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Waste immobilization and environmental sustainability in glass-ceramics glazes development

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Abstract. The current work investigated the formulation of glazes using recycled CRT (Cathode Ray Tube) waste glass powder mixed with basalt, kaolin and other additives. New glaze compositions can be crystallized in order to improve the mechanical and chemical properties of fast-fired glazed tiles. These glazes are characterized by high resistance to abrasion.

1 Introduction

Glazes can be defined as a stable glassy coatings applied to ceramic earthenware and formerly obtained by cooling oxides or minerals applied and melted on the surfaces of ceramic objects. The large increase in demand for tiles with improved and advanced properties, such as high resistance to abrasion, higher hardness, lower closed porosity and improved chemical resistance is observed [1]. A glass-ceramic glaze must provide precursor frit which is technically and commercially compatible with the fabrication conditions normally used in industrial production, where glazes should be obtained by fast firing process. Densification is achieved by sintering in the presence of a viscous flow at temperatures slightly higher than the glass transition temperature (Tg), resulting in a compact layer nearly free of porosity. During fast firing process sufficient crystallization occurs. It resulted in the appearance of crystalline phase in glaze obtained [2]. Moreover the phase composition and structure development under the heat treatment are very important, and fulfill strict requirements in the linear expansion coefficient of the glaze. The greater the difference in the thermal expansion of the ceramic support and the glaze, the faster defects will appear [3]. Glaze suspensions are composed of different types of raw materials such as: plastics, non-plastics, and additives. Plastic materials include clays e.g. kaolin and bentonite, whereas the non-plastic materials consist of oxides, pigments, feldspars and frits. The additives are used to optimize the glazing process are dispersing and deflocculanting agents, binders and defoaming agents [4]. The potential of replacing natural components in ceramics glaze production with wastes is well documented in literature [5]. Replacing fluxes with cullet has been reported in Youssef and Tarvornpanich [6]. P Ketboonruang studied the potential use of Municipal solid waste (MSW), soda lime silica cullet and borax in a low firing temperature glazes production. This allowed them to avoid strong fluxing such as a very toxic lead oxide [7]. This underscore the importance of recycling cullet which will not only turn waste to wealth but will also reduce the stress and cost of seeking fluxes for ceramic glazes. Glass is found to be in different types and properties, moreover there are some types of glass cullet which is more of a nuisance to the environment [8]. Thus for the purpose of this research, exploring the composition and effect of Cathode Ray Tube (CRT) cullet on the glaze properties will significantly reduce the environmental impact of the ceramic glaze production process. CRTs are composed of three different parts: the viewing section known as the screen or panel, made of silica barium-strontium glass; the funnel glass and the neck glass, both of which contain lead oxide which absorbed X-ray radiation [9,10,11]. Various different compositions of glasses used for CRT create obstacles to the increased recovery the glass [12]. Moreover the specific glass composition forbid their recycling in the glass industry for the production of containers, domestic glassware and glass fibers, if crushed and mixed together it cannot be even recycled as cullet, for TV glass, on the other hand there are no manufactures of CRT glass in Europe anymore [13]. The use of CRT cullet as a replacement of float glass and feldspar in glazes production will be a very promising initiative as it will strongly contribute to sustainable development of ceramics industries. Our studies will enhance the use of wastes and also sustain the environmental benefits of the society.

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2 Experimental

The chemical compositions of CRT glass, float glass, basalt, borosilicate glass and feldspar are presented in table 1. Chemical composition of raw materials used in this experiment was analyzed by X-ray Fluorescence (XRF) with use of spectrometer WDXRF Axios mAX , PANalytical. The thermal linear expansion coefficient was measured on the blocks prepared from the powdery glazes and frits just as shown in table 2. The dilatation of the materials was measured using dilatometer Bahr Thermo Analyse DIL 801 L-Germany with a heating rate 5 K min^{-1}. The kind of crystalline phases which were formed via the thermal treatment of selected glazes at the temperature 1130°C, were examined by XRD method with use of Philips X'Pert X-ray diffractometer with CuKα radiation source. The morphologies of crystalline phases developed under glazes firing were examined by scanning electron microscope (SEM, Nova Nano SEM 200, FEI Company). SEM tests were performed with an attachment for chemical analysis of specimens in micro-areas with energy dispersive x-ray spectroscopy (EDAX). The observations were carried out in low vacuum conditions in the secondary electron mode. The samples were covered with a carbon layer. The abrasion resistance was determined according to the EN-ISO 1545-7 standard (PEI method). Abrasion test was based on a visual assessment of changes in the glazed surface, and wherein the rotational movement moving the shearing load of 100 to 12000 times in comparison with the surface of the tiles.

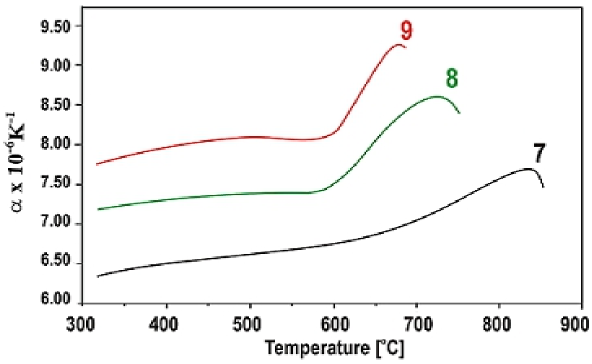

Figure 1. TMA expansion curves of studied glazes 7-9.

Raw materials for the production of glazes were shredded and mixed, then milled in a porcelain ball mill. The raw materials were wet milled for 40 minutes and the milling time was chosen experimentally to obtain expected sieve residue of less than 0.1%. The resulting mixture was applied to a ceramic tile by hand and heated at a rate of 25°C/min up to the firing temperature 1130°C. The entire firing cycle lasted 52 minutes. Tiles after firing were cooled with the furnace. Enamel surfaces were examined visually in terms of surface defects, surface smoothness and gloss. For the determination the basic physical and chemical properties of selected glazes the water absorption and abrasion resistance were tested. Determination of water absorption was performed according to the method described in the standard [PN-EN ISO 10545-3: 1999 Ceramic tiles. Determination of water absorption, porosity and density of the total p.5.1. Water saturation. Cooking method]. After cleaning and drying, the samples were weighed. Distilled water was used to impregnate the samples. Impregnation of samples was carried out by boiling the liquid within 2 hours. After the test, the samples were weighed again.

3 Results and discussion

CRT glass cullet was used in order to formulate in laboratory scale compositions of ceramic glazes as substitute to frit and feldspar in 1-9 glazes series designed and as a partial substitut of these two components in case of 10-14 glazes. As is reported in [14] CRT panel glass is a typical silicate glass containing barium and strontium and shows a tendency to not crystallize with a low melting nature, confirmed by low softening and transition temperatures (respectively Ts=559°C, Tg=490°C) and high thermal expansion coefficient (α=10.3·10^{-6}/°C). The high value of the thermal expansion coefficient of CRT glass cullet does not allow to use this kind of cullet itself for glazes production. The glaze compositions 1-6 prepared after firing showed crazing defect and spot resistance; however the presence of kaolin in glazes 3-6 decreases the intensity of the defect but did not avoid it. Therefore a re-modulation of the raw materials was necessary to obtain a better agreement between glaze and ceramic body dilatometric coefficient. For the laboratory tests different formulations using CRT glass, kaolin and basalt ranging in 20–40, 5 and 10–15 wt.%, respectively, were prepared. It permitted to obtain a glaze No 7 characterized by the by a lower thermal expansion coefficient (6.39·10^{-6}/°C^{-1}) (Fig.1).

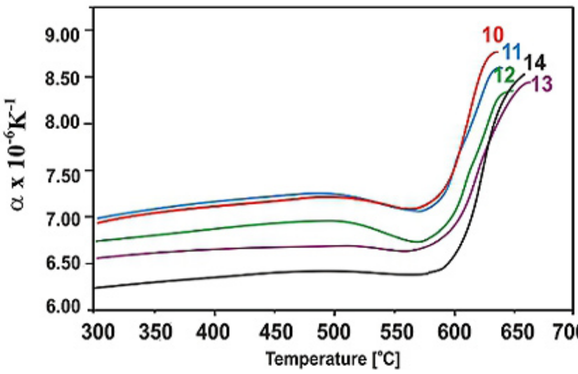

Figure 2. TMA expansion curves of studied glazes 10-14.

The glaze 7 prepared contains 50% of vitreous fraction, substituted only by CRT glass. The glaze appeared to be matt, thus to obtain glossy glaze the second group of glaze compositions was designed (10-14). The glaze 14 prepared contains 85 wt. % of vitreous fraction, substituted by 40 wt % of CRT glass, 30 wt. % of M4 borosilicate glass and 15 wt. % of float glass. The thermal expansion coefficient of glaze 14 was reduced by the addition of 15 wt. % of kaolin and 30 wt. % of M4 borosilicate glass (Fig.2).

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Table 1. Chemical composition of gazes components [wt.%].

Component	CRT glass cullet	Feldspar	Float glass cullet	Glass M_4	Basalt
SiO_2	61,82	68,30	71,70	79,00	44,46
CaO	-	0,90	13,00	-	10,53
MgO	0,013	-	-	-	10,88
Al_2O_3	2,0305	18,80	1,30	-	14,95
Fe_2O_3	0,065	0,10	-	-	11,16
Na_2O	7,95	5,80	12,80	-	4,38
K_2O	7,35	6,40	1,20	2,50	1,45
BaO	7,273	-	-		-
B_2O_3	-	-	-	18,50	-

Table 2. The compositions of glazes designed.

	The compositions of designed glazes [wt%]						
Symbol of glazes	**CRT glass cullet**	**Glass M_4**	**Feldspar**	**Float glass cullet**	**Kaolin**	**Basalt**	**Firing parameters and appearance**
1	100	-	-	-	-	-	1130°C, 1h Matt glazes
2	50	50	-	-	-	-	
3	80	-	-	-	20	-	
4	70	-	-	-	30	-	
5	60	-	-	-	40	-	
6	50	-	-	-	50	-	
7	50	-	-	-	40	10	
8	50	-	-	-	35	15	
9	50	-	-	-	30	20	
10	35	-	20	30	5	10	1130°C, 1h Glazes with gloss
11	35	-	25	35	5	-	
12	15	-	35	45	5	-	
13	10	5	35	45	5	-	
14	40	30	-	15	15	-	

Borosilicate glasses are known for having very low coefficients of thermal expansion (~$5\cdot10^{-6}$/°C at 20°C), making them resistant to thermal shock, more so than any other common glass) [15]. By reducing the value of α, B_2O_3 contributes to the density structure of the glazes, making them more chemically resistant (Fig. 2). The tendency to crystallization depend on, among other factors, the chemical composition of the glaze [16]. The glaze 7 crystallize easily because contains basalt. The crystallization is enhanced by the significant amount of the iron oxides and of the oxides of bivalent metals present. As the molar ratio SiO_2:RO is increased from 2-2.5 (glazes 7-9) in the presents of the alkalis the crystallization capability of the glaze decreases. The kind of the crystallizing phases was confirmed by the XRD technique. The XRD pattern of the glaze 7

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fired at 1130°C revealed the presence of a three crystalline phase: $KAlSi_3O_8$ - 67% -Sanidine (JCPDS No.99-101-1680),Al_2SiO_8 - 22%-Sillimanite (JCPDS No.99-100-0721) and $BaAl_2Si_2O_8$-11%-Paracelsian (JCPDS No.99-100-0994). The intensity of lines corresponding to $KAlSi_3O_8$ and Al_2SiO_8 phases are narrow indicating the existence of well-developed crystals (Fig.3).

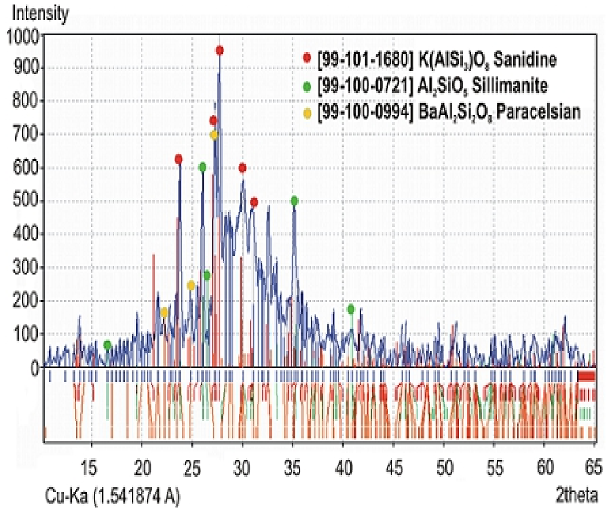

Figure 3. XRD pattern of glaze no. 7 after firing at 1130°C, 1h.

The appearance of not significant amount of $BaAl_2Si_2O_8$, can be explain by its an extenisve polimorphism [17]. Under XRD the crystalline phases in glaze 14 were not detected, enables us to conclude that glaze most probably being amorphous (Fig.4).

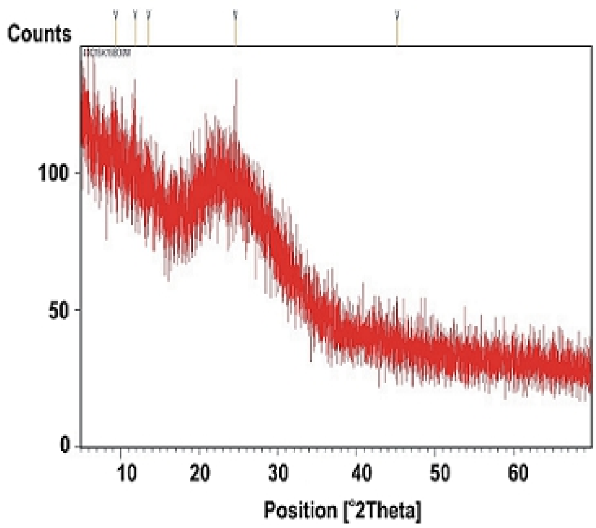

Figure 4. XRD pattern glaze no. 14 after firing at 1130°C, 1h.

Morphology of glaze 7 surface fired at 1130°C analyzed by SEM shows smooth surface with very fine crystals on the surface as shown in Figure 5. Si, Al and K were the major elements analyzed by EDS. That consistent with the results of phase analysis by XRD that shows crystalline phases: $KAlSi_3O_8$, Al_2SiO_8 and not significant amount of $BaAl_2Si_2O_8$ in glaze 7 (Fig.3). Glaze 14 fired at 1130°C shows glassy surface (Fig. 6),

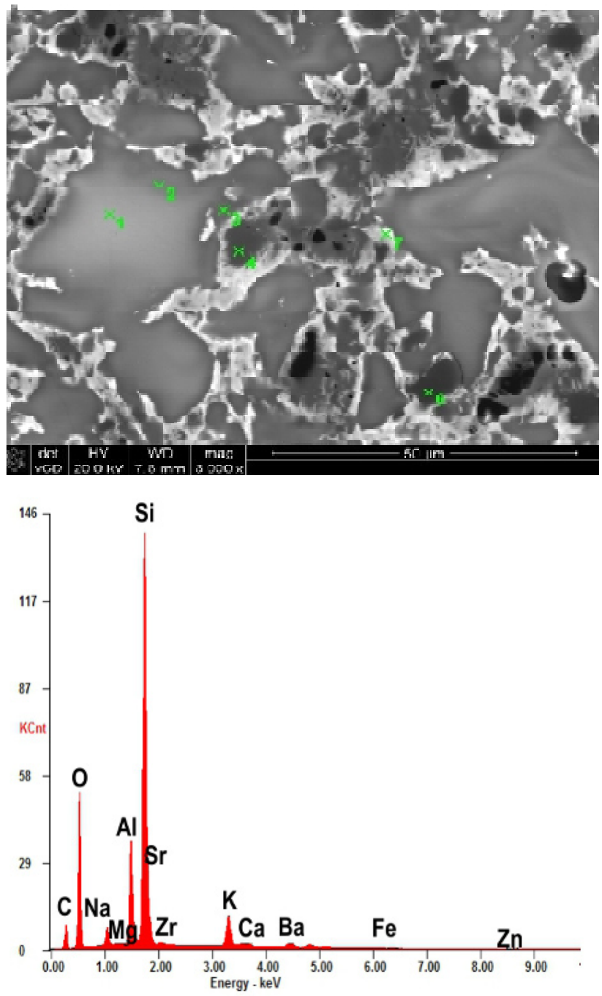

Figure 5. SEM photograph and EDS analysis of glaze 7 (the analysis performed in point 7).

SEM analysis did not show any crystalline phases. EDS revealed more Ca and Na content due to float glass cullet in the glaze composition. The resistance of the glaze tile to mechanical damage resulting from the impact of the abrasive factor was tested. The glazes were divided into abrasion resistance grades (PEI) with a specified number of rotations, of the device that rubs the surface of the glazed tiles after which the permanent traces of abrasion become visible. Based on the abrasion test the glaze 7 is assigned to the class 3 (number of rotations 1500) and glaze 14 (number of rotations 12000) to the class 4. Glaze 3 can be apllied on the tiles for flooring in domestic housing with considerable traffic and normal footware, where small abrasive material may ocassionally be carried out. Glaze 14 can be subjected for more frequent pedestrian traffic. The results of water absorption are presented in Table.3. Water absorption (N) was calculated by the following formula (1):

$$N = \frac{m_2 - m_1}{m_1} \cdot 100\% \qquad (1)$$

where:
m_1 - mass of the dried sample [g]
m_2 - mass of the sample saturated with liquid [g]

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Table 3. Water absorption

Type of sample	Number tiles	Water absorption (%)	Water absorption average (%)
Glaze 7	1/073 2/073 3/073	5,9 6,1 6,0	6,0
Glaze 14	1/013 2/013 3/013	4,9 4,9 5,0	4,9

4 Conclusion

The aim of the study was to support, by an environmental point of view, the recycling solution in the ceramic field successfully experimented for the CRT panel glass. In the ceramic industry, CRT cullet used as a raw material in glaze for low-fired products were found possible for CRT glass recycling. Glazes for low firing area with firing temperature of 1130º C utilised up to 50 wt % CRT panel glass. The identification of this limit percentage is related to the importance of avoiding defects like cracking, bubbling. Moreover the attention was paid toward the thermal expansion coefficient that tends to be elevated. The re-modulation of the raw materials in formulating the glaze composition becomes fundamental to obtain acceptable values of this parameter. The matt and amorphous glazes obtained have very similar to originals not containing CRT glass. Based on the surface abrasion tests it was observed that the introduction of CRT panel glass into the formulation meets the requirements of the standard product. However, research conducted have been the starting point for the study with the environmental impact of technologies for the production of ceramic glazes and will contribute to the rational development of the waste and re-introduce it to the market as a full value secondary raw material.

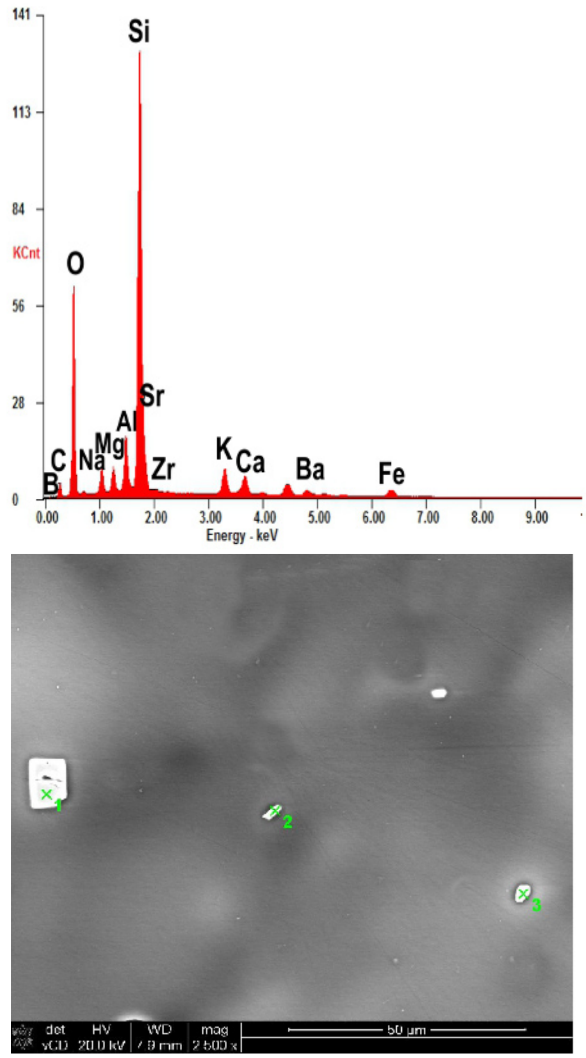

Figure 6. SEM photograph and EDS analysis of glaze 14 (the analysis performed in point 2).

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