EXPERIMENTĂRI PENTRU REALIZAREA UNOR VITROCERAMICI DIN DEŞEURI DE STICLĂ DE LA TUBURI CATODICE - CRT

EXPERIMENTS TO OBTAIN GLASS-CERAMICS FROM GLASS WASTE RESULTED FROM CATHODE RAY TUBES - CRT

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Our experiments on the recovery of the glass waste resulted from cathode ray tubes - CRT were focused to designing compositions of glass-ceramic from glass waste with possible applications in composite materials. The recipes were calculated using as much waste as possible, using various nucleating agents and varying percentages, showing in this study the influence of ZrO_2. The report of CRT glass used for the neck:funnel:panel components were 5:30:65%, identical to the ones in CRT. We determined the following physical and mechanical properties: density, porosity, absorption, thermal expansion, hydrolytic stability. In order to characterize in terms of compositional and microstructural, the analyses were carried out by X-ray diffraction and scanning electron microscopy measurements, showing the influence of the nucleating agent and thermal treatment temperature on the properties of the glass ceramics.

Experimentele noastre privind recuperarea deşeurilor de sticlă rezultate din tuburi catodice - CRT, s-au concentrat pe proiectarea de compoziţii de vitroceramici din deşeuri de sticlă cu posibile utilizări în materiale compozite. Reţetele au fost calculate utilizând cât mai mult posibil deşeuri, folosind diferiţi agenţi de nucleaţie şi procente diferite ale acestora, în acest studiu prezentându-se influenţa ZrO_2. Raportul sticlă CRT pentru părţile componente gât:con:panou frontal folosit a fost 5:30:65%, identic cu cel din CRT. S-au determinat următoarele proprietăţi fizico-mecanice: densitatea, porozitatea, absorbţia, dilatarea termică, stabilitatea hidrolitică. Pentru caracterizarea din punct de vedere compoziţional şi microstructural au fost efectuate analize de difracţie cu raze X şi determinări de microscopie electronică de baleiaj, evidenţiind influenţa agentului de nucleaţie şi a temperaturii de tratament termic asupra proprietăţilor vitroceramicii.

Keywords: *glass-ceramics, cathode ray tubes, waste, composites*

1. Introduction

Glass-ceramic materials can be defined as polycrystalline solids containing vitreous phase obtained by controlled crystallization of a glass product made for this purpose [1-3].

The flexibility of the process for obtaining glass-ceramic is manifested by the fact that many wastes were used as raw materials for glass-ceramics, including fly ash from thermal power plants [4, 5], metallurgical slags [5, 6], red mud from the production of alumina [5, 7], residues of tungsten from tungsten minerals [8], E-glass fibres [2, 3], rice husk ash [9], waste products from sugarcane [5,10], glass wastes from CRT [5, 11, 12], TFT-LCD waste [13, 14] and other waste and glass products [5].

A recent issue regarding industrialized countries is the management of electronic waste of which 80% came from television-sets and computer monitors [12]. Electronic products are one of the segments of consumer goods in rapid expansion, and technological innovation and increased market availability facilitates the process of replacing the existing models [15]. There are many reasons to increase the amount of waste to be used or reused. Firstly, the disposal costs are minimized; secondly, the area that is reserved for the disposal and storage is reduced, thus allowing other uses of the land; in the third row, there may be financial gains from the sale of products or at least offsetting the cost of processing and disposal, and fourthly – the products can replace some limited or costly natural resources [5].

The ability of oxide systems to form glass-ceramic materials is conditioned by two groups of factors: intrinsic (chemical composition and structural features of glasses) and extrinsic (a number of parameters associated with the processing conditions of synthesis of the precursor glass for glass-ceramic, namely, the history of melting and controlled crystallization process, thermal history) [16].

To exploit these wastes, this paper presents

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preliminary results on the ability to turn the CRT glass into glass-ceramic with possible applications in composite materials.

2. Experimental

To produce a material suitable for the crystallization is often necessary to add correction compounds within the waste. Generally, because the main objective is to reuse the waste, the quantity of pure material added to improve performance should be as small as possible [1].

The objectives of the experimental part were:
- the development of glass-ceramic compositions using CRT glass waste;
- to obtain samples through the technique of pressing - sintering;
- the characterization of the samples and interpreting the obtained results.

2.1. Raw materials

For the preliminary attempts to obtain glass-ceramics we established the following recipes:
- Control sample, made only with glass powder.
- Samples of glass powder with 2% and 5% ZrO_2 as nucleating agent.

In order to obtain the glass powder we used the fractions of glass founded in the CRT: 5% neck, 30% funnel and 65% front panel.

2.2. Operating mode

In order to obtain the test specimens metal moulds with the dimensions of 30x10x7 mm were used. Based on previous work [3], we established by calculation and experiment the quantity of powder required. The material was weighted then mixed with poly-vinyl-alcohol in a porcelain mortar for 5 minutes. Poly-vinyl-alcohol acted as a bonding material for powder during the pressing.

From the prepared mixture we took the necessary quantity to fill the mould then the specimen was subjected to uniaxial cold pressing in a hydraulic press with a force of 50 MPa. After that the specimen was form-released and placed on a ceramic substrate. The stages were performed for all the specimens.

We obtained three specimens for each type of the samples: glass powder and glass powder with ZrO_2, 2% and 5%, a total of 9 specimens. The obtained samples are shown in Figure 1.

The specimens were then subjected to a sintering treatment. It was established by testing the optimal sintering temperature lying between 700ºC and 800ºC. The thermal treatment, at 700ºC, 750ºC and 800ºC, was carried out according to the following curve: 10°C/min up to a temperature of the thermal treatment and plateau for 30 minutes. Some of the specimens obtained after the sintering treatment are shown in Figure 2.

The specimens were subjected to the tests carried out for the determination of the ceramic and the physical-mechanical properties and microstructural characterization.

We determined the density, the porosity, the absorption, the hydrolytic stability and the thermal properties. At the same time the structural analyses were performed by X-ray diffraction and, respectively, scanning electron microscopy.

2.3. Apparent density

Density determination was performed by the hydrostatic weighing method based on weighing the specimens in air (m_{aer}) and then in water ($m_{apă}$). The density of the samples was obtained taking into account the density of water ($d_{apă}$), with the equation (1):

$$d = \frac{m_{aer}}{m_{aer} - m_{apă}} d_{apă} \ (\text{g/cm}^3) \qquad (1)$$

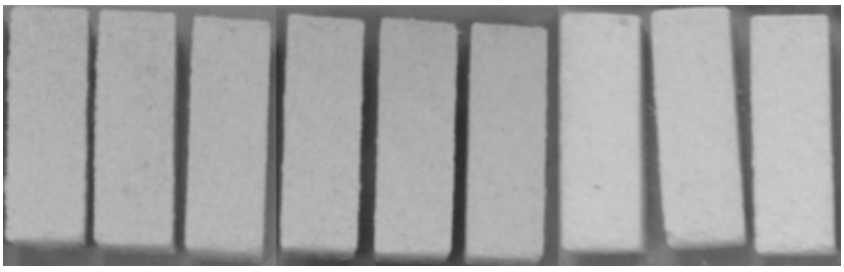
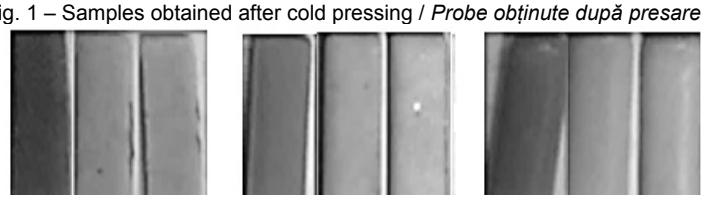


Fig. 1 – Samples obtained after cold pressing / *Probe obţinute după presare la rece.*



700°C 750°C 800°C

Fig. 2 – Samples after sintering / *Probe după sinterizare*.

2.4. Absorption

The absorption was determined by the boiling method, in which the samples are boiled in water for 4 hours and then cooled in water for 1-2 hours. The samples are weighed before (m_{aer}) and after boiling ($m_{fierbere}$), and the results were obtained using relation (2):

$$A = \frac{m_{aer}}{m_{aer} - m_{fierbere}} \cdot 100 \ (\%) \qquad (2)$$

2.5. Porosity

The porosity, P, was calculated with the equation:

$$P = d \times A, (\%) \ (3)$$

(d – density, g/cm^3; A – water absorption, %), the saturation liquid being water.

2.6. Hydrolytic stability

Like any other material, glass or glass-ceramic can react more or less with different chemical reagents or other materials with which it comes into contact. Since the glass/glass-ceramic is used in most cases for practical purposes as a material that should not chemically interact with the substances, interest is to measure the extent to which it can interact.

For the measurement of hydrolytic stability, the conductometric method was used to measure the change in conductance of a powder suspended in the water function of time, retaining constant for every determination the temperature, the amount of powder used and its specific surface area and the amount of water in the suspension.

The sample was ground in a porcelain mortar and then passed through two sieves with different mesh sizes. The fraction between the two sieves was chosen and 1 gr of it was weighed at analytical balance. The procedure was repeated for all samples analysed.

2.7 Thermal expansion

Thermal expansion is one of the properties which determine to the highest degree the behaviour of glass matrix on thermal stresses.

The expansion curve allows us to assess significant temperatures that characterize the glass-ceramic and to calculate the linear thermal expansion coefficients necessary to evaluate mainly the thermal shock stability.

We performed the thermal expansion curves using a DIL 402 PC Netzsch dilatometer with software that allows calculation of the coefficient of thermal expansion and the main temperature points specific for solid oxide materials. The temperature increase rate was 3°C/min.

2.8. Compositional and microstructural characterization

In order to characterize in terms of composition and microstructure we performed X-ray diffraction analyses and scanning electron microscopy measurements.

The phases formed on thermal treatment was examined by X-ray diffraction, in the range of 2θ=10-60°, using CuKα radiation, with a Shimadzu 6100 device.

Scanning electron microscope studies were conducted on "bulk" samples using a Hitachi S 2600 N type microscope. The samples were covered with a thin layer of gold; metallization time was 80 second and current 60 mA.

3. Results and Discussion

3.1. Apparent density

The results obtained are shown in Figure 3 as the average values for all 3 samples with the addition of a nucleating agent.

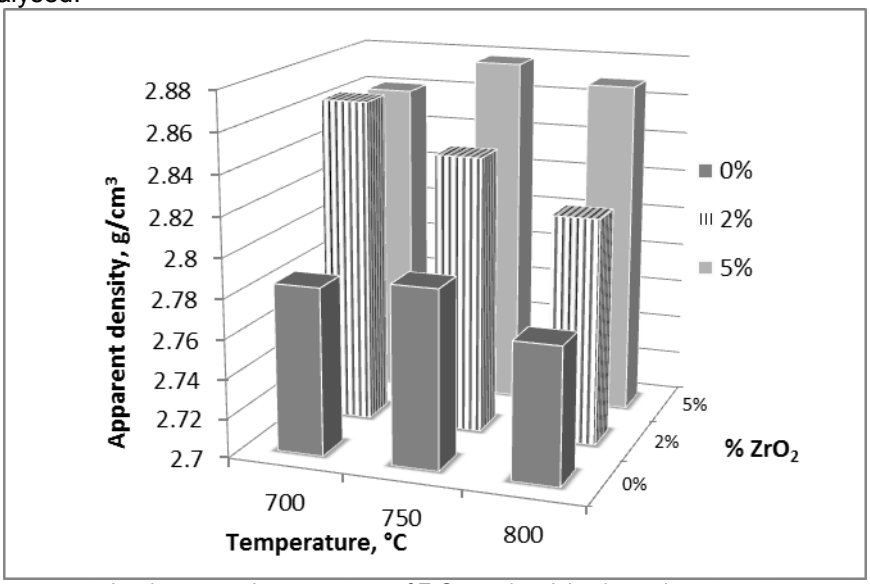


Fig. 3 – Variation of the apparent density versus the percentage of ZrO_2 used and the thermal treatment temperature / *Variația densității aparente funcție de procentul de ZrO_2 utilizat şi de temperatura de tratament termic .*

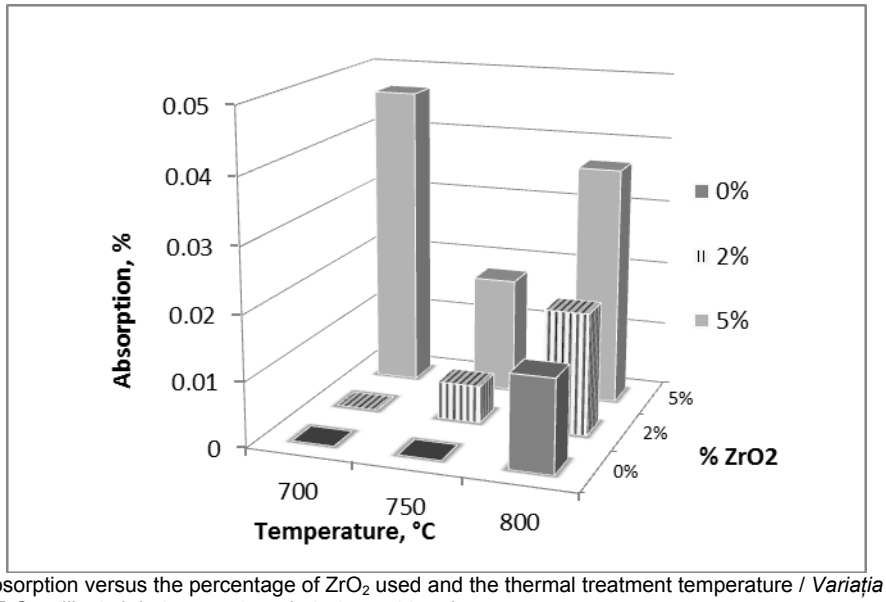


Fig. 4 – Variation of absorption versus the percentage of ZrO_2 used and the thermal treatment temperature / *Variația absorbției funcție de procentul de ZrO_2 utilizat şi de temperatura de tratament termic.*

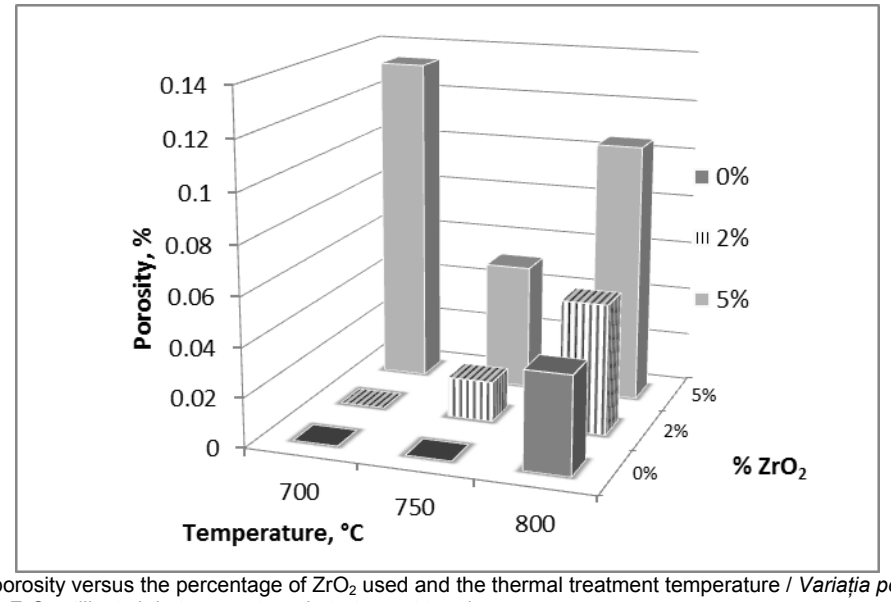


Fig. 5 – Variation of porosity versus the percentage of ZrO_2 used and the thermal treatment temperature / *Variația porozității funcție de procentul de ZrO_2 utilizat şi de temperatura de tratament termic.*

There is evidence that the density varies significantly, both for the control sample and function of the quantity of nucleating agent used. We noted higher values for samples with addition of 5% nucleating agent compared to samples with 2% agent due to the higher amount of nucleating agent. Also, there is a higher density of samples with addition of ZrO_2 compared to the control samples, caused by the high density of ZrO_2 (5.68 g/cm^3).

3.2. Absorption

The results obtained are shown in Figure 4 as average values.

It is observed that the samples show a very low absorption of water, less than 0.1%. As the sintering temperature increases, the control sample has a loose structure containing pores, which determines the absorption noted for the thermal treatment on 800°C, while for the samples with addition of nucleating agent the optimum temperature for the sintering is closer to 750°C, where absorption is minimal.

3.3. Porosity

The results obtained are shown in Figure 5.

We observe for the samples with addition of ZrO_2 that the porosity is minimal, close to 0. Due to the crystalline structures, more porous, which are formed inside the material, there is an increase in porosity for samples with addition of 5% nucleating agent compared to those with 2% ZrO_2. In correlation with the density and absorption tests, we can say that a low porosity provides a better densification of samples and a low absorption.

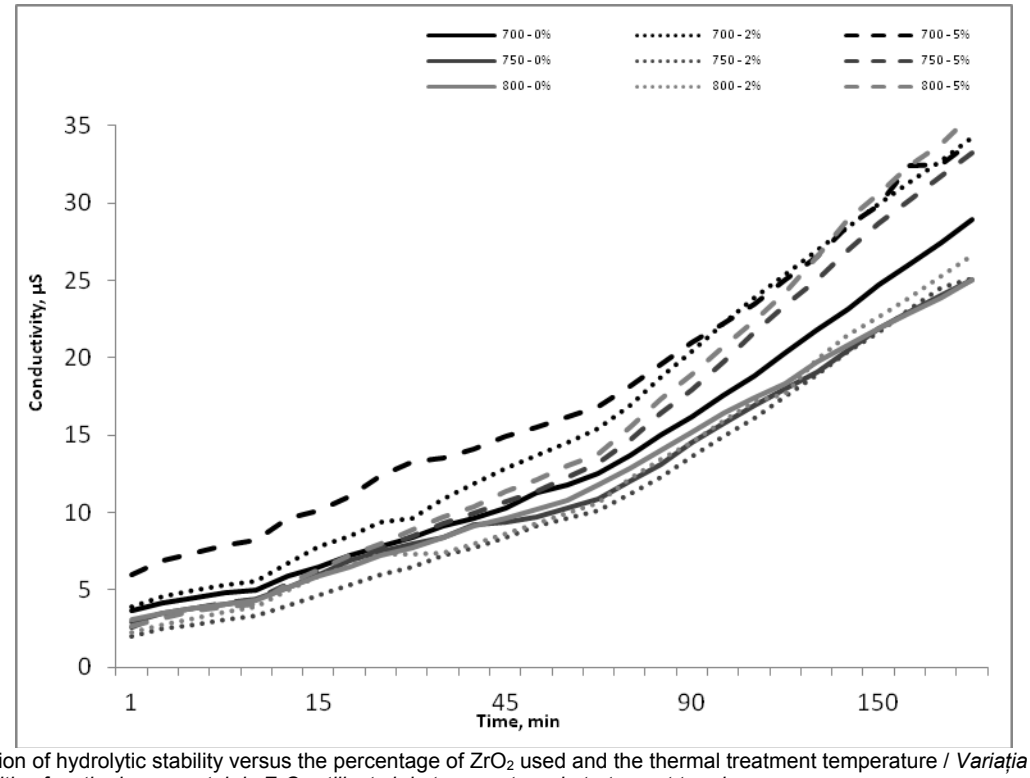


Fig. 6 – Variation of hydrolytic stability versus the percentage of ZrO_2 used and the thermal treatment temperature / *Variaţia stabilităţii hidrolitice funcţie de procentul de ZrO_2 utilizat şi de temperatura de tratament termic .*

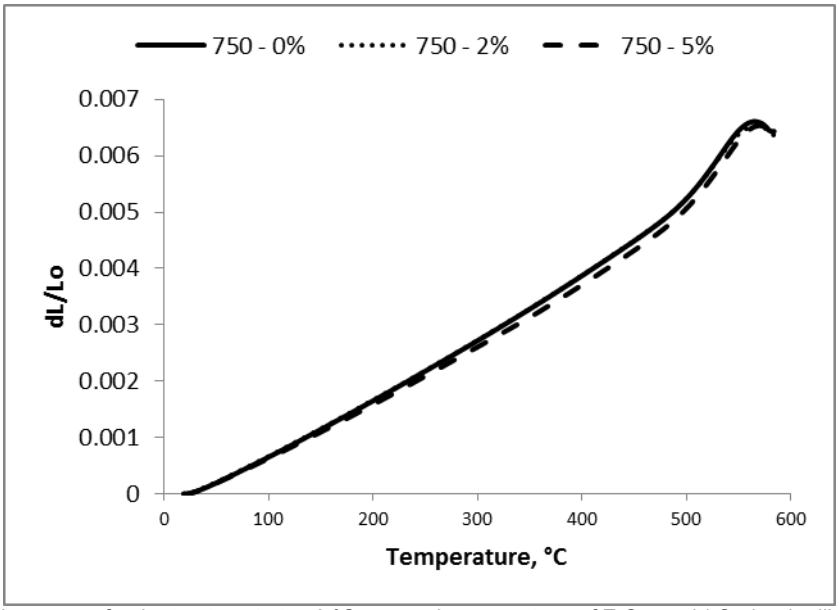


Fig. 7 – Thermal expansion curves for the treatment at 750 °C versus the percentage of ZrO_2 used / *Curbe de dilatare termică pentru tratamentul la 750 °C funcţie de procentul de ZrO_2 utilizat .*

3.4. Hydrolytic stability

The results obtained are shown in Figure 6. A more compact structure with minimum porosity and absorption and maximum density will present a good stability. We noted a greater stability (minimum conductivity) for the samples with 2% nucleating agent, treated at 750 and 800° C, while the samples with 5% ZrO_2 have minimal stability, the latter also having higher porosity and absorption.

3.5. Thermal expansion

We present for example, in Figure 7, compared, the expansion curves for the control sample and samples with ZrO_2, at 750°C, the temperature considered optimal for the sintering treatment.

From the thermal expansion curves we determined the coefficients of thermal expansion, α_{20}^{300}, shown in Table 1.

Table 1

Coefficients of thermal expansion [α_{20}^{300} ×10^7 K^{-1}] of the samples versus the percentage of ZrO_2 and the thermal treatment temperature used / *Coeficienţi de dilatare termică* [α_{20}^{300} ×10^7 K^{-1}] *ai probelor funcţie de procentul de* ZrO_2 *utilizat şi de temperatura de tratament termic utilizată*

ZrO_2 content / Thermal treatment temperature	0%	2%	5%
700°C	96.95	93.12	96.57
750°C	97.08	97.35	93.10
800°C	96.29	96.17	95.79

The control samples show a specific behaviour for glasses, with glass transition and dilatometer softening temperature clearly seen on the curve, while the samples with nucleating agent present a dimmed specific inflection of the glass transition and a dilatometer softening temperature shifted to higher temperatures and not very well defined, suggesting the presence of significant amounts of crystalline phase formed after the thermal treatment.

3.6. SEM and XRD

X-ray diffraction revealed, along with the specific spectra for vitreous structures, the presence of sharp peaks for samples with 5% nucleating agent attributed to ZrO_2 and, for the thermal treatment at 750 and 800°C, of wider peaks (which signifies the presence of small crystals) assigned to barium silicate and lead silicate.

Scanning electron microscopy revealed the formation of crystalline structures, even in the control sample, in the absence of nucleating agent, the formations being more developed for the thermal treatment of 800°C, where porosity was highest for these samples. In the case of samples with ZrO_2, crystalline phase is present in greater amount, crystals concentration being more clearly defined, especially for samples treated at 750°C. In all cases, the crystals are small and have been developed especially in the pores of the vitreous material, where the temperature of the thermal treatment allowed their growth, as we can see in Figure 8.

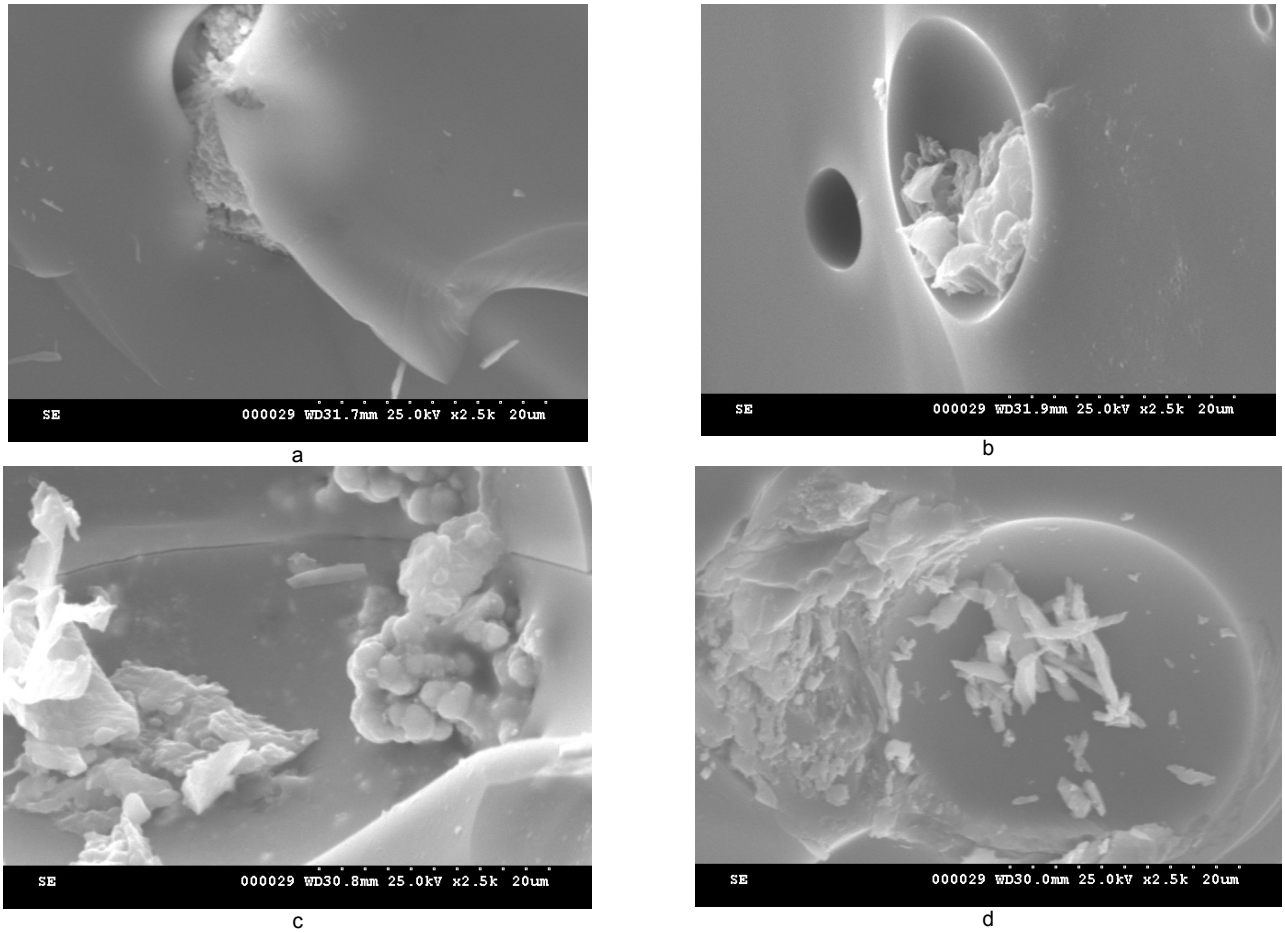


Fig. 8 – SEM microscopy for the control sample and samples with nucleating agent / *Microscopii SEM pentru proba martor şi probe cu agent de nucleaţie:* a) 750°C-0%, b) 800°C-0%, c) 750°C-5%, d) 800°C-2%

4. Conclusions

This paper presents the experimental results on the development of glass-ceramic compositions using CRT waste glass and ZrO_2 as a nucleating agent in a proportion of 2% and 5%. The processing technique was uniaxial cold pressing of the powder mixture (glass waste - nucleating agent), followed by a sintering treatment.

The samples were characterized regarding the density, porosity, absorption, hydrolytic stability and thermal expansion, X-ray diffraction analysis and scanning electron microscopy. The analysis of the results shows that:

- The density of the samples varies significantly, higher values standing out for samples with addition of 5% nucleating agent compared to samples with 2% due to the higher amount of nucleating agent.

- Due to the crystalline structure formed, an increase in porosity occurs for samples with the addition of 5% nucleating agent compared to the samples with 2% agent. In correlation with the density and absorption tests, there was a greater stability for the samples with 2% nucleating agent, treated at 750 and 800°C, a dimmed specific inflection of the glass transition and of the dilatometer softening temperature, which suggests the presence of a significant amount of crystalline phase formed after the thermal treatment.

- For the samples with nucleating agent, X-ray diffraction revealed the presence of small crystals assigned to barium silicate and lead silicate, confirmed by the SEM analysis, which highlighted the development of crystals, in particular in the pores of the vitreous material, where the temperature of the thermal treatment allowed their growth.

A unique advantage of sintering can be found in the incorporation of a reinforcement phase, leading to glass-ceramic matrix composites with a very good efficacy and low costs. It should be noted that the glass-ceramic matrix composites are generally made by a nucleation treatment and growth of glass-ceramic crystals previously obtained.

The reuse of CRT waste glass to obtain glass-ceramics has a great advantage: manufactured materials may be useful in higher absorption of wastes, with uses in composite materials.

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