STUDII ASUPRA CRISTALIZĂRII UNOR COMPOZIȚII DE STICLĂ CU CONȚINUT SCĂZUT DE OXID DE BARIU

STUDIES REGARDING THE CRYSTALLIZATION OF SOME GLASS COMPOSITIONS WITH LOW BARIUM OXIDE CONTENT

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In recent years, electronic equipments containing cathode ray tubes (CRTs) have ceased to be produced in developed countries and were replaced by modern equipment, more economical and lighter. The glass waste resulting from the cathode ray tube is a valuable raw material which can be used to obtain other materials such as glass-ceramics, with different applications.

Present paper aims to study the crystallization of CRT glass with low barium oxide content with 15% by weight added nucleating agent (TiO_2, ZrO_2 and ZnO). For the obtained samples X-ray diffraction analysis were carried to determine the crystalline phases and scanning electron microscopy to examine the microstructure and the resulting phases from heat treatment. Thus, the influence of nucleating agent and heat-treatment temperature on the properties of the glass ceramic were revealed.

The material has applicability in constructions, e.g. decorative or insulation tiles. Its advantages result from the high percentage of waste reused, with positive impact on the environment, and from the low temperature needed for manufacturing [1-3].

În ultimii ani echipamentele electronice care au în componența lor tuburi cinescoape (CRT) au încetat să mai fie produse în țările dezvoltate și au fost înlocuite de echipamente moderne, mai economice și mai ușoare. Deșeurile de sticlă rezultate din tubul cinescop reprezintă o materie primă valoroasă care poate fi utilizată pentru obținerea altor materiale cum ar fi vitroceramică, cu diverse aplicații.

Această lucrare are ca scop studiul cristalizării unor sticle CRT cu conținut scăzut de oxid de bariu cu adaos de nucleatori (TiO_2, ZrO_2 și ZnO) în proporție de 15%. Pe probele obținute au fost efectuate analize de difracție de raze X pentru determinarea fazelor cristaline și microscopie electronică de baleiaj pentru a examina microstructura și fazele rezultate prin tratament termic. Astfel, s-a evidențiat influența agentului de nucleație și a temperaturii de tratament termic asupra proprietăților vitroceramicii.

Materialul poate fi aplicat în domeniul construcțiilor, de exemplu ca plăci decorative sau izolante. Avantajele sale rezultă din reutilizarea unui procent mare de deșeu, cu impact pozitiv asupra mediului, și din temperatura redusă la care este obținut [1-3].

Keywords: *cathode ray tubes, glass-ceramics, low barium oxide content*

1. Introduction

The growth rate of the electronic and electrical equipment wastes (WEEE) has become alarming. The high amount of WEEE and the great variety of the materials they contain (a lot of them has the potential to be hazardous for environment and population) has drawn the attention in the management and reuse of wastes. WEEE has been proved to be a great source of valuable metals like copper, aluminium and gold; when these materials are not reused, other ones must be extracted with negative effects for the environment due to the mining and processing [1].

Cathode ray tubes (CRTs) contained in the older generation TV-sets and computer monitors are made from 85% glass, the rest of 15% being represented by metals and plastics [4, 6]. The glass components are divided in 4 types: the front panel (made from glass with barium and/or tin oxides), the funnel or cone (glass with lead oxide), the bonding glass (that contains about 85% lead oxide) and the neck (glass rich in lead oxide) [6, 7]

Based on the latest law in the environment domain, the Romanian authorities bring new methods to track down the companies in the electronic and electrical equipment market. The operators must ensure a collection rate of 40% for 2016; 45% for 2017-2020 and 65% for 2021 [8].

In this context, the CRT wastes that cannot be recycled to produce new cathode ray tubes represent a valuable raw material that can be used to produce new materials such as glass-ceramics, with different applications.

2.Samples preparation

To produce a glass-ceramic material, CRT waste resulted from crushing the whole CRT panel was used as raw materials. These wastes have

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almost free barium oxide (BaO) content [9]. The glass powder was obtained by grinding glass shards coming from the front panel (50% wt) and funnel (50% wt). In addition, the following nucleation agents were used: TiO_2, ZrO_2 și ZnO; as 15% in the final mixture, this being the highest concentration tested as revealed in a literature study [10]. The raw materials were dosed and homogenized by mixing in a mortar for 10-15 minutes. Polyvinyl alcohol drops were added in the mixture to maintain the integrity of the samples after cold pressing. Based on previous experience [11], the mixture was introduced in the die and pressed uniaxially at 75 MPa. 15 samples were made and then heat treated at 700 and 900°C for 4 hours and at 800 °C for 6, 8 and 10 hours in order to study the effect of the nucleating agents and the crystallization time on the glass-ceramic structure.

3. Results and discussions

3.1. X-ray diffraction

The phases formed after the heat treatment were identified by X-ray diffraction, in the 2θ=10-70 ° domain, using CuKα radiation, with SCHIMADZU XRD 6000 diffractometer.

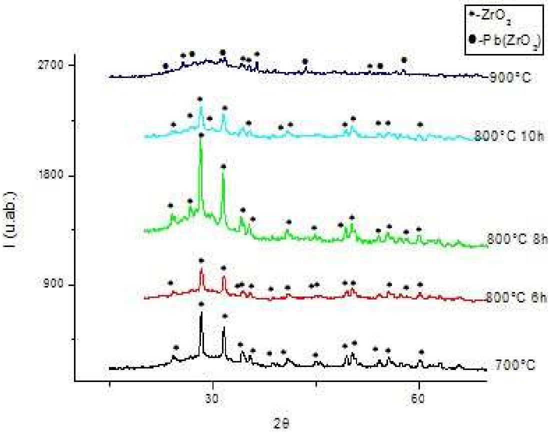

Fig. 1 - X-ray diffractions patterns for samples containing ZrO_2 for various heat treatments / *Difracțiile de raze X pentru probele care conțin ZrO_2 la diverse temperaturi.*

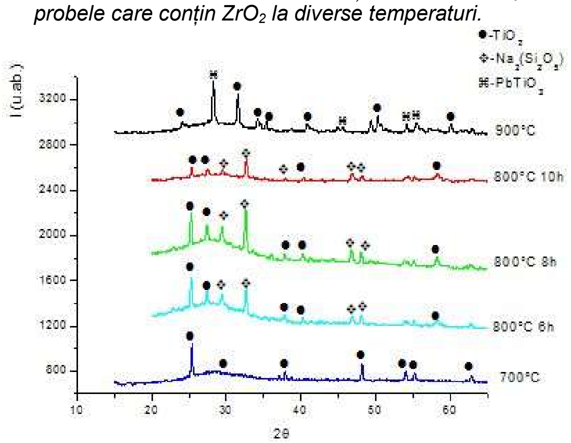

Fig. 2 - X-ray diffractions patterns for samples containing TiO_2 for various heat treatments */ Difracțiile de raze X pentru probele care conțin TiO_2 la diverse temperaturi.*

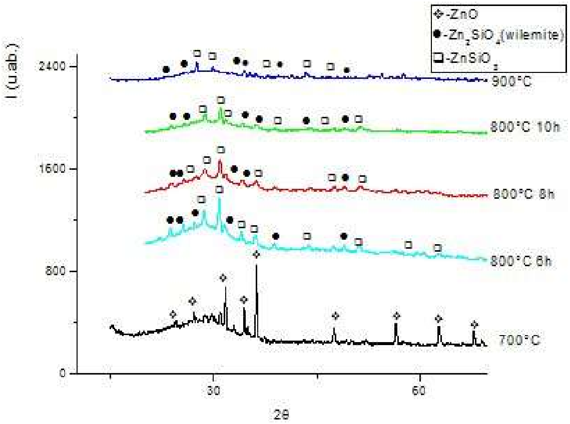

Fig. 3 - X-ray diffraction patterns for samples containing ZnO for various heat treatments / *Difracțiile de raze X pentru probele care conțin ZnO la diverse temperaturi.*

From the X-ray diffraction analysis, it can be observed that the 700°C treatment had no effect, thus only the nucleator's crystalline phase could be identified.

The samples with ZrO_2 treated at 800°C did not show the growth of other crystalline phases, regardless the time allowed. This may be caused by the insufficient temperature to obtain crystalline compounds in the CRT glass mixed with this nucleator. At 900°C the sample containing ZrO_2 formed a solid solution of lead zirconate and ZrO_2.

The samples containing TiO_2 crystallized at 800°C forming $Na_2Si_2O_5$. After the heat treatment at 900°C a solid solution of lead titanate, $PbTiO_3$, and TiO_2 resulted.

The samples with ZnO formed at 800 and 900°C two compounds: willemite Zn_2SiO_4 and $ZnSiO_3$, respectively.

3.2. Scanning electron microscopy

The analyses were made on bulk samples with HITACHI S 2600 N and Versa 3D Dual Beam microscopes. The samples were covered with a thin layer of gold, the metallisation time was 60 seconds and the current was 60 mA. The following images present the SEM pictures of the samples that contains the nucleators (TiO_2, ZrO_2 and ZnO) heat treated at different temperatures (700, 800 and 900°C).

At 700°C it can be observed in all the cases the presence of two phases (one crystalline and one vitreous) and porosity (due to the too low sintering temperature). The crystalline phase belongs to the nucleators and the vitreous phase is formed by the sintered CRT glass. This shows that the temperature is too low for the appearance of the nuclei and their crystallization, respectively.

The SEM images of the samples treated at 800°C show a vitreous phase that covers the crystalline phase like a matrix. Likewise, not all the samples crystallized equally. The sample with TiO_2 crystallized the most, followed by the one with ZrO_2,

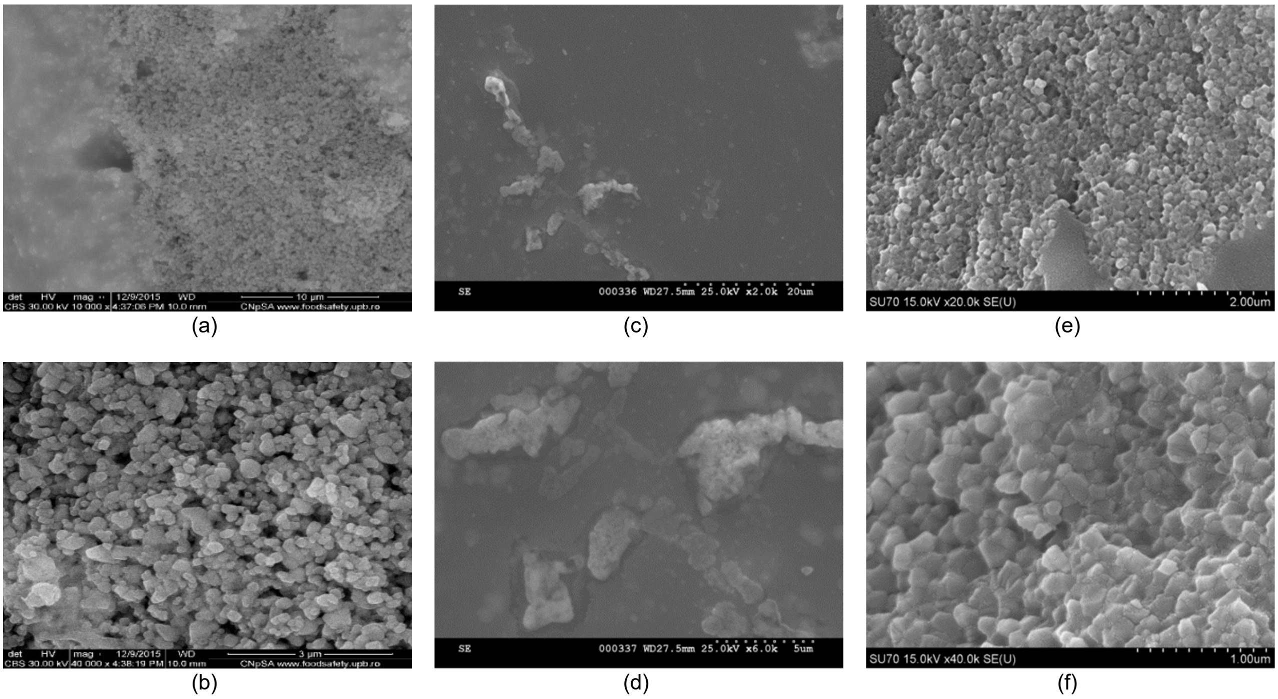

Fig. 4 – SEM images of samples containing TiO_2 treated at various temperatures: (a) and (b) at 700°C; (c) and (d) at 800°C; (e) and (f) at 900°C / *Imagini SEM ale probelor care conțin TiO_2 tratate la diverse temperaturi : (a) și (b) la 700°C; (c) și (d) la 800°C; (e) și (f) la 900°C.*

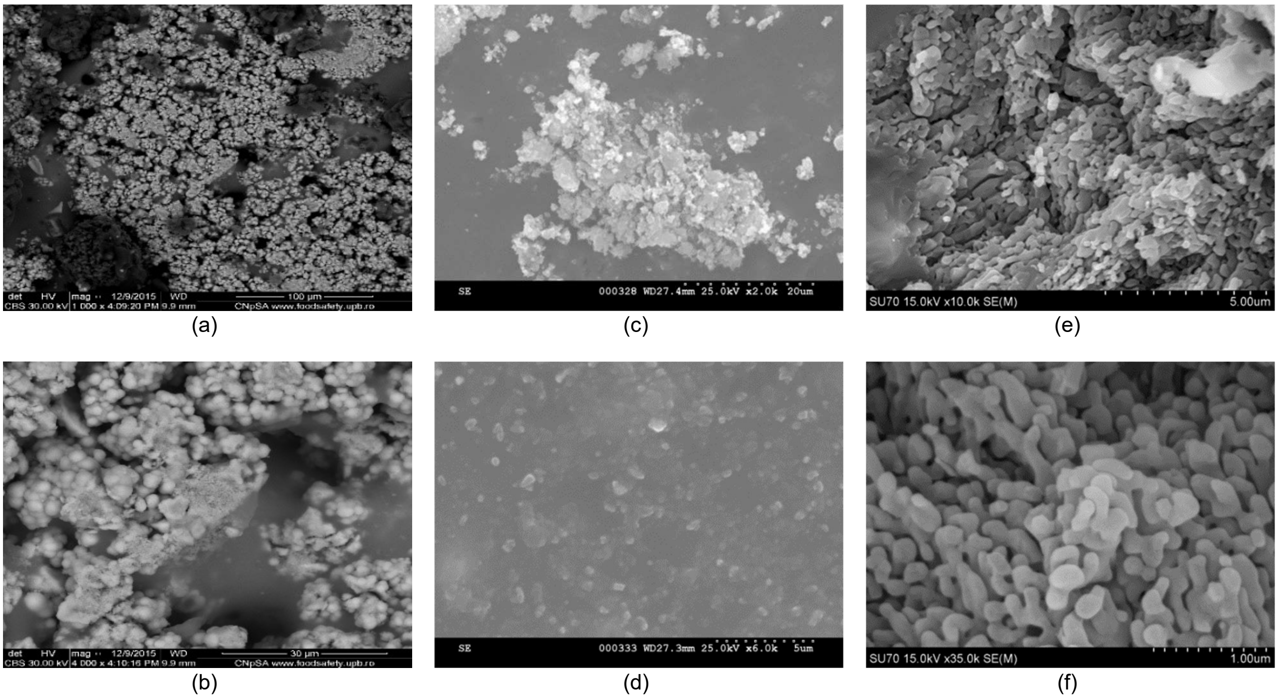

Fig. 5 - SEM images of samples containing ZrO_2 treated at various temperatures: (a) and (b) at 700°C; (c) and (d) at 800°C; (e) and (f) at 900°C / *Imagini SEM ale probelor care conțin ZrO_2 tratate la diverse temperaturi : (a) și (b) la 700°C; (c) și (d) la 800°C; (e) și (f) la 900°C.*

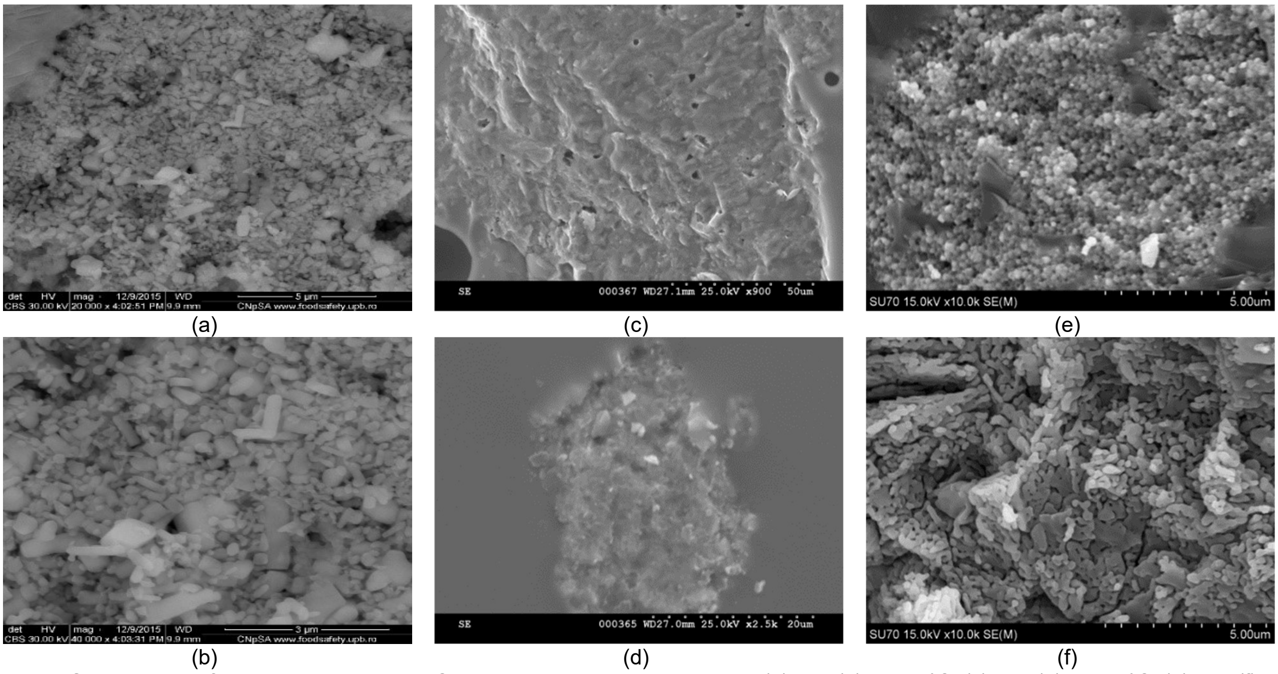

Fig.6 - SEM images of samples containing ZnO treated at various temperatures: (a) and (b) at 700°C; (c) and (d) at 800°C; (e) and (f) at 900°C / *Imagini SEM ale probelor care conțin ZnO tratate la diverse temperaturi : (a) și (b) la 700°C; (c) și (d) la 800°C; (e) și (f) la 900°C.*

while the sample with ZnO presents small crystals covered by the vitreous phase.

All the samples subjected to heat treatment at 900°C present two phases, as well, but the crystalline phase is more pronounced that the vitreous one and also much clearly visible. The crystals are numerous and have a similar characteristic morphology. For this temperature, ZnO seems to give the best results - the sample that includes 15% by mass of ZnO developed a structure with agglomerates made from small crystals, distinctive for glass-ceramics.

4. Conclusions

Present paper presents the results of the experiments conducted in order to obtain the optimum conditions of temperature and time for the single step heat treatment to obtain glass-ceramics, using as raw materials CRT wastes and different nucleation agents. The goal was to obtain a material at the lowest possible temperature in order to reduce its cost.

After the tests were done and interpreted, we can state that the 700°C temperature is not appropriate for crystallization. At 800°C ZrO_2 did not form any other crystalline phases, due to the low temperature for this type of nucleator in conjunction with the complex oxide system of the CRT glass. At 900°C the samples that contains TiO_2 and ZrO_2 formed solid solutions with PbO. ZnO had the best results, this nucleator being one of the best in the oxide system the CRT glass is part of. Further, our study proposes that the obtained material to be used as a building material, as decorative or insulating tiles. The advantages of this material are given by the high percent of contained CRT waste and, subsequently, the smaller cost to obtain it, in comparison with the products made from natural raw materials.

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