature level for the water and volatile compounds removal, followed by structural reformation and the last the vitrification processes at more than 1400°C. The structural re-formation processes are well seen at 250°C, 400°C and 670°C.

4. Conclusions

The SEM-EDX analyses evidentiates that the coprecipitation procedure obtains a phase distribution at higher temperatures.

The particle morphology is vitro-ceramic type with the two different phases, internal (doped ZnO grains) and external one (dispersive medium of Sb, Bi oxydes).

The pigment has a uniform granulometry, high coloration and covering power, chemical and thermal resistance.

The thermogravimetric data confirms that the pigment is resistent in time and at high temperatures.

The obtained pigments can be used for mosaics and stained glass.

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