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Glass-ceramic, using TV screen and galvanic wastes as raw materials

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Abstract*— *The glass is used for the production of electronic components mainly as microchips, diodes, capacitors and screens of televisions as Plasma Display Panel (PDP). At present, PDPs have a constant production increase around 30% by year. This increase in the PDP market generates as well an increase with regard to industrial waste of the components of vitreous composition, and this waste tends to be directed to confinement because the glass contains lead. An alternative of advantage of these waste, is to introduce it as raw material in a glass-ceramic process, that tends to be means in which the polluting elements, under suitable treatment is possible to include it in the ceramic structure. With this scene, this work offers the first results of the incorporation of this kind of glass waste as main source of SiO_2 in the elaboration of glass-ceramic materials of SiO_2-Al_2O_3-X (X=ZnO, ZnO-CaO, CaO and MgO) systems.

Key words: **Glass-ceramics, Plasma Display glass waste, recycle glass**

I. INTRODUCTION

A Plasma Display Panel (PDP), which makes up a TV screen, is an electronic device that functions through the phenomenon of liberation of UV rays of noble gases when voltage is applied. When they interact with phosphors, some visible rays are produced. Cells are contained between two glass plates which have metal oxide layers vacuum sealed, that contain a mixture of noble gases (xenon, neon, argon, and helium) and passes through a pair of horizontal electrodes and one vertical electrode. These are arranged in a hollow configuration with many small dividing barriers, with a space between them for containing the discharge gas and the structure is sealed by pressure. After charging the PDP with gas into the gap between upper and lower plates, ultraviolet rays are generated through an electric discharge and are induced to the phosphor layer to produce visible light [1]

Plasma Display Panel (PDP) market is growing at an incredible rate; it is considered that PDP television loads will increase in 30% per year, generating 25 million units by the end of this year. Research in the development PDP´s predicts that market will increase a 11.4% per year from 2006 to 2010, because of demand growth for larger size televisions (larger than 40 inches), and the emergence of new media markets, increasing by 16 million dollars in volume for 2010 [1]. Together with this production increase, hazardous and non-hazardous wastes are generated due to the strict quality system made and glass is of particular concern since its vitreous matrix has barium and/or lead impurities, elements which have the function of absorbing high energy radiation, produced in the process of image creation. PDP residual glass is provided for direct confinement [2], making a thermal stabilization treatment. Material is not recycled because of its lack of technology, which is necessary for its recovery.

There is a background of the Cathode Ray Tube (CRT) glass recovery processes [3], but these methods cannot be used directly in PDP glass recovery for removing the coating layers because they do not contain the same chemical elements[4-5] besides, the process of removing chemical substances to PDP glass is different to the coating process of CTR glass, so it is a great global concern in which alternatives of using this type of wastes are taken, taking advantage of the chemical elements presence that confer to elaborated materials particular properties[6] porcelain stoneware [7], glass-ceramics[8-11]. Parallel to this, another waste material is generated in the metal coating industrial process, conformed by aluminum salts as sulfates and hydroxides, which are similarly confined and in previous studies, it has been possible to use them as an alternative source of Al_2O_3 substitute in the field of glass-ceramic materials [12] and foam glass [13-15].

This article is directed to feasibility of TV plasma display panel residual pulverized glass as a source of SiO_2 and anodizing plant waste, as a substitute of Al_2O_3 in glass-ceramic systems of SiO_2-Al_2O_3-X base system, where X= ZnO, ZnO-CaO, CaO and MgO. Also it is directed to assess the effect on nucleation crystallization process of different chemical elements that are included in vitreous pieces that make up a TV screen.

II. EXPERIMENTAL PROCEDURE

The chemical composition of mayor and trace elements of pulverized PDP screen glass residue (frontal and back) were characterized via X-Ray Fluorescence (XRF) using a Siemens SRS 3000 Spectrometer (Rh tube and Be 125 μm window). Later on, four compositions of traditional glass-ceramic materials are selected; SiO_2-Al_2O_3-X (X=ZnO, ZnO-CaO, CaO and MgO), industrial waste is used as a substitute to traditional raw material; PDP screen glass waste and residual aluminum salts as SiO2 and Al2O3 [Al(OH)3 as Gibbsite and Bayerite] sources, respectively; and TiO2 as nucleating agent. Table 1 shows the weight percent of each component. The selected raw materials are taken to grinding, mixing and homogenizing, and after that, to two thermal treatments in high Temperature Furnace 46100 Thermolyne at 5 °C/minute of heating speed. The first thermal treatment corresponds to crystal fusion-nucleation-growth; 900 °C/60 min (gas elimination) + 1450°C/2 h (fusion) + 900 °C/1 h (nucleation)

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+ 1000 °C/4 h (crystal growth).The second was made at 900 °C/10 h using a heating rate of 5°C/min.

Table 1. Chemical Composition (% w/w)

GC	Waste		Oxides			
	Glass TV	Aluminium Salts	ZnO	TiO_2	CaO	MgO
GC-1	50.9	23.2	18.5	7.4	--	--
GC-2	53.4	17.7	7.8	11.1	10	--
GC-3	53.4	17.7	--	11.1	17.8	--
GC-4	42.8	30.2	--	13	--	14

The crystalline phases present in glass-ceramic materials obtained was determined by X-Ray diffraction. The XRD patterns were obtained with a D8 Bruker diffractometer coupled to a Cu anode X-ray tube in Bragg−Brentano configuration. The $K\alpha_1$ wavelength was selected with a diffracted beam Ge monochromator, and the compounds were identified conventionally using the Joint Compounds Powder Diffraction Standards (JCPDS) database. The microstructural analysis was performed using Scanning Electron Microscope with a Leica Stereos can 440.

III. RESULTS AND DISCUSSION

A. Chemical composition of precursors

Table 2 and 3 shows the results of XRF, as it can be seen the chemical composition of frontal glass presents as predominant compounds; SiO_2, Al_2O_3, CaO, BaO, Na_2O, and K_2O; while on the back glass, SiO_2, Al_2O_3, CaO, BaO, SrO, Na_2O, and K_2O are the main compounds. In view of the results of the percentage composition of SiO_2 on both glass residues, we can consider using them in the same way. The main difference is in the concentration of trace elements (see Table 3) where the concentration of trace elements as Nd, V, Cr and Ni are higher in the frontal side while the concentration of trace elements like Cr and Co are higher in the back glass. Taking it into account, the samples were prepared using a homogenous mixture of both sides in the selected formulations.

Table 2. Chemical composition (mayor elements) in % w/w of PDP screen glass waste

Oxides	Frontal	Back	Oxides	Frontal	Back
SiO_2	54.034	52.294	P_2O_5	0.263	0.015
TiO_2	0.177	0.066	SO_3	0.06	0.06
Al_2O_3	6.503	6.125	SrO	9.6	11.5
Fe_2O_3	0.185	6.125	BaO	7.33	8.35
MnO	0.01	0.013	ZrO	2.23	2.57
MgO	1.881	1.839	ZnO	0.893	0.427
CaO	4.404	4.356	Bi_2O_3	ND	1.55
Na_2O	4.58	4.229	PbO	1.14	ND
K_2O	6.085	6.021	PXC	0.4	0.4

Table 3. Chemical composition (trace elements) in ppm of PDP screen glass waste

Element	Frontal	Back
Nd	19	6
V	56	ND
Cr	96	181
Co	62	174
Ni	29	ND

B. Glass-Ceramic materials obtained

In the XRD patterns of samples after crystallization at 900 °C for 10 hours, it is possible to identify a number of crystalline phases which vary in proportion and composition to each material. Predominantly, elements such as zinc, calcium, aluminum, silicon, barium and iron crystallize as Gahnite ($ZnAl_2O_4$), Barium Aluminum Silicon Oxide ($\alpha Ba_{0.808}Al_{1.71}Si_{2.29}O_8$), Perovskite ($CaTiO_3$) and Dropsied ($CaMgSi_2O_6$), and the presence of vitreous phase by the bottom-broadband.

Figure 1 show the XRD patterns for GC-1 and GC-2 samples, respectively. As it can be seen, for the sample with ZnO/CaO; GC-1 (SiO_2-Al_2O_3-ZnO), the predominant crystalline phases are Perovskite ($CaTiO_3$), Gahnite ($ZnAl_2O_4$) and Barium Aluminum Silicon Oxide ($\alpha Ba_{0.808}Al_{1.71}Si_{2.29}O_8$) and Diopside ($CaMgSi_2O_6$) and Calcium Zinc Aluminum Silicate ($Ca_{0.97}Zn_{0.032}Al_{0.63}Zn_{0.37}Si_{0.69}Al_{0.312}O_7$) are present in low proportion. However, for the GC-2 (SiO_2-Al_2O_3-ZnO-CaO) samples, three similar crystallines phases present in the GC-1 sample are identified; Barium Aluminum Silicon Oxide, Perovskite and Calcium Zinc Aluminum Silicate and appears and additional phase identified as Calcium Aluminum Silicon Titanium Oxides ($Ca_3TiSi_2Al_2Si_5Ti_{0.5}O_{14}$).

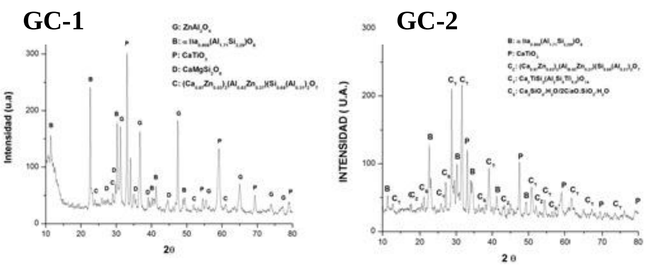

Fig 1. X-Ray diffraction patterns of glass-ceramic GC-1 and GC-2 crystallized at 900 °C/10 hours

Figure 2 shows the SEM images of the different glass-ceramic materials; GC-1 sample (after the amorphous SiO_2 is removed). The microstructure is composed by a Perovskite ($CaTiO_3$) dendritic network, forming a fully ordered crystalline mosaic, in the case of the sample with CaO rhombohedral crystals of gahnite ($ZnAl_2O_4$) were identified by EDS analysis. Generally, a dendrite shaped crystal is generated when the activation energy for the crystal growth is low and the latent heat is high [16]. These materials present a more defined and homogeneous crystalline structure using Calcium and/or Zinc, the thermal treatment favoring the crystallization process in each system and the variety of

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crystallization forms interconnected by the vitreous phase formed mainly by SiO_2,

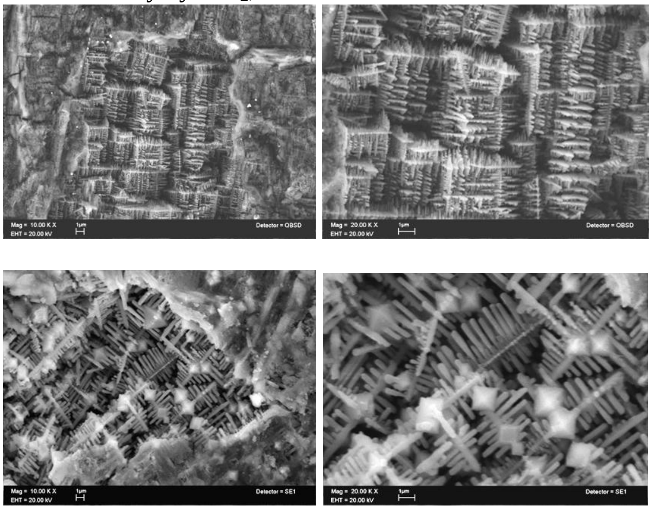


Fig 2. SEM micrographs of glass-ceramic GC-1 and GC-2 crystallized at 900 °C/10 hours

The materials with CaO/MgO; GC-3 (SiO_2-Al_2O_3-CaO) presents Gahnite, Barium Aluminum Silicon Oxide, Deerite ($Fe_6Fe_3O_3Si_6O_{17}(OH)_5$) and Senaite ($Pb_{0.83}Ti_{13.66}Fe_{6.34}MnO_{38}$). Finally, the GC-4 ($SiO_2$-$Al_2O_3$-CaO-MgO) presents Gahnite, Diopside, Lead Aluminum Silicate ($PbAl_2Si_2O_8$) and Pseudobrookite (Fe_2TiO_5). The Figure 3 shows the XRD patterns of samples GC-3 and GC-4. It should be considered the industrial waste that provide variety of elements that act as nucleating agents or fluxes within glassy phase and a heat treatment of 10 hours, allowing the defining predominant crystalline phases (Figure 3).

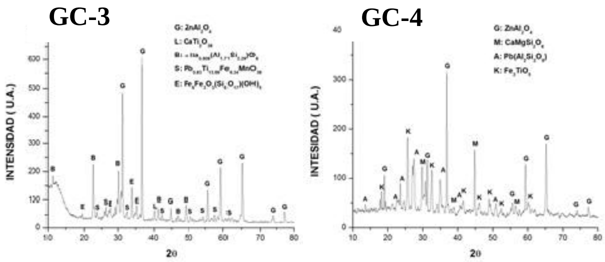
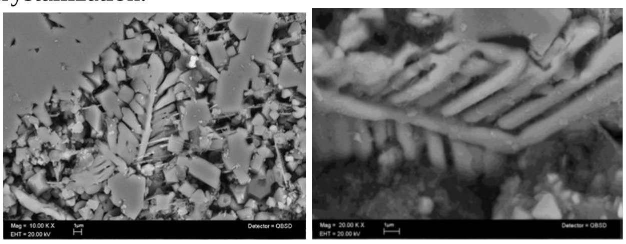


Fig 3. X-Ray diffraction patterns of glass-ceramic GC-3 and GC-4 crystallized at 900 °C/10 hours

Figure 4 shows the microstructure of two last kind of glass-ceramic that present mainly gahnite ($ZnAl_2O_4$) crystals, GC-3 shows a dendritic network and the formation of a fully ordered crystalline mosaic; and GC-4 displays a polyedric crystallization.



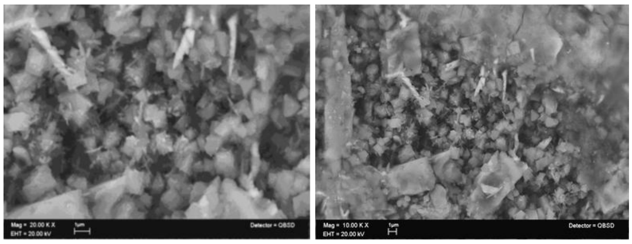


Fig 4. SEM micrographs of glass-ceramic GC-3 and GC-4 crystallized at 900 °C/10 hours

IV. CONCLUSIONS

According to the obtained results, it has been possible to attain a variety of glass-ceramic materials using PDP screen glass residues as a source of SiO_2, along with anodized plant residues as alternate source of Al_2O_3. Stable materials have been achieved after a 10 hrs treatment at 900°C with defined crystallization. The systems containing the combination ZnO-TiO_2 present better result due to the better definition and homogenization of crystalline phases. The use of this kind of residues is considered acceptable in the elaboration of glasses for ceramic coating which, after thermal treatment, promote the formation of crystalline phases that enhance the properties of ceramic materials used for construction, for example, floor tiles and/or bricks. By this process, residues acquire an industrial value, their confining cost is minimized, and the use of natural non-renewable raw materials (SiO_2 and Al_2O_3) decreases.

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