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# OBTAINING AND CHARACTERIZATION OF VITROCERAM BY CHEMICAL DOPED ZnO FOR ART MOSAIC

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## ABSTRACT

*This paper presents the obtaining and the characterization of ZnO doped vitroceramic, used as photo and termoresistive pigment for art mosaic. The coprecipitation involves two sequential steps, first of ions* $Zn^{2+}_{(aq)}$, $Cr^{3+}_{(aq)}$, $Co^{3+}_{(aq)}$ *and* $Mn^{3+}_{(aq)}$, *as oxihydroxides in predetermined molar reports: 98:0,6:0,7:06, followed by maturation, forced filtration and redispersion of the granules in distilled water, after which, by ion exchange is precipitated as intergranular film of* $Sb^{3+}_{(aq)}$ *and* $Bi^{3+}_{(aq)}$ *ions. After forced filtration and drying, the material is subjected gradually to a thermal process, according to a curve with three levels: 20 - 110℃, 110 - 360℃ şi 360 - 950℃, with a heating rate of 3℃/min., each level keeping a constant temperature while varying between 4 and 8h for nanostructures processes of crystalls reform. The vitroceramic was characterized by SEM-EDX, microFTIR and termic derivatography, after treatment at 110℃ and respectively 950℃, underlining uniformity of grains and revealing their heterojonctional structure in cross-section.*

KEYWORDS: vitroceramic material, pigment, mosaic, SEM-EDX, IR, microFTIR, TG/DTA/DTG/DSC

## 1. Introduction

Zinc oxides doped as frit pigment for artistic mozaic are polycrystalline ceramics containing minor dopants and additives [1, 2].

The zinc oxide is a synthetic white pigment used in paintings after 1834 [3].

Compared to titanium dioxide (introduced in the market for painting much later, after 1916) it has the advantage of low cost manufacturing, but compared to it and other inorganic pigments, it has an important number of disadvantages, such as low coverage degree (transparent in thin layers), variable degree of white in time under the influence of environmental factors, low photo- and temperature resistance, while as vitroceramic pigment it has a high reactivity, it induces the thermoluminescent effect and manifests incompatibility to a number of other types of metal oxide pigments.

However, as a ceramic pigment, zinc oxide has several advantages by doping the granules and their surface additive: it can be stabilized both photochemically and thermoresistively, it can get very different stable shades, indexed CIE L*a*b* [4], can be used as a pigment for oil or water painting and also to achieve artistic mosaics and stained glass. Compared to frit pigments, particularly used to achieve polychrome based mortars finishes, mosaics and stained glass art, ceramic pigments have several major advantages: high climate and mechanical resistance, compatibility with organic and inorganic binders and glass [5, 6].

Speculating data from scientific research to get the material for ceramic varistors based on zinc oxide, there have been performed different studies on the doping processes of ZnO grains and their surface additive, in order to obtain chromophore structures with stable photochemical and thermal shades which by glazing glass process allow obtaining tessers for mosaics and stained glass, thus elaborating a first procedure for obtaining a green pigment for this purpose [5]. As in the varistor case too, the question arises to optimize the two processes: the doping and the additive.

With the only difference that in case of new vitroceramic pigments there are requirements to be respected, to obtain uniform coloring, photo- and thermoresistance, compatible with the glass glazing performance. Since the two processes are difficult to control and vitroceramic pigments field is not sufficiently known, this paper seeks the submission of relevant information from literature used in developing technology for obtaining a varistor ceramics based on zinc oxide, in order to allow interpretation of experimental data obtained on newly synthesized vitrocerams, involving two stages: doping of zinc oxide by coprecipitation $Zn^{2+}$ions in mixture with other cations of transitional metals, likely forming chromophore structures, and the addition of granules resulting from coprecipitation on these structures surface of cations of block "p" metals to form uniform and continuous intergranular films, photochemically and thermal by stable and strong reactive at surface, able to interact with glass by the glazing processes.

## 2. Theoretical aspects on the obtaining of vitroceram

The precise role of the oxidic components of vitroceramic material used up to date in manufacturing pigments technology for art mosaic is difficult to assess [7-11]. Except for zinc oxide, considered a major phase, the others are grouped in dopants or additives. Their involvement by inserting in the crystallites structure of ZnO in these technologies clearly indicates the need to create two types of structures with different functions.

Precipitation processes by which those structures are obtained are based on two types of insertions: *subtractive* or *intercrystalline doping*, forming polychromatic phases and surface or interface (intergranular) additive, where they get into *congruents, eutectics* and *intermediate phases*. By doping, white zinc oxide turns colored, while the additive forms on the surface grain or intergranular, clusters, adductions or connecting nanostructural bridges. Hence, obtaining pigments such vitroceram likely to be further glazed on glass, requires two sequential processes: first, a doping one to form chromophore groups, then the surface additive one, to form the reactive film with a dual role: stabilization of the chromophore and glazing.

E.g., for the green pigments, the first obtained are the doped ZnO grains, mainly with MnO and CoO, after which they are submitted to $Bi_2O_3$ and $Sb_2O_3$ additive, forming the intergranular film reactive to the subsequent glazing process. Manganese and cobalt oxides bring back the color of zinc oxide granules by producing photochemical by and thermally stable chromophore structures [8, 12, 13], while those of bismuth and antimony supply uniform distribution, continuity and density of intergranular film, allowing stabilization of chromophores and glazing [7, 12]. As seen, the role of doping and of the additives is largely evident, but the processes taking place in the two stages of production: the precipitation/polymerization and the calcination/sintering/vitrifying, are much more complex, develop different crystalline, eutectic and congruent phases, technologically unmanageable.

It is known that zinc oxide is a very poor type “n” extrinsic semiconductor, that by doping with block “d” metal oxides from the center of the first series of transition in stable oxidation states ($Cr_2O_3$, MnO, $Fe_2O_3$, CoO, NiO), becomes electronically conductive by populating with electrons the Additional Donor Band (ADB), the thermoluminescent effect being diminished.

On insertion by additive of thus obtained granules with oxides of block “p” ($Bi_2O_3$, $Sb_2O_3$, PbO, $SiO_2$), a series of polycrystalline dielectric structures result, with electron depletion of the additive band, transforming it into an Additional Acceptor Band (AAB) and taking a big distance from the Valence Band (VB), allowing their glazing and bindering on the glass. Furthermore, the low voltage resistivity increases due to ZnO-$Bi_2O_3$ eutectic formed after sintering/vitrifying processes at temperatures above 750°C [14] that allow stabilizing of the shade and fading of the thermoluminescent effect. As $Bi_2O_3$ is non-dispersible in ZnO at room temperature coprecipitation processes, it will segregate, be on the surface of a ZnO grain, or at interface between two ZnO grains, having the shape of an amorphous 1-2 nm film rich in bismuth oxide [15]. Previous studies [1, 2, 5, 16-19] showed that the distribution, uniformity and granulometry of polycrystalline structures on the surface of the doped zinc oxide granules depends on bismuth oxide content, which increases the film grain, leading to its discontinuity.

In contrast, antimony oxide, which is a grain growth inhibitor, forms with zinc oxide spinels and pirochlore type phases at the grains surface, which provides continuity and uniformity to the intergranular film [20-22]. Thus, antimony oxide serves to bind the granules of zinc oxide and allows, when obtaining tessers for mosaics or stained glasses art, vitroceramic pigment adhesion to glass surface by glazing.

Regarding the transitional metal oxides, the cobalt and manganese have a well known role in granules of zinc oxide coloration [5, 7, 10]. These oxides are dispersable in ZnO solution, as they are kinetic and thermodynamic compatible, having the same oxidation state (II). Both cobalt oxide and the manganese one are colored materials, that allow the sintering to give chromophore structures with zinc oxide. Very important for ceramic pigments used in the mosaics and stained glass, is the distribution and uniformity of colored granules, but also the intergranular film thickness and continuity [5].

It is absolutely necessary that both phases - precipitation/polymerization and the sintering/vitrifying one, at the most lowest temperature, give optimal distributions of colored microgranules and intergranular films. An important role in structural reform of intergranular polycrystalline film in the sintering/vitrifying processes have the spinel structures and pirochlore type phases that inhibit granules growth and compactize them at temperatures higher than 950°C [7], up to 1100°C [5].

Previous studies [21, 22] focused on the role of certain dopants concentration on certain tinctorial and thermoluminescent properties. It was noted that doping achieved through colloidal milling physical processes is effectively lower at the sintering-vitrifiying, while the one achieved by the processes of precipitation / polymerization remains constant [7, 23]. A comparative analysis of the transitional metal oxides behavior used in doping processes in terms of kinetic and thermodynamic compatibility with zinc oxide, which is typical amphoter, taking into account the three types of reactivity: acid-basic (which is dominant), complexing and redox, allow their grouping in the following alkalinity series: CrO>MnO>FeO>CoO>NiO; $Mn_2O_3$ (weak basic)>$Cr_2O_3$ (amphoteric)> $Fe_2O_3$(very weak acid)>$Co_2O_3$(weak acid)>$Ni_2O_3$(weak acid).

These series allow assessing the stability of double, mixed or saline oxides likely to appear at the precipitation or the sintering/vitrifying precesses. Thus, the next two double oxides are very stable: $Fe_3O_4$ (feroferic oxide, $FeO.Fe_2O_3$) and $Mn_3O_4$ (manganomanganic oxide, $MnO.Mn_2O_3$) and three saline oxides: $ZnCr_2O_4$, $ZnNi_2O_4$, $ZnCo_2O_4$, followed by the less stable, saline oxides type: $ZnMn_2O_4$ (coming from amphoteric oxide and a very weak basic one) and $ZnFe_2O_4$ (derived from an amphoteric oxide and a very weak acid) and then the unstable ones, double oxides type: $Cr_3O_4$, $Ni_3O_4$ and $Co_3O_4$. If during the processes of precipitation only the very stable are formed, the sintering-vitrifying processes are also likely to form some less stable oxides. It is interesting that some occur in the precipitation phase, but disappear at sintering-vitrifying, or vice versa, are formed at high temperatures, but reversible change at the cooling in primary byproducts occurs.

Since the kinetics of these processes is much more complex, further there are introduced some issues from the specialized literature related to the interactions that take place in the two phases, the precipitation and sintering-vitrifying, having carefully formed components and structural features of intergranular films.

Together with the formation of zinc oxide doped particles, their surface resulting in a series of congruents spinel $Zn_7Sb_2O_{12}$ type and pyrochlore type phases, bismuth oxide-rich in the form of 1-2 nm thick intergranular films. Moreover, to highlight the role of oxides in the two processes, besides the main components for doping (CoO and MnO) and the additive ($Bi_2O_3$ şi $Sb_2O_3$), were used in small quantities other transition metal oxides too, stable in +III oxidation state, such as $Cr_2O_3$ [16], $Fe_2O_3$, $Co_2O_3$ and $Ni_2O_3$ [20], giving rise in precipitation to ZnO interactions, somewhat different of oxides in the oxidation state +II. They interact better with zinc oxide in sinterizing-vitrifying. Thus, thermal processes enable a series of reactions leading to congruents and different polycrystalline phases [8]. Final composition of the final microstructure depends on the existence and development of such reactions occurring in sintering and vitrifying, and also on selecting an optimal strategy for achieving a structure with exactly the tinctorial and bindering desired properties [28]. It is known that hue and bindering capacity by glazing is directly proportional to the average grain size of ZnO [29, 30]. It is therefore necessary a rigurous control of microstructural development degree of conductive grains and intergranular film, both in precipitation stage and in the sintering-vitrifying one. In 1975, *Wong* [31] first suggested a possible reactions sequence involving formation of a pyrochlore-type compound $Bi_2(Zn_{4/3}Sb_{2/3})O_6$. At higher temperatures, this phase reacts with ZnO pellet, which is easily accessible in the matrix bulk, to form a spinel-type compound and a liquid phase rich in bismuth oxide. So, zinc oxide replaced in pyrochlore an equivalent amount of bismuth oxide, without disrupting the substructure ($Zn_{4/3}Sb_{2/3}$), according to the reaction:

$$Bi_2(Zn_{4/3}Sb_{2/3})O_6 + ZnO \rightarrow Zn(Zn_{4/3}Sb_{2/3})O_4 + Bi_2O_{3(liq)} \qquad (1)$$

The presence of liquid phase leads to film densification, zinc oxide grain is reduced and spinel formed will act as grain growth inhibitor [16].

Later, in 1980, *Inada* [32] proposed a similar sequence of reactions in two stages, that occurs in a ternary oxide system, first at temperatures below 900°C and the second, between 900°C to 1050°C, according to the following reactions:

$$2ZnO + 3/2Bi_2O_3 + 3/2Sb_2O_3 + 3/2O_2 \rightarrow Zn_2Bi_3Sb_3O_{14} \qquad (2)$$

$$2Zn_2Bi_3Sb_3O_{14} + 17ZnO \rightarrow 3Zn_7Sb_2O_{12} + 3Bi_2O_{3(liq)} \qquad (3)$$

According to Inada, the reaction (3) is reversible on cooling, although the presence of certain doping, as the oxides of Cr, Mn, Co and Ni, tend to stabilize the spinel structure and to prevent their decomposition in pyrochlore type phases. There is a disagreement between the chemical composition of pyrochlore-type phases proposed by Inada and suggested by Wong. Prevalence of the first reaction was confirmed in 1989 by *Kim et al*. [33] and recently reaffirmed by *Mergen & Lee* (1997) [34]. *Kim* states that both the binary systems of reaction ($ZnO\text{-}Sb_2O_3$ and $ZnO\text{-}Bi_2O_3$), and the ternary ($ZnO\text{-}Sb_2O_3\text{-}Bi_2O_3$), allow dielectric film densification, being closely related to the formation of pyrochlore type phases and the liquid ones (eutectic).

A very important role plays the relationship between the Sb oxide and Bi oxide. For $Sb_2O_3/Bi_2O_3 = 1$, it will correspond to stoechiometry of pyrochlore phase formation.

A ratio greater than unity leads to the formation of liquid phases (around 740°C), as a result of interaction between ZnO and $Bi_2O_3$ with formation of eutectic [33, 35]. On the other hand, a lower ratio than 1 delays eutectic liquefaction at higher temperatures, up to pyrochlore phase decomposition (reaction 3).

Based on previous studies from the 1990s on the influence of nature and the doping concentration, of sintering-vitrifying temperature, of heating and cooling rates on the development and microstructural reform of vitroceram, *Olsson* [5] suggested the existence of an additional reaction that explains the increasing of volumetric fraction for spinelic structures at $Sb_2O_3/Bi_2O_3$ ratios > 1.

In 1996, *Leite et al.* [37] proposed the following sequence of reactions to explain the role of additives in the formation of intergranular dielectric film:

$$Sb_2O_3 + O_2 \rightarrow Sb_2O_{5(liq)} \quad \text{(which takes place at 527°C)} \qquad (4)$$
$$Sb_2O_{5(liq)} + ZnO \rightarrow ZnSb_2O_{6(s)} \quad \text{(between 700 and about 850°C)} \qquad (5)$$
$$ZnSb_2O_{6(s)} + 6ZnO \rightarrow Zn_7Sb_2O_{12(s)} \quad \text{(temperatures at higher than 800°C)} \qquad (6)$$
$$3ZnSb_2O_{6(s)} + 3Bi_2O_{3(s)} + ZnO \rightarrow Zn_2Bi_3Sb_3O_{14} \qquad (7)$$

The last sequence takes place at temperatures between 700°C and 900°C.

Based on previous work of *Kim et al.* [36] and *Krasevec et al.* [38], who suggested a mechanism of evaporation-condensation of antimony oxide at about 500°C, *Leite et al.* [37] proposed that at first Sb(III) oxide is oxidised to Sb(V), which is liquid at this temperature. Further, pentoxide vaporizes, and the vapors condense over ZnO solid particles to form intermediate phases of rutile type, $ZnSb_2O_6$. Such a phase, whose existence was mentioned above by *Inada*[32] and *Kim et al.* [33], and, then reacts with ZnO adjacent particles to form spinel structures or with ZnO and $Bi_2O_3$, when appear the pyrochlore phases, which later transform into spinels (reaction 3). However, the presence of oxide of Sb(V) is controversial because the compound decomposes at around 380°C, releasing oxygen.

Thus, *Ott et al.* [22] and *Kumari et al.* [39] rejected this hypothesis and rewrote reactions (4) and (5) into a single one:

$$ZnO + Sb_2O_3 + O_2 \rightarrow ZnSb_2O_{6(s)} \quad \text{(which takes place between 600 and 800°C)} \qquad (8)$$

Ott et al. have noted, however, the presence of spinel structures $ZnSb_2O_{6(s)}$ is unclear, since the direct reaction itself could explain the additional formation of spinel [22], according to the process:

$$7ZnO + Sb2O3 + O2 \rightarrow Zn_7Sb_2O_{12(s)} \text{(at temperatures above 800°C)} \qquad (9)$$

This option was rejected by *Kumari et al.* [39], who proposed the following rection taking place in the binary system:

$$ZnO + Sb_2O_3 + O_2 \rightarrow ZnSb_2O_{6(s)} \quad \text{(temperatures at higher than 600°C)} \qquad (10)$$
$$ZnSb_2O_{6(s)} + 1{,}33ZnO \rightarrow Zn_{2.33}Sb_{0.67}O_{4(s)} + 0{,}67Sb_2O_3 + 0{,}67O_2 \qquad (11)$$

Reactions that would take place at temperatures above 800°C, whereas that after 900°C a structural reform should take place, according to the reaction:

$$3Zn_{2.33}Sb_{0.67}O_{4(s)} \rightarrow Zn_7Sb_2O_{12(s)} \qquad (12)$$

By trimerizing $Zn2.33Sb0.67O4_{(s)}$, which is nestoechiometric, it results a stoichiometric spinel structure, corresponding to the formula $Zn_7Sb_2O_{12(s)}$, but with a cubic symmetry instead of an orthorhombic one. Spinel transformation could be avoided by the presence of some soluble additives.

Reactions from (1) to (12) are some of the proposals in the specialized literature to explain the formation of the intergranular film during the sintering-vitrifying process.

Lack of accurate descriptions of the entire vitroceramic manufacturing process has imposed the writing of this paper, focused primarily on highlighting the phenomena that occur both in the precipitation-polymerization processes and at the sintering-vitrifying, taking into account the formation from pure oxides of eutectic type phases, pyrochlore, spinel and intermediate phases.

## 3. Expermental Part

*Chemical Analysis*

A newly synthesized product was analyzed by classical chemical methods, determining by mass atomic spectroscopy the metal cations as key components on the basis of which the composition of oxides was calculated. Hygroscopic and chemically bound water was determined by gravimetric methods, subjecting the sample to a static heat treatment. This correlates, as we shall see, with data obtained by thermal derivatography.

*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.

*TG/DTA*

In the thermal 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.

*Micro-FT-IR and IR*

The spectra have been recorded with a FT-IR Spectrophotometer coupled to a HYPERION 1000 microscope, both pieces of equipment from Bruker Optic, Germany.

FT-IR spectrometer is a TENSOR 27, which is an advanced flexible bentchtop instrument suitable for routine applications as well as laboratory research. TENSOR 27 is designed for measurements mainly in the mid – infrared region.

The IR spectra have been recorded with a IR Spectrophotometer SPECORD M, between 200 – 4000 cm$^{-1}$, information correlated to spectra obtained by microFTIR.

## 4. Results and Discutions

The pigment of vitroceramic type, newly synthesized, with green-pale color, was first characterized by chemical analysis (Table 1).

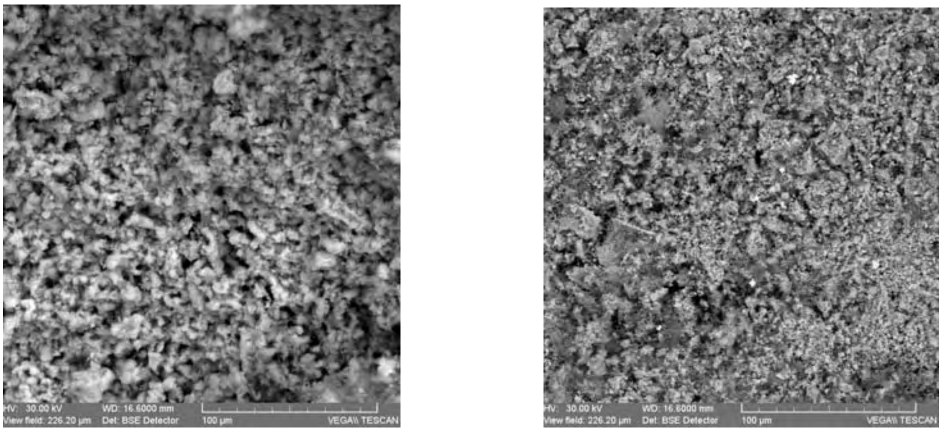
***Table 1.*** *Data on the chemical composition of newly synthesized vitroceramic Chemical compozition in main components as oxide*

| **Chemical compound**, (%) | | **Samples I** | **Samples II** |
|---|---|---|---|
| ZnO | Theoretical | 87.77 | 88.55 |
| | Practical | 87.752 | 87.932 |
| MnO | Theoretical | 0.77 | 0.62 |
| | Practical | 0.760 | 0.617 |
| CoO | Theoretical | 1.63 | 1.23 |
| | Practical | 1.606 | 1.221 |
| $Cr_2O_3$ | Theoretical | 1.65 | 1.33 |
| | Practical | 1.628 | 1.309 |
| $Sb_2O_3$ | Theoretical | 3.14 | 3.17 |
| | Practical | 3.106 | 3.148 |
| $Bi_2O_3$ | Theoretical | 5.05 | 5.10 |
| | Practical | 4.991 | 5.059 |
| $H_2O_{(higroscopic)}$ | Theoretical | - | - |
| | Practical | 6.964 | 0.586 |
| $H_2O_{(chimic)}$ | Theoretical | - | - |
| | Practical | 1.193 | 0.117 |

Samples I – pigment after precipitation stage with ammonia solutions;
Samples II – pigment sintering and vitrifying stage.

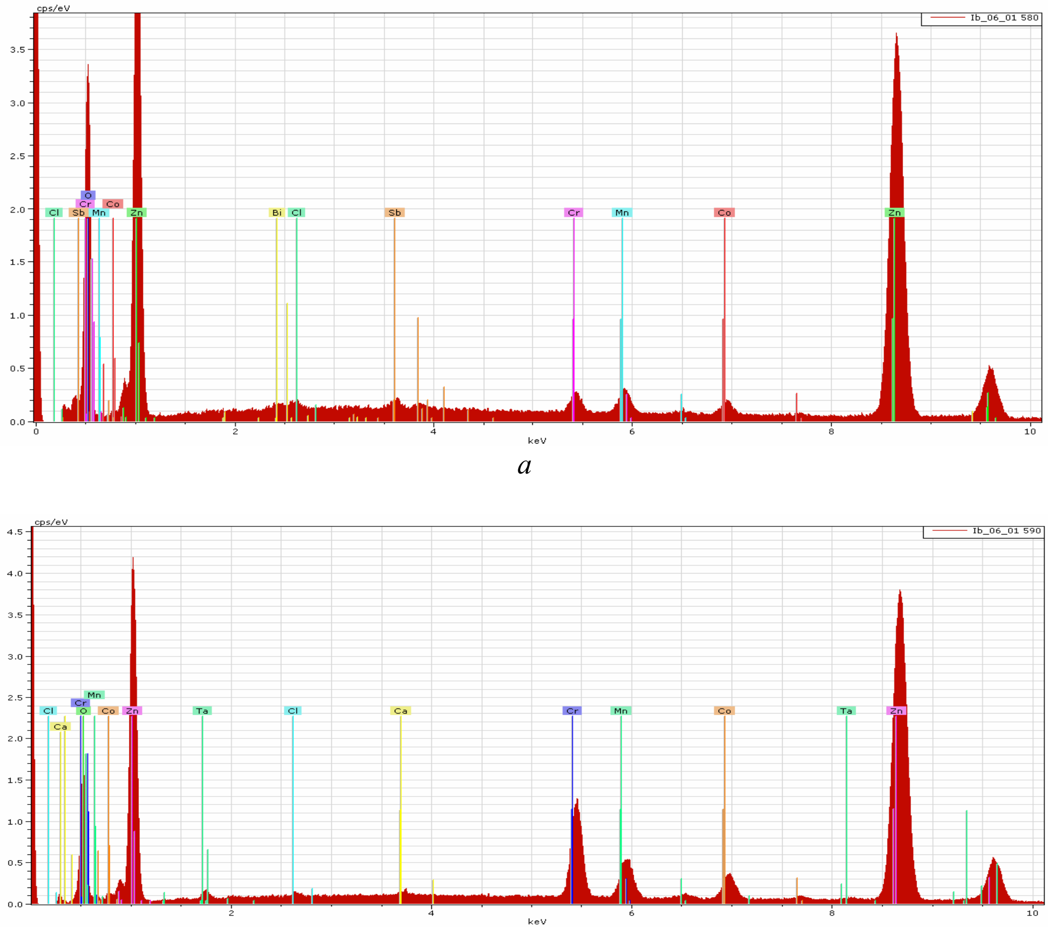
By comparing the theoretical ratio of main components with the chemical analysis data, these results allowed a confirmation, so that it was achieved the total coprecipitation of all chemical compounds, the values obtained by chemical analysis being very close to the theoretical ones.Product composition in the two stages of processing does not differ greatly, the only component that has wide variations being the water under the two forms, hygroscopic or physically bound water and the constitution water or chemically bound water.

Therefore, the product was further characterized by SEM-EDX, IR spectroscopy and thermal derivatography.



*a* *b*

***Fig.1**. SEM image of newly sinthesized vitroceram, 1000X BSE:*
*a – before vitrifying-sinterizing; b – after vitrifying-sinterizing.*



*a*

*b*

***Fig.2.** EDX Spectra of newly sinthesized vitroceram:*
*a – before vitrifying-sinterizing; b – after vitrifying-sinterizing.*

***Table 2.*** *Composition of the vitroceramics: left table is after precipitation and right table is the composition of a bluk of doped ZnO*

| Element | Weight, % | Atoms, % | Error in % |
|---|---|---|---|
| Zinc | 64.58572 | 37.09885 | 1.849272 |
| Oxygen | 25.02373 | 58.74673 | 7.219001 |
| 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 |

| Element | Weight, % | Atoms, % | Error in % |
|---|---|---|---|
| Zinc | 66.32515 | 40.41063 | 1.777766 |
| Oxygen | 19.62508 | 48.86934 | 3.40265 |
| Chromium | 9.136397 | 7.000575 | 0.292687 |
| Cobalt | 2.843064 | 1.922008 | 0.110038 |
| Manganese | 1.155598 | 0.838036 | 0.103717 |
| Chlorine | 0.386475 | 0.434311 | 0.046599 |
| Calcium | 0.52823 | 0.525105 | 0.048067 |

The thermogravimetric analysis took 100 mg of product, very finely crushed, dried in oven at 110±5°C for 4 hours and then subjected to dynamic thermal analysis. Figure 3 presents the derivatograma of the product.

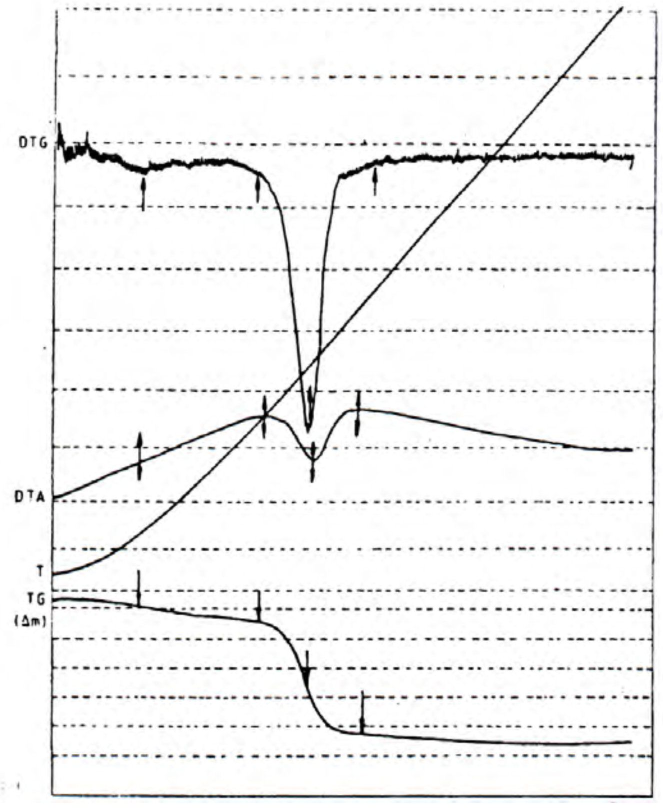


***Fig.3.*** *Derivatogram of the vitrified-sinterized product*

***Table 3.*** *Data on the nature of thermal effects on temperature ranges*

| **Product** | **Temperature ranges** (ºC) | **Nature of the dominant thermic effect** | **Charateristic temperature** (ºC) |
|---|---|---|---|
| G(I) | 30-110 | exothermic | max. at 70 |
| | 110-210 | highly exothermic | max. at 170 |
| | 210-240 | highly endothermic | min. at 220 |
| | 240-400 | exothermic | max. at 270 |

From Figure 3 and the corresponding data listed in Table 3 for the newly synthesized product, after vitrifying-sintering stage, the following conclusions:

- On heating under dynamic can be drawn, it has up to 110°C, a thermal process with a dominant weak exothermic effect, corresponding to the elimination of ammonia and of reversible hygroscopic water (the sample was heated at 110±5°C, hydroscopic water coming from the residual and the reversible water, taken after the initial thermic treatment) and of a quantity of oxygen absorption from the atmosphere; so, in this area, specific mass loss (0.18%) corresponds to the three processes: dehydration, ammonia elimination and oxygen uptake;
- Over 110°C, the product has a highly exothermic effect at 170°C, when it is eliminated a portion of the crystallization water and the coordinative;
- Endothermic dominant processes corresponding to the disposal of constitution water (of the OH groups and of those of coordinating left) are found at 220 ºC;
- Last highly exothermic effect corresponding to crystalline reforming processes, takes place at 270°C, attributed to the fact that the product structure shows a higher concentration of congruent structures of spinel type, with high thermal stability;
- Thermal analysis under dynamic which shows that coprecipitation procedure in ammonia system allows redistribution phase at high temperatures, thus creating optimal conditions to achieve eutectoid of oxides of antimony and bismuth, as a dispersion medium for spinel grains.
- In Figure 4 there are comparative spectra IR of the newly synthesized product after precipitation and drying stage, when the product is white-gray-brown (thick curve) and respectively after step by step treatment of calcination and sintering at 1200°C, when the product is pale green (thin curve).

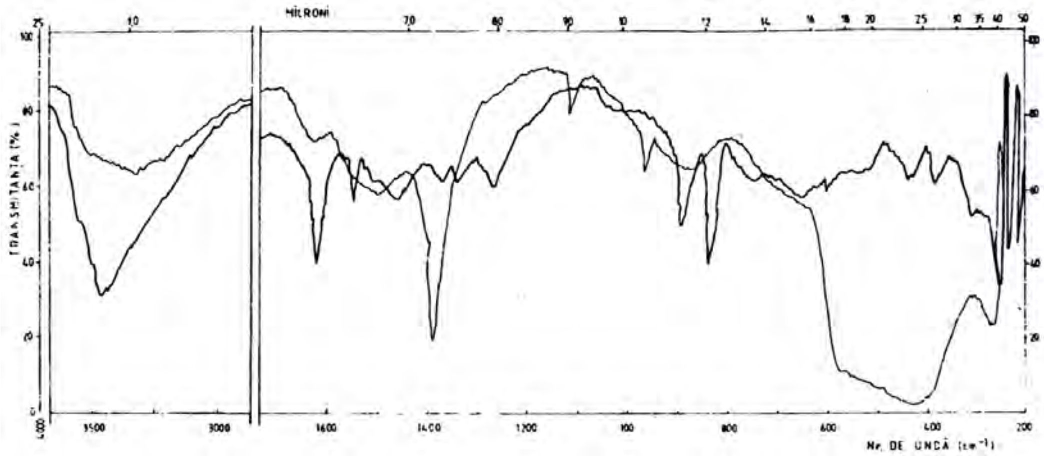


***Fig. 4.*** *IR spectra for the product G(I): thick line – product after precipitation and drying stage; Thin line – product after calcination-sinterizing.*

To characterize these products by IR spectroscopy were used characteristic group vibrations of the main structural components, in particular groups: Zn(II)-O, Zn(II)-OH, Mn(II)-O, Mn(II)-OH, Co(II)-O, Co(II)-OH, Cr(III)-O, Cr(III)-OH, with Bi(III)-O and Sb(III)-A [171, 195, 198, 199, 292 and 293].

If the oxidic systems of the cations of Zn(II), Mn(II), Co(II), Cr(III) have a few crystalline changes, very stable, oxides of Sb(III) and Bi(III), presents a more complex allotropy, whose stability depends on the summative oxidic system in which it takes part. Because they are easily fusible oxides, other oxides are dispersed by physical and chemical processes, when congruent hardly fusible structures are formed,.

From IR spectra, stands some specific features major phase, zinc oxide (Table 4).

It should noted that the product analyzed after precipitation and drying has representative characteristic group frequencies in the 3380-3430 cm-1 range, specific to each type of water, those at 1380$cm^{-1}$ and 250$cm^{-1}$, corresponding hidroxocomplexes of transition metals, in exchange, the same products after the sintering stage, are subjected to changes of absorption bands in fields 380-440 $cm^{-1}$, 500-570 $cm^{-1}$, 1380 $cm^{-1}$ şi 3380-3440 $cm^{-1}$. It should be noted that there is a clear difference between the spectra produced in the two stages: precipitation and calcination-sintering. At first, there also are shown the corresponding bands to amino complexes, the thick line spectra (1620-1630 $cm^{-1}$, 830 $cm^{-1}$ şi 860-880 $cm^{-1}$), which are strongly attenuated in the process of calcination.

***Table 4.*** *Characteristic group vibrations –specific to diverse structural units*

| **Chimical Compound** | **Characteristic frequency showed like wave numbers** (cm$^{-1}$) |
|---|---|
| ZnO | 230<br>420-450-500<br>1380 |
| MnO | 350<br>405-420<br>660 |
| CoO | 220<br>390-460<br>590<br>670 |
| $Cr_2O_3$ | 320<br>530<br>650-670 |
| $Sb_2O_3$ | 212<br>390<br>540 |
| $Bi_2O_3$ | 260<br>505<br>1480-1520<br>1550 |

In conclusion, IR spectra show the presence of two groups of oxide systems, transition hardly fusible metals and fuses easily fusible of Sb and Bi, which after sequential coprecipitation process in ammonium hydroxide medium originally formed some type of coordinative oxiammino or oxihidroxidice species, which after the gradual thermal processes, lead to elimination processes of volatile components (water and ammonia), segregation, diffusion and microstructural reform, resulting multicomponent dispersed phase, thermally and photochemically stable.

## 5. Conclusions

New vitroceramic material was synthesized to help obtaining tessers for mosaic and stained by single or double glazing [6]. Through chemical analysis, combined with SEM-EDX data, the thermogravimetric and IR spectrocopy, coprecipitation process revealed that the ammonia system allows redistribution phase at much higher temperatures, and the pigment has a uniform particle size, coloration and coverage of high power, high chemical, thermal and photo resistance, with good preservation of color over time. This pigment has a color degradation rate (shift to grey), very low compared with other green mineral pigments as chromophore groups form intragranular and intergranular film which stabilizes the color and protects it photochemically and thermally.

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