VITROCERAMICI DIN DEŞEURI DE STICLĂ CRT CU TiO_2 CA AGENT DE NUCLEAȚIE

GLASSCERAMICS FROM CRT GLASS WASTE WITH TiO_2 AS NUCLEATING AGENT

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The recovery of glass waste resulted from CRT (cathode ray tubes) in glass ceramic materials can have possible uses in composite materials. The recipes were calculated using as much waste as possible, using 2% and 5% TiO_2 as nucleating agent. The ratio 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, thermal expansion, hydrolytic stability. In order to characterize in terms of composition and microstructure, the analyses were carried out using 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 ceramic.

Recuperarea deşeurilor de sticlă rezultate din tuburi catodice – CRT se poate realiza şi în materiale vitroceramice cu posibile utilizări în materiale compozite. Rețetele au fost calculate utilizând cât mai mult posibil deşeuri, folosind TiO_2 ca agent de nucleație în proporții de 2 şi 5%. Raportul sticlă CRT pentru părțile componente gât:con:panou frontal folosit a fost 5:30:65%. S-au determinat următoarele proprietăți fizico-mecanice: densitatea, dilatarea termică, stabilitatea hidrolitică. Pentru caracterizarea din punct de vedere compozițional şi microstructural au fost efectuate analize de difracție cu raze X şi determinări de microscopie electronică de baleiaj, evidențiind influența agentului de nucleație şi a temperaturii de tratament termic asupra proprietăților vitroceramicii.

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

1. Introduction

We can define the glass-ceramic materials as polycrystalline solids containing a vitreous phase. They can be produced via the controlled crystallization of glass [1-3]. The mechanism of the process is related to the type of catalyst and the chemical composition of the parent glass. Different types of nucleating agents greatly promote the crystallization process of glass and enhance the formation of a fine-grained microstructure. Generally, the controlled crystallization of glass is induced by nucleating additives (e.g. noble metals, fluorides, TiO_2, ZrO_2, P_2O_5, Fe_2O_3 or Cr_2O_3). Titanium oxide (TiO_2) is an efficient nucleating agent commonly used in the fabrication of glass-ceramic. This oxide is believed to be highly soluble in glass melts; however, its high ionic field strength encourages the liquid–liquid phase separation phenomenon to occur during the subsequent heat treatment of the solid glass. Upon cooling, it can precipitate in the form of small titanium oxide crystals or titanium compound species that act as nuclei, facilitating the development of the main crystalline phases [4, 5]. Zirconia (ZrO_2) is another conventional nucleating agent widely used in several silicate systems. In many glass-ceramic systems, more than one kind of nucleating agent is used to obtain the optimum microstructure and properties.

On the other hand, cathode ray tubes (CRT) are specifically designed to be high resistant to crystallization [6]. There are several issues around CRTs which create obstacles to the increased recovery of the glass. The lead content can mean that the glass is classified as a hazardous material and the glass stream is a mixture of panel and funnel glass, making it difficult to reuse in new CRTs [7-9].

Two ways to reuse the CRT glass are often used in recent literature: re-melt of glass cullet followed by a controlled crystallization with nucleating agent [4, 7] or sintering of the glass powder, also with the aid of a nucleating agent [10, 11].

To exploit the potential of these wastes, this paper presents preliminary results on the ability to turn the CRT glass into glass-ceramic with possible applications in composite materials using TiO_2 as

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nucleating agent and a mixture of neck, panel and funnel glass.

2.1. Experimental

We kept the quantity of nucleating agent added as small as possible because the main objective is to reuse the CRT waste.

The objectives of the experimental part were:

- to develop glass-ceramic compositions using as much as possible CRT glass waste;
- to obtain samples through pressing - sintering technique;
- the complex characterization of the samples.

2.1 Raw materials

We established the following recipes in order to obtain glass-ceramics:

- the etalon, glass powder;
- the samples of glass powder with 2% and 5% TiO_2 as nucleating agent.

The mixture of neck, panel and funnel glass was the ratio of 5:30:65%, identical to the one in CRT.

2.2 Experimental

Based on previous works and on the chemical compositions of the glasses present in the CRT [3], we made specimens with the dimensions of 30x10x7 mm [3, 12]. The milled CRT glass powder that passed through a 0.22 mm mesh sieve was homogenised with poly-vinyl-alcohol for 5 minutes. The specimens were shaped using cold pressing with a force of 50 MPa.

We obtained three specimens for each type of the samples: glass powder and glass powder with TiO_2, 2% and 5%, a total of 9 specimens. Then, the specimens were sintered at 700°C, 750°C and 800°C with a heating rate of 10°C / min and a plateau of 30 minutes.

We determined the hydrolytic stability and the thermal properties. The thermal expansion curves were draw 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.

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

Scanning electron microscope studies were conducted on "bulk" samples using a Hitachi S 2600 N type microscope.

3. Results and Discussion

3.1 Hydrolytic stability

The results obtained are shown in Figure 1.

As the thermal treatment temperature increases the stability in water also increases for all the samples. This denotes the existence of some compounds more stable as the temperature increases. We observed a good stability (minimum conductivity) for the samples with 5% nucleating agent, treated at 750 and 800°C, while the samples with 2% TiO_2 are less stable in water. This suggests that a higher amount of TiO_2 can stabilize the glass-ceramic network.

3.2. Thermal expansion

In Figure 2 are shown, as example, the expansion curves for the etalon and samples with TiO_2.

We determined the coefficients of thermal expansion, α_{25}^{500} , shown in Table 1.

The samples with higher amount of TiO_2 show a dilatometer softening temperature shifted to higher values and a less visible glass transition. Also, the coefficients of thermal expansion decrease, suggesting the presence of crystalline phase formed after the thermal treatment.

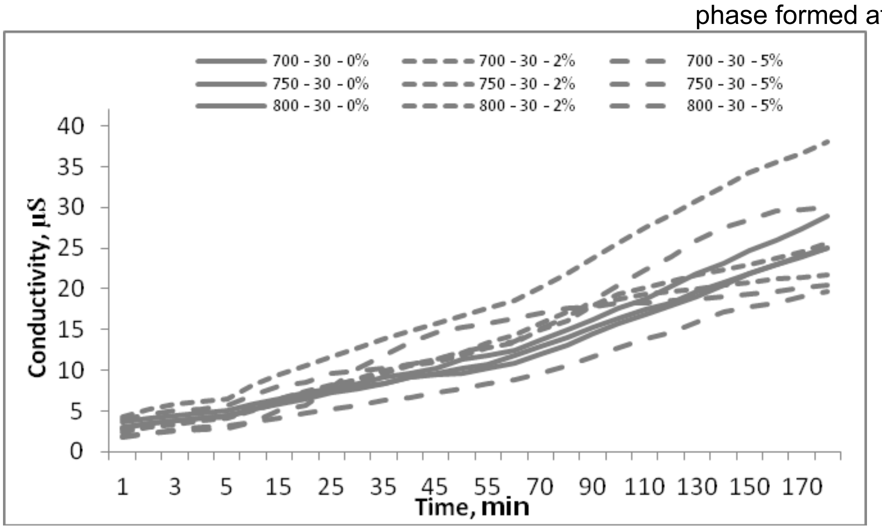
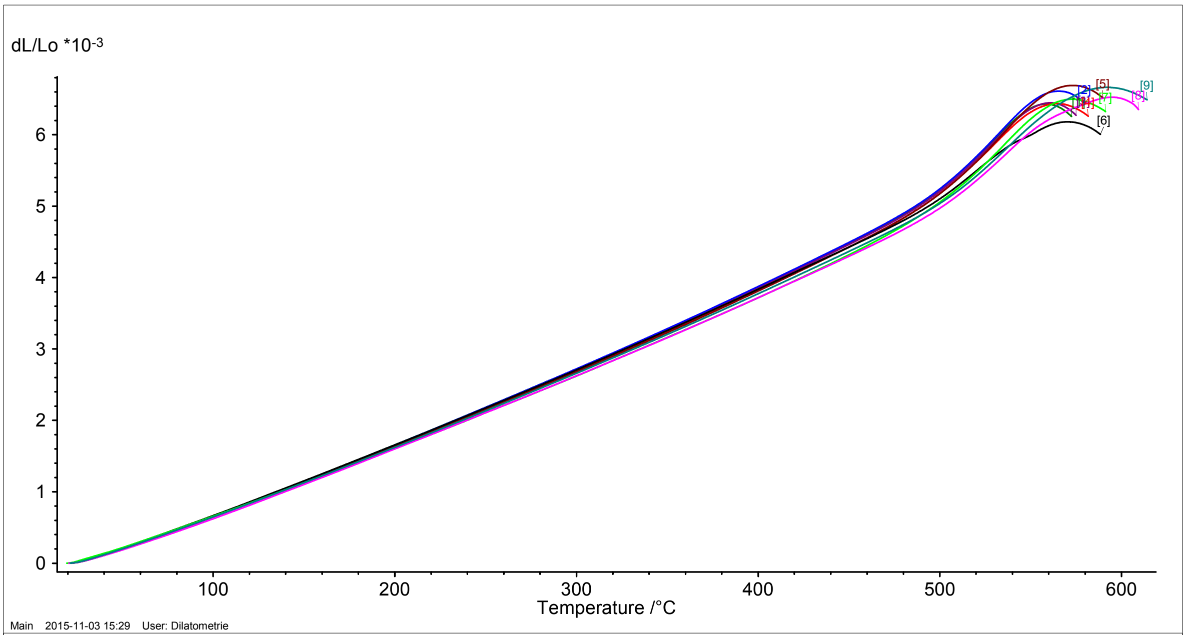


Fig. 1 - *Variation of hydrolytic stability versus the TiO_2 percentage and the thermal treatment temperature. /* Variaţia stabilităţii hidrolitice funcţie de procentul de TiO_2 utilizat şi de temperatura de tratament termic.



[#] Instrument	File	Date	Identity	Sample	Length/mm	Segment	Range	Atmosphere	Corr.
[1] DIL 402 PC	Ioana_Et_700_30.dl4	2014-01-20	Ioana_Et_700_30	Ioana_Et_700_30	29.000	1/1	20/3.0(K/min)/900	---/---	020
[2] DIL 402 PC	Ioana_Et_750_30.dl4	2014-01-22	Ioana_Et_750_30	Ioana_Et_750_30	29.440	1/1	20/3.0(K/min)/900	---/---	020
[3] DIL 402 PC	Ioana_Et_800_30.dl4	2014-01-23	Ioana_Et_800_30	Ioana_Et_800_30	30.040	1/1	20/3.0(K/min)/900	---/---	020
[4] DIL 402 PC	TiO2_2_700_30.dl4	2014-01-24	TiO2_2_700_30	TiO2_2_700_30	29.250	1/1	20/3.0(K/min)/900	---/---	020
[5] DIL 402 PC	TiO2_2_750_30.dl4	2014-02-06	TiO2_2_750_30	TiO2_2_750_30	29.170	1/1	20/3.0(K/min)/900	---/---	020
[6] DIL 402 PC	TiO2_2_800_30.dl4	2014-03-18	Ioana_rectangular	Ioana_rectangular	29.650	1/1	20/3.0(K/min)/900	---/---	020
[7] DIL 402 PC	TiO2_5_700_30.dl4	2014-01-29	TiO2_5_700_30	TiO2_5_700_30	29.200	1/1	20/3.0(K/min)/900	---/---	020
[8] DIL 402 PC	TiO2_5_750_30.dl4	2014-02-07	TiO2_5_750_30	TiO2_5_750_30	29.200	1/1	20/3.0(K/min)/900	---/---	020
[9] DIL 402 PC	TiO2_5_800_30.dl4	2014-02-13	TiO2_5_800_30	TiO2_5_800_30	29.210	1/1	20/3.0(K/min)/900	---/---	020

Fig. 2 - *Thermal expansion curves versus the percentage of TiO_2 used* / Curbe de dilatare termică funcție de procentul de TiO_2 utilizat.

Table 1

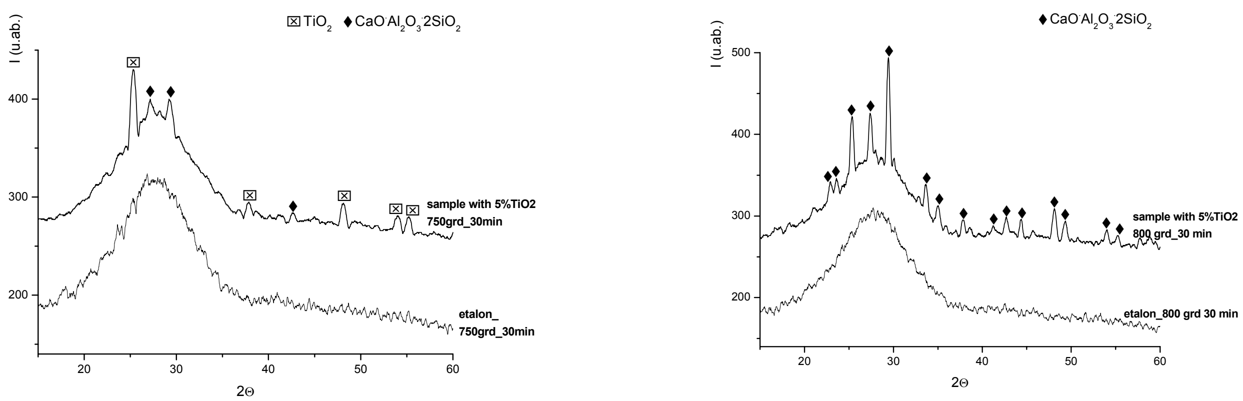
Coefficients of thermal expansion α_{25}^{500} of the samples versus the percentage of TiO_2 and the thermal treatment temperature used

Coeficienți de dilatare termică α_{25}^{500} ai probelor funcție de procentul de TiO_2 utilizat şi de temperatura de tratament termic utilizată

TiO_2 content / Thermal treatment temperature	0%	2%	5%
700°C	$109.96\cdot10^{-7}$ K^{-1}	$108.66\cdot10^{-7}$ K^{-1}	$105.89\cdot10^{-7}$ K^{-1}
750°C	$110.06\cdot10^{-7}$ K^{-1}	$108.57\cdot10^{-7}$ K^{-1}	$104.39\cdot10^{-7}$ K^{-1}
800°C	$109.41\cdot10^{-7}$ K^{-1}	$107.09\cdot10^{-7}$ K^{-1}	$105.78\cdot10^{-7}$ K^{-1}

3.3. SEM and XRD

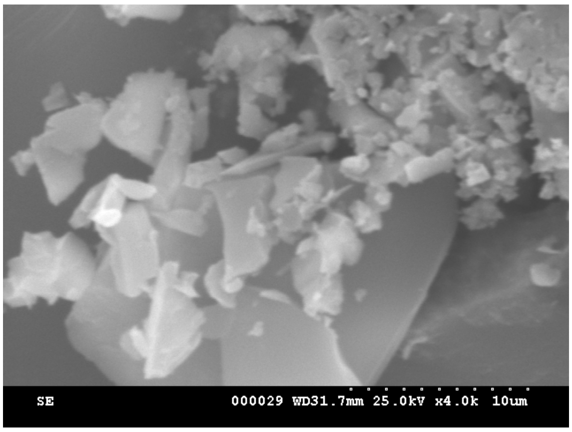
XRD spectra are presented in Figure 3a and 3b.



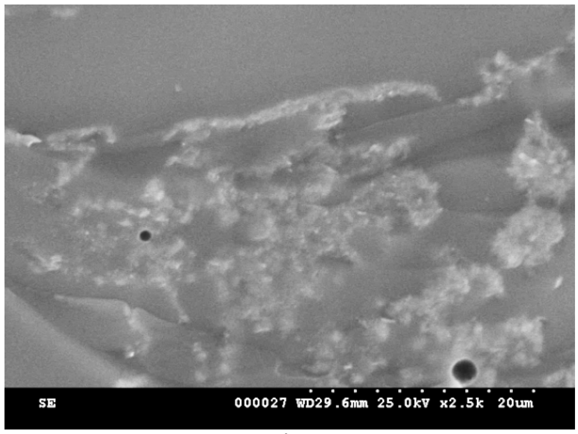
a

b

Fig. 3. X-ray spectra for the etalon sample and with nucleating agent/ *Spectre DRX pentru proba etalon şi cea cu agent de nucleație:* a) 750°C, b) 800°C.



a



b

Fig. 4 – SEM microscopy for the samples with nucleating agent / *Microscopii SEM pentru probe cu agent de nucleaţie* – a) 750°C-5%, b) 800°C-5%

X-ray diffraction revealed, in case of the etalon, the specific spectra for vitreous structures, with a single large centred peak around 2θ = 28°. The sample with 5% TiO_2 heat treated at 750°C have, along with the specific peaks of the nucleating agent, peaks which were attributed to a small amount of anorthite. In case of the sample with 5% TiO_2 subjected to 800°C for 30 min the peaks are specific to the anorthite, the compound with the highest rate of crystallization from the CRT at this temperature.

Scanning electron microscopy shows the formation of crystalline structures, the crystalline phase being present in greater amount and the crystals concentration more clearly defined especially for samples treated at 800°C. The anorthite crystals are quite small and they develop around the TiO_2 nuclei, as we can see in Figure 4b.

4. Conclusions

The article presents the experimental results on the development of glass-ceramic compositions using CRT waste glass and TiO_2 as a nucleating agent in proportions of 2% and 5%.

The analysis of the results shows that:

- There was a good stability and a decrease of the coefficients of thermal expansion for the samples with 5% nucleating agent, treated at 750 and 800°C, which suggest the presence of crystalline phase formed after the thermal treatment.

- For the samples with 5% nucleating agent, x-ray diffraction revealed the presence of anorthite along with a large amount of vitreous phase. The small anorthite crystals grown around the TiO_2 nuclei have the highest rate of crystallization at this temperature, fact that is revealed by the SEM analysis, too.

The use of CRT waste glass to obtain glass-ceramics could offer a great advantage: the obtained manufactured materials would incorporate wastes with applications in composite materials as matrix.

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