



# Thermal Stability of Inorganic Pigments Synthesized from Galvanic Sludge

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**Abstract:** *Pigments used in ceramic glazes have been obtained by chromium ions extraction from galvanic sludge and their precipitation as barium chromate and lead chromate from technological solutions. The chemical composition was determined by XRF method. Complex thermal analysis TG-DSC, XRD and SEM methods have been used for microstructural characterization and thermal treatment behaviour evaluation, in order to establish the compatibility with the ceramic matrix. XRD spectra have highlighted only lead chromate specific interferences in the monoclinic phase and barium chromate in the orthorhombic phase, suggesting an advanced degree of purity. Weight losses of 2.2% for barium chromate and 3.1% for lead chromate have been recorded on the TG curve at 800°C. As a result of thermal treatment, barium chromate has changed its colour from yellow to green.*

**Keywords:** *galvanic sludge, inorganic pigments, thermal stability*

## 1. Introduction

The industrial developments cause an increasing in the concentrations of heavy metal ions from industrial effluent, such as electroplating sludge [1]. The pollution with heavy metals represents an important global issue because of their extremely toxic effect even at low concentrations and one of the highest environmental risk is the omnipresence of heavy metals due to their toxicity, persistence and lack of biodegradation [2-4]. There are various methods for neutralization and recovery of electroplating sludge, namely: methods of incorporation/inertisation of the sludge (also heavy metals) in stable matrices and methods for the extraction of valuable components (metal ions) and their exploitation such as inorganic pigments or raw materials in various industries [5].

Inorganic pigments are used in many industries. Pigments used in the ceramic industry are inorganic compounds such as metal oxides, mixture of metal oxides or metal salts [6]. Generally, the quality of ceramic pigments depends on their crystalline structure, chemical composition, purity and physical characteristics [7]. Ceramic industry is on the rise and constant competitiveness in this sector and is leading manufacturers and researchers to find solutions in order to reduce raw materials costs and, at the same time, to develop new products. In recent years, a particular attention was given to the recycling of industrial waste, which are a source of alternative and less expensive raw materials [8,9]. Various methods were developed in order to synthesize pigments from high metal ion containing sludge such as: green and pink pigments synthesized from high-chromium galvanic sludge [10]; red, green, pink ceramic pigments synthesized from sludge from various metal coating processes and having high aluminum and chromium content [8]; red-brown and black pigments obtained from high chromium and iron sludge resulting from the treatment by electrocoagulation of wastewater from metallic coatings and tested in transparent ceramics [11]; yellow and brown pigments obtained from metallurgical dust and tested in glazes and angobes [12] or gray-black ceramic pigments synthesized from sludge resulted from chromium/nickel/cooper metal coating activities [13]. The latest research in the field has focused on the synthesis of ceramic pigments from tannery wastewater treatment sludge [14-16].

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In this work, we focus on the characterization of yellow and orange chromium based pigments such as barium chromate and lead chromate, synthesized from galvanic sludge. The main purpose of the research was to study the microstructural characterization and thermal treatment behavior of pigments, in order to establish the compatibility with the ceramic matrix. Generally, these pigments have a good thermal stability and coloring strength [17]. Their use is limited by the Restriction of Hazardous Substances (RoHS) Directive, therefore researches on their valorization has focused on obtaining ceramic materials for decorative use that do not come into contact with food.

## 2. Materials and methods

### 2.1. Pigments synthesis

Chromium based pigments were extracted from a sludge which is the result of the treatment of mixed wastewaters derived from various metal finishing processes (copper plating, cadmium plating, zinc plating, etc.). The sludge presented a complex chemical composition, the content in metals being the following: 8.00% chromium; 21.3% iron; 2.44% zinc; the content of Ni, Cu, Cd, Pb, Mn, Ca, Mg, Na being below 1% for each element [18]. Sludge samples were dried at 105°C in Binder oven to constant weight, about 6 h and milled in ball grinding mill in order to obtain particles with average diameters of about 20 µm.

The chromium recovery process was based on the solubilisation of trivalent chromium by alkaline oxidation with 12% sodium hypochlorite and 20% sodium hydroxide added to provide a strong alkaline medium ( $pH = 12.0-12.5$ ); reaction temperature was 80°C, reaction time 30 min, with stirring throughout the reaction. Reagents consumption was calculated from chemical reactions, the amount of sludge processed and its chromium content. The samples were filtered with a vacuum pump resulting a sodium chromate solution from which the chromium-based pigments were extracted. The extraction efficiency of chromium ions was 84.20% in one stage [19]. Lead chromate was obtained by precipitation process with lead acetate [ $Pb(CH_3COO)_2 \cdot 3H_2O$ ] and barium chromate was obtained by precipitation with barium chloride [ $BaCl_2 \cdot 2H_2O$ ]. The precipitates were vacuum-filtered, the cakes were washed stepwise in order to remove the soluble salts adsorbed on the cake, dried and prepared by grinding [20].

### 2.2. Methods of investigation

The chemical composition of both pigments was determined by XRF spectrometry using an X-Ray Fluorescence Supermini instrument. The purity of synthesized pigments from sludge was also determined by X-ray diffraction analyzes using a D8 Advance Diffractometer in the  $\theta-2\theta$  configuration with Cu  $K\alpha_1$  radiation ( $\lambda = 0.154060 \text{ \AA}$ ). The data were obtained by scanning in the range of  $2\theta = 10 - 70^\circ$  with a step of  $0.02^\circ$ . The morphology of both lead chromate and barium chromate raw and thermal treated at 700°C respectively 800°C was investigated by scanning electron microscopy (SEM) using a Hitachi SU-70 FE-SEM model. DSC (Differential Scanning Calorimetry) and TG (Thermo Gravimetry) analyzes at different temperatures according to the particularities of the materials and their chemical composition was performed in order to investigate the behavior of the pigments at heating (phase transformations and mass losses). Heating behavior of pigments was studied using a Netzsch STA 449 F5A. The TG and DSC curves were recorded in nitrogen atmosphere using alumina crucibles. The investigated temperature range was 25-800°C (or 850°C) at a heating rate of 10°C/min.

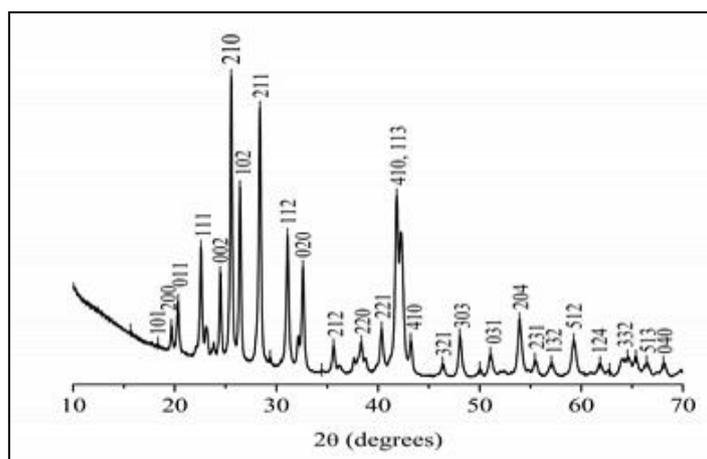
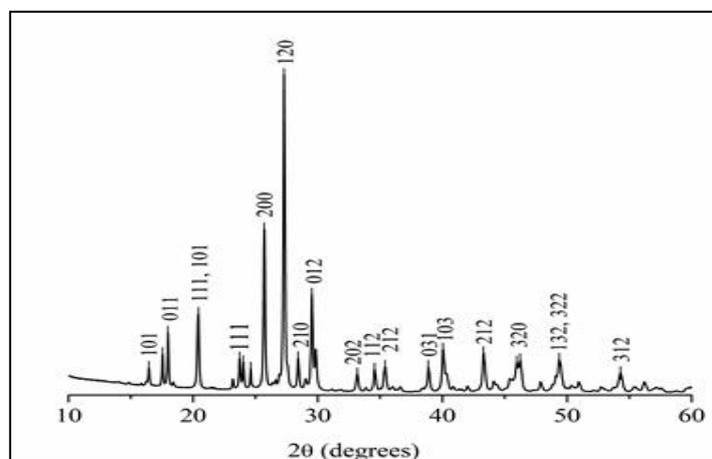
## 3. Results and discussions

The chemical composition of both barium chromate and lead chromate pigments determined by XRF analyses is presented in Table 1.

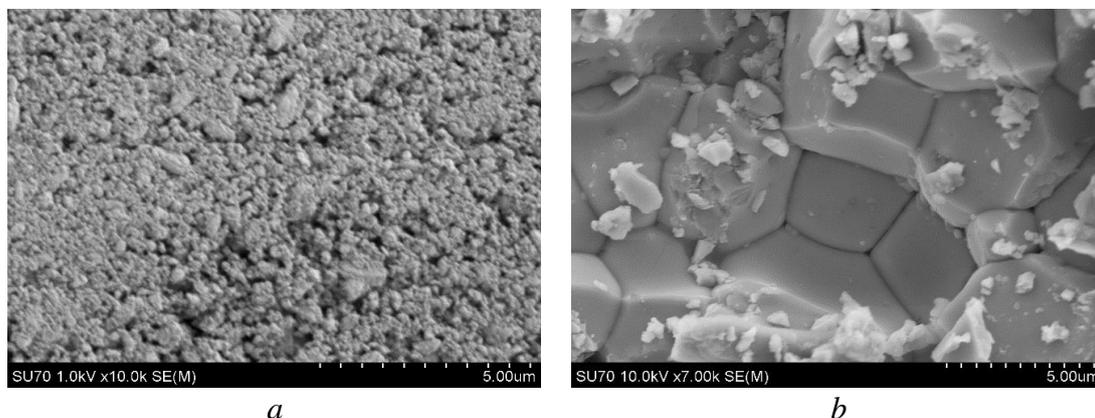
**Table 1.** Elemental composition of barium chromate and lead chromate

Pigment	Elemental composition (mass %)				
	Cr	Ba	Pb	S	Minor components
Barium chromate	25.1	72.8	-	1.3	0.8
Lead chromate	23.6	-	75.2	-	1.2

The XRF results highlight the purity of the synthesized inorganic pigments. Thus, the barium chromate pigment contains mainly barium (72.8%) and chromium (25.1%). The 1.3% of sulfur derived from synthesis process and the rest of the components does not exceed 1%. The lead chromate pigment contains lead as major component (75.2%) and chromium in proportion of 23.6%, the minor components does not exceed 1.2%. The XRD patterns of synthesized barium chromate particles are presented in Figure 1. The sharp diffraction peaks indicate that the product is well crystallized. Accordingly, to ICDD (International Centre for Diffraction Data) database all the interferences were perfectly indexed as orthorhombic phase of barium chromate with lattice parameters of  $a=9.103 \text{ \AA}$ ,  $b=5.526 \text{ \AA}$  and  $c=7.337 \text{ \AA}$ . On the x-ray pattern the interferences belonging to other phases are not recorded indicating that the minor components appeared during the synthesis reaction are poorly crystallized. For the lead chromate patterns presented in Figure 2, all the interferences were indexed as a single phase of monoclinic lead chromate [space group  $P21/n (14)$ ] with lattice parameters  $a = 7,12 \text{ \AA}$ ,  $b = 7,43 \text{ \AA}$ ,  $c = 6,79 \text{ \AA}$  and  $\beta = 102,420^\circ$  consistent with the reported data (JCPDS 73-2059).

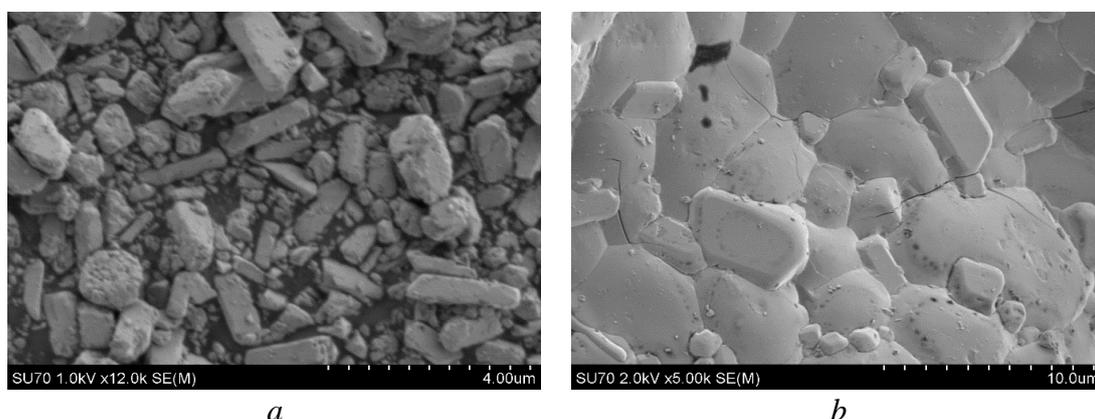
**Figure 1.** XRD spectra of barium chromate pigment**Figure 2.** XRD spectra of lead chromate pigment

The morphology of both barium chromate and lead chromate raw and thermal treated at 800°C respectively 700°C was investigated by scanning electron microscopy (SEM). In Figure 3 are presented the SEM images of raw and thermal treated barium chromate at 800°C, The raw barium chromate powder has a fine texture and a unimodal distribution of the grains, with agglomeration tendency of the very small size particles. After sintering at 800°C (Figure 3b), results a pore-free structure, in which the polyhedral granule (with well-defined sides and edges) are about 5µm in size.



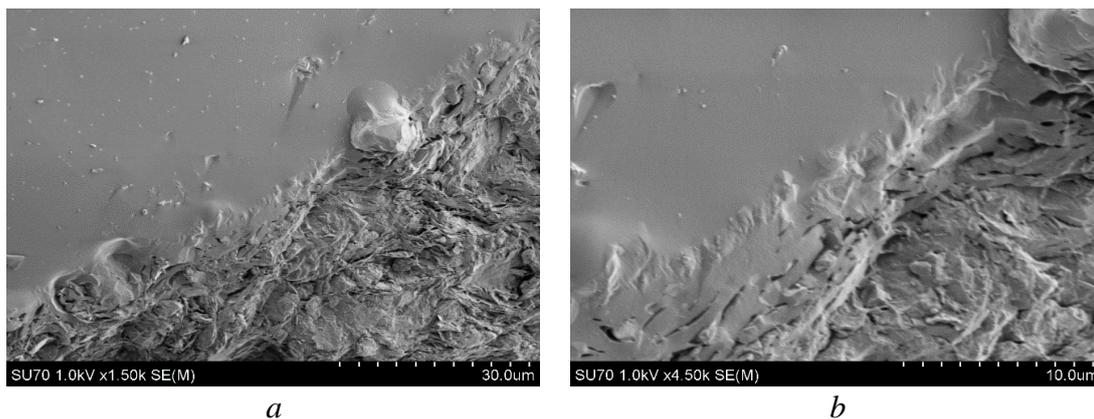
**Figure 3.** SEM images of barium chromate, raw (a) and thermal treated at 800°C (b)

The micrographs of raw lead chromate, presented in the Figure 4, evidence polyhedral granules which exhibit a bimodal distribution, without agglomerations; the size of the large particle varies between 1µm to 2µm and the small particles do not exceed 0.4µm. The sintering at 700°C ensure the formation of a compact structure, through an intimate grains linkage, with visible intergranular boundaries and triple junctions (Figure 4b). The particle sizes may reach up to 8µm, highlighting the positive temperature effect on the grain growth rate. Araújo et al. has evidence a high rate of the granule growth, hence a good reactivity of lead chromate, by thermal treatment up to 700°C [21].



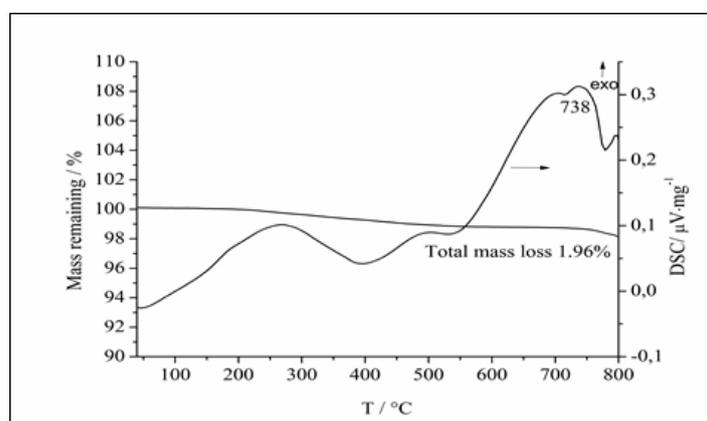
**Figure 4.** SEM images of lead chromate, raw (a) and thermal treated at 700°C (b)

SEM images of the ceramic body interface with the transparent glaze, containing 5% barium chromate are presented in Figure 5. The fixing of the glaze on the ceramic body surface was accomplish by heating at 1100°C. At the interface area the glaze diffuses into the surface layer of the crystalline and porous ceramic body (Figure 5b).



**Figure 5.** SEM image of the ceramic body interface with glaze containing 5% barium chromate, at different magnifications.

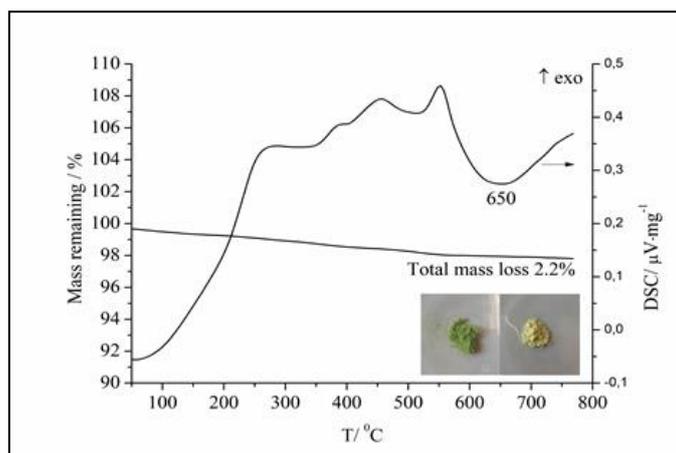
The thermal stability of the pigments was studied in nitrogen medium by complex thermal analysis. In Figure 6, TG-DSC curves corresponding to lead chromate are presented.



**Figure 6.** DSC-TG curves of the lead chromate, synthesized from galvanic sludge

There is an exothermic effect indexed on DSC curve, with a maximum to 738°C, accompanied by a mass loss of 0.72%. The thermal effect corresponds to the phase transformation of the monazite-structure in the high temperature baryte form. The total mass loss registered on TG curve of the lead chromate was 1.96%. From scientific data, pure lead chromate, obtained by synthesis, presents at high temperature two phase transitions: from the low temperature monazite structure passes at 706°C into the  $\beta$  - barite form and at 782°C into the  $\gamma$  - barite [22]. In this case lead chromate, obtained by synthesis from galvanic sludges, contains 1.2% minor components, which could be the reason of why the temperature at which it undergoes phase transformations may be different. Knight reported that the phase transition from the monazite structure of synthetic lead chromate in the barite structure was achieved at 795°C, and the process was accompanied by a mass decrease of 1.6% [23].

DSC curve of the barium chromate recorded a thermal effect between 570°C and 770°C (with a maximum at 650°C), to which it corresponds a mass loss of 0.25% (Figure 7).



**Figure 7.** DSC-TG curves of the barium chromate, synthesized from galvanic sludge

Unlike lead chromate, the color of barium chromate, at the end of the analysis, changed from yellow to green, suggesting its decomposition into the nitrogen atmosphere. There are various data regarding the thermal stability of barium chromate in different gaseous environments. Decomposition of barium chromate is accompanied by oxygen release and reduction of chromium [24]. In some papers research it is mentioned that barium chromate is thermally stable up to 850°C [25]. In other sources it states that between 800 and 900°C, it decomposes into a mixture of  $\text{BaCr}_2\text{O}_4/9\text{BaO}\cdot4\text{Cr}_2\text{O}_3\cdot\text{CrO}_3$ , according to the  $\text{BaO}\text{-Cr}_2\text{O}_3$  phase diagram [26]. In air, barium chromate has thermal stability up to 1400°C; partial oxygen pressure could inhibit the decomposition mechanism of barium chromate [10]. By vacuum sintering at 1050°C, barium chromate changes its color from yellow to green, suggesting its decomposition and formation of  $\text{BaCr}_2\text{O}_4$  [11]. In this case, the decomposition of barium chromate is accelerated by the reducing character of the nitrogen atmosphere. The total weight loss recorded at the end of the determination was 2.2%.

#### 4. Conclusions

The XRF analyses highlighted the purity of the synthesized pigments: the major component of lead chromate pigment is lead (75.2%), followed by chromium (23.6%); Barium chromate pigment contains mainly barium (72.8%) and chromium (25.1%). In both cases the amount of impurities is very low (less than 1.2%). The XRD analyses highlighted single phases of monoclinic lead chromate and orthorhombic barium chromate. For lead chromate the DSC/TG analyses highlighted an exothermic effect with a maximum at 738°C, accompanied by a mass loss of 0.72% corresponding to the phase transformation of monazite-structure into barite form. For barium chromate, the DSC curve recorded a thermal effect between 570 and 770°C with a mass loss of 0.25%. At the end of the thermal treatment the color of barium chromate, changed from yellow to green, suggesting its decomposition. The total weight loss recorded at the end of the determination was 2.2%. The SEM images of raw lead chromate highlights dispersed polyhedral grains, bimodal distributed while the sintered pigment exhibits a compact structure, through an intimate grains linkage, with visible intergranular boundaries and triple junctions. The SEM images of raw barium chromate highlights a powder with fine texture and a unimodal distribution of grains, with agglomeration tendency of the very small size particles. The sintered sample at 800°C presented a pore-free structure, in which the polyhedral granule (with well-defined sides and edges) are about 5μm in size.

From microstructural point of view, at the ceramic/glaze matrix interface, a transition area can be delimited where the glaze, by diffusion mechanisms, has been fixed to the ceramic body surface.



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