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Sinthesis and Properties of Marble-Like Glass-Ceramics Using of Ash from Thermal Power Plants

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Abstract

Color marble-like glass-ceramic materials were obtained through thermal treatment of glasses of the system CaO-Al_2O_3-SiO_2 by using natural materials with the introduction of waste materials - ash from thermal power plants (TPP). The melting of the glass batch was in corundum crucibles at 1450°C with an isothermal hold of 60 min. The glasses obtained was fritted in distilled water and dried for 6 hours at 100°C, then completely crushed and divided into fractions with grain size of 0.8 mm, 1.0 mm, 2 mm, 2.5 mm and over 2.5 mm. It was found that the use of ash from TPP lead to higher values of degree of transformation (crystallization) than using base composition. Values of Avramy parameter's in the range n=1,0 ÷ 1,6 are showed that crystallization of the glass frit is largely heterogeneous and crystal growing starts from the surface. The introduction of ash from TPP to native glasses carry out to significant reduction of energy of crystallization by Ec=289 kJ/mol to Ec=221 kJ/mol. The glass-ceramic materials were obtained through a one stage crystallization - 1050÷1070°C and an isothermal hold of 60 min., colored white, yellow brown to dark brown. The main crystalline phase in glass-ceramics is β-vollastonite with needle habit, size of crystals - Í = 40 ÷ 120 μm and d <5 μm in quantities 37 ÷ 42%. As secondary phases depending on the amount of ash have been identified - the anorthite, gehlenite and α-quartz with prismatic habit were appeared. The obtained glass-ceramic materials have a marble-like effect and technical parameters compared with natural granite and marble and have higher values of density, micro hardness, speed grinding, bending strength and chemical resistance. That's why they can be used in construction such as lining materials.

Keywords: Glass-ceramic; Crystallization; Crystal growing; Marble-like effect.

1. Introduction

Glass-ceramics, intended for building applications, constitute an undoubtedly well-developed and widespread way to absorb glasses obtained from the treatment of several wastes. In addition to the environmental advantage of immobilizing wastes into materials with a generally high chemical resistance (like glasses), a certain economic benefit may be found in entering the large market of construction materials. The first and most important example was certainly that of Russian Slagsitalls, developed as early as the 1960s, by employing several slags of ferrous and non-ferrous metallurgy, ashes and wastes from mining and chemical industries [1, 2]. Lately, several combinations of wastes have been proposed [3-5], sometimes leading to materials with excellent properties [6].

Conventional glass-ceramics start from a two-step thermal treatment of nucleation and crystal growth. Although undoubtedly widespread, this route presents some disadvantages: the treatment is quite difficult and expensive, and sometimes particularly slow, so that catalysts (TiO_2, Cr_2O_3, etc.) are needed [1, 2]. In addition, the removal of defects (like gas bubbles) in the parent glass is essential for the achievement of strong glass ceramics, so that long fining times are required.

A secondary glass-ceramics manufacturing route, that of sintered glass-ceramics, has been established since the 1960s. Finely powdered glass is generally pressed and sintered, the crystallization occurring together with densification [7-9]. Since free glass surfaces are preferred sites for devitrification, crystallization may occur without catalysts, especially for small grains [7], thus configuring a ''surface mechanism''. The sintering approach may lead to a pleasant ''marble-like'' appearance of the glass-ceramics, much superior to that of Slagsitalls.

Commercial examples of this approach are the wollastonite-based ''Neoparies'', developed in Japan since 1970s [1, 2]. Sintered pyroxene-based glass-ceramics from cheaper and more accessible raw materials has been developed, in Bulgaria [10] and in Italy [11-13], since the early 1990s. The parent glass being provided in powdered form, long fining times are not needed, thus drastically reducing the costs of preliminary glass-making; in addition, very limited processing times may be advantageous in avoiding the volatilisation of dangerous oxides (like those of heavy metals) which may be dissolved in glasses when obtained from wastes. Recently, the Kingdom of Saudi Arabia has started investi-gating the use of its local resources for this purpose, withrelated achievements being seen in the glass–ceramics andceramics fields [14, 15].

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2. Material and Method

The chemical composition of the employed waste and natural resources is available in Tables 1 and 2. The waste were mixed in the proportion 0%–30%–50% by weight.

Table-1. Chemical composition of the starting waste and natural products

Oxide	Ash of TPP	Lime stone	Sand	Feldspar
SiO_2	47.41	0.30	99.83	69.98
Al_2O_3	19.47	0.32	0.12	18.02
CaO	7.31	52.54	-	0.78
Na_2O	0.67	-	-	9.87
K_2O	2.21	-	-	0.15
MgO	2.73	1.63	-	0.84
MnO	0.12	-	-	-
Fe_2O_3	12.04	0.06	0.03	0.15
TiO_2	1.04	0.01	0.02	0.21
P_2O_5	0.11	-	-	-
SO_3	1.46	-	-	-
L.O.I (1100^{o}C)	5.43	45.14	-	-

Table-2. Oxides included in the initial glasses

Oxide	GPR-0	GPR-30	GPR-50
SiO_2	58.68	56.46	53.79
Al_2O_3	6.98	6.79	11.10
CaO	16.89	16.21	12.80
R_2O	4.98	4.46	3.47
MgO	0.58	1.24	1.75
MnO	-	0.03	0.05
Fe_2O_3	0.07	3.54	5.76
TiO_2	-	0.30	0.55
P_2O_5	-	0.03	0.05
B_2O_3	0.99	0.96	0.91
BaO	3.95	3.77	3.71
ZnO	6.39	6.18	6.06
Sb_2O_3	0.49	-	-

The particular combination was chosen in order to approach the composition of wollastonite-based ‘‘Neoparies’’ [1]; the high content of alkali, with respect to ordinary wollastonite-based glass-ceramics was compensated by a remarkable amount of alumina, in order to determine alumino-silicate secondary phases.

Melting of mixtures is held in high temperature oven type Naber 2 HT 16/R17 with rate of temperature rise about 300^{o}C/h. Upon reaching the maximum temperature, one hour isothermal soaking is held which is needed of mixing and degassing of the melt in the crucibles. After isothermal soaking dishes are removed and fused glass with low viscosity is poured into a container with cold water.

Glasses, not including defects were obtained by melting of blends at the following time- temperature conditions: - temperature 1500°C, isothermal soaking - 60 min.

The degree of the phase transformation, Avrami’s parameter and activation energy of crystallization are determined by isothermal method by heat treatment of initial glass in the temperature range 1000 ÷ 1070^{o}C at different times of isothermal hold (20÷540min.).

The scanning electron micrographs (SEM) were taken using scanning electron microscope Karl Zeiess Yena (Germany) in regime of secondary electrons and acceleration of 30 kV

The X-ray analyses were carried out by the method of powder diffraction using X-ray apparatus D2 Phaser (Germany) with CuK_α radiation (30kV, 10mA), Ni filter. The X-ray diffraction scanning angle is from 10° to 60°.

Glass frit is subjected to heat treatment as follows: GP0 – 1070^{o}C/60min., GP1-30 and GP2-50 1050^{o}C–60 min.

Micro hardness was determined by the Vickers method of PMT-3 apparatus using samples in the shape of plate (20 x 20 mm) with polished surfaces.

The speed of smoothing of glasses is determined by using the polished machine "Joke".

Determination of the chemical resistance. Glass-ceramics grains sized 0,40 – 0,50 mm were used for the determination of their chemical resistance, measured by the weight difference before and after 1h treatment with 0,01n HCl and 0,01n NaOH (at 100°C).

3. Results and Discusion

To explain the kinetics of crystallization of super cooled melts the so-called Avrami equation usually is used [2, 16].

$\alpha(\tau) = 1 - exp(-gI_0U^{n-1}\tau^n)$ (1)

where α(τ) is degree of transformation at time τ, g is a shape constant, I_o is the rate of steady-state nucleation, U is the rate of crystal growth and n is a integer number which depends on the growth direction numbers, the mechanisms of nucleation and crystal growth.

By taking the logarithms of "(1)" twice, the value of the Avrami constant, *n*, may be calculated by the slope of the experimental curve.

In the case of crystals growth from a previously formed constant number of nuclei the Avrami constant only depends on the crystallization growth. In this case, using isothermal results obtained at different temperatures, the activation energy of crystal growth, *Ec*, can be evaluated assuming an Arrhenious temperature dependence, i.e.

$U = Uo \exp[-Ec/(RT)]$, "(1)" can be rewritten as:

$\ln \tau_\alpha = Ec(RT) - \ln(\text{const } Uo^n)/n - [\ln - \ln(1 - \alpha)]/n$ (2)

where τ_a is the time, corresponding to a certain value of α.

If the logarithm of τ_a is plotted against *1/T*, the slope gives *Ec/R* value.

As previously demonstrated [17], the degree of the phase transformation can be evaluated by using density measurements, through the following equation:

$\alpha = [(\rho_{\chi(\tau)} - \rho_g)\rho_{x(tot)}] / \{[\rho_{x(tot)} - \rho_g)\rho_{x(\tau)}]$ (3)

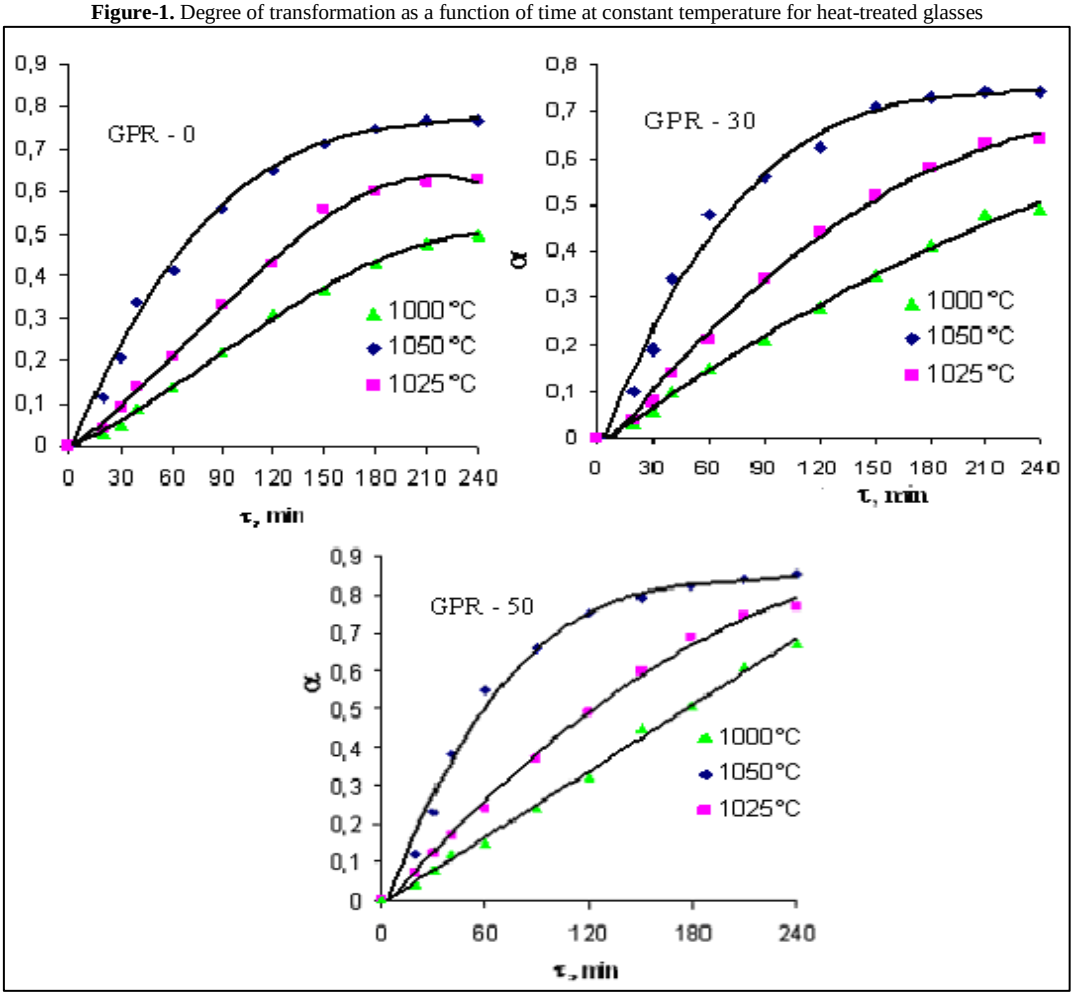
where ρ_g is the density of the initial glass, $\rho_{\chi(\tau)}$ is the density at time τ and $\rho_{x(tot)}$ is the maximum density at the end of the crystallization process.

The wt. % crystal phase formed, *x*, can be evaluated through the relation [17]:

$x = 100(1/\rho_g - 1/\rho_{gc}) / (1/\rho_{g(c)} - 1/\rho_c)$ (4)

In this case ρ_{gc} is the density of the glass-ceramic, ρ_c is the density of the crystal phase formed and the $\rho_{g(c)}$ is the density of a glass, having the same composition as the crystal phase formed.

Figure-1. Degree of transformation as a function of time at constant temperature for heat-treated glasses

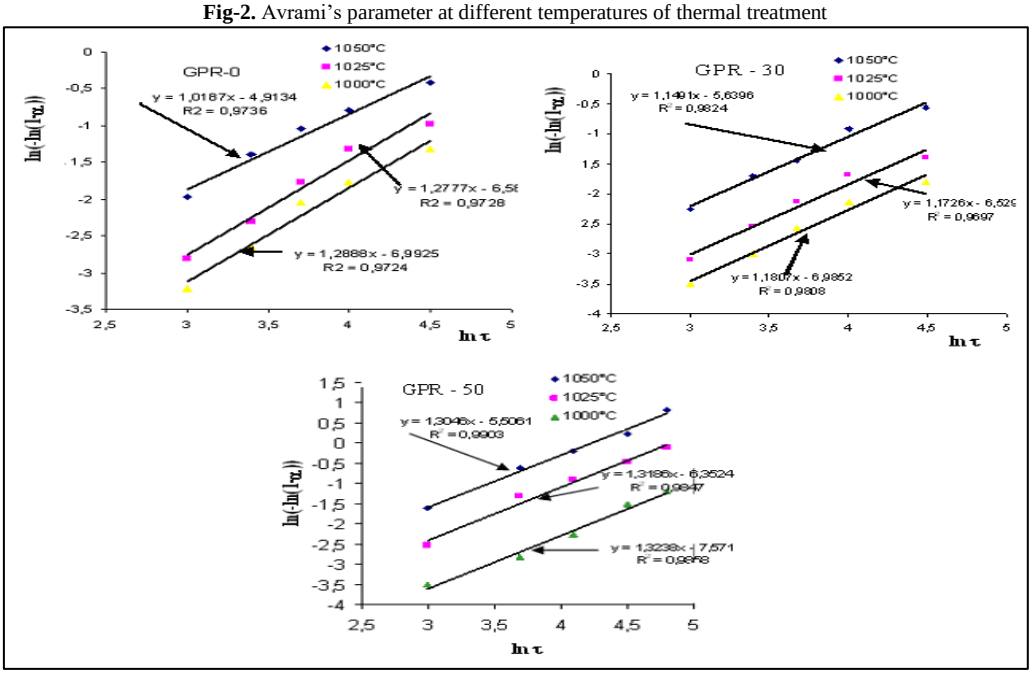


The degree of the phase transformation (α) is calculated using equation (3) The pycnometer was used for determining the density of heat-treated glass at a constant temperature for different times. Figure 1 shows the levels of transformation as a function of time at a constant temperature.

By plotting the graph ln (-ln (1-α)) as of the services of the ln τ can be obtained Avrami's parameter (*n*) of slope of the experimental linear regression. Figure 2 shows the values of *n* obtained under different thermal glasses. Values of *n* for GPR-0, GPR-30 and GPR- 50 in the range 1.0 - 1.3 correspond to a single dimensional of crystal growth mechanism [2, 18].

The activation energy of crystallization was calculated by equation (2) using isothermal results obtained under different temperature of glass thermal treatment.

Fig-2. Avrami's parameter at different temperatures of thermal treatment



The activation energy of crystallization was calculated from the slope of the curve obtained by plotting the dependence of $ln\ \tau_\alpha$ as a function of 1 / T (Fig. 3).

Figure-3. Activating energy of crystallization determined by isothermal method

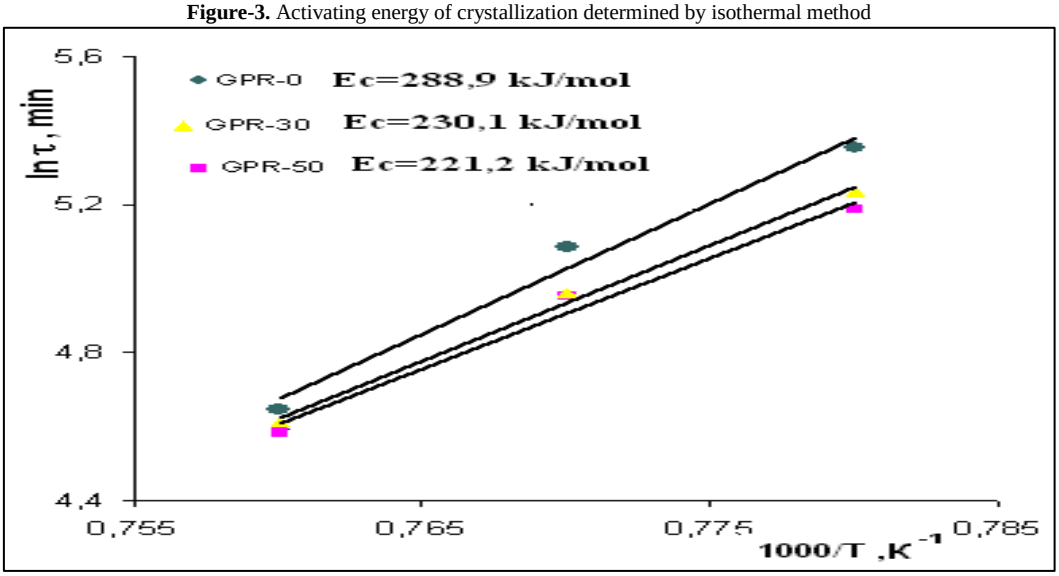
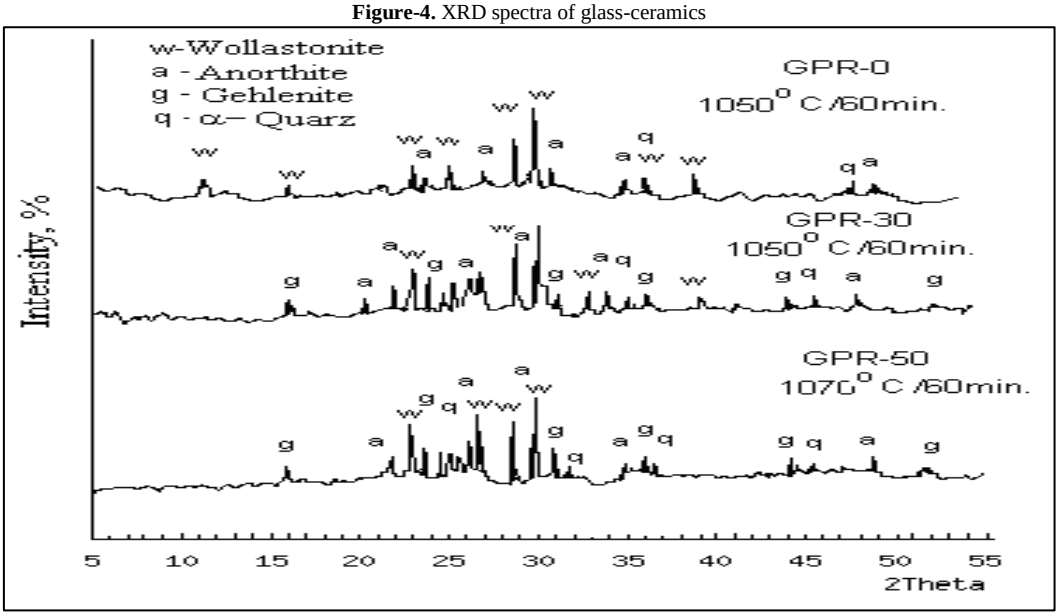


Figure-4. XRD spectra of glass-ceramics



By introducing a certain percentage of ash to the main glass *Ea* decreased from 289 to 221 kJ / mol, which is probably due to the formation of crystalline phases with different phase composition.

The different crystalline phases developed in heat treated samples were identified by X-ray diffraction (XRD) analysis. The results are shown in figure 4. The main crystalline phase in heat-treated samples appears β-wollastonite ($CaSIO_2$), as a secondary – anorthite ($Ca(Al_2Si_2O_8)$), gehlenite ($Ca_2Al(Al(SiO_7))$ and α-quartz (SiO_2) .

Samples' structure was determined by SEM (Fig. 5). There are two types of crystals - needle (wollastonite), and prismatic (anorthite, gehlenite and α-quartz) having been primarily wollastonite type. By increasing the amount of ash number of crystals grow but reduces their size from 120 to 40μm и d <5 μm.

Figure-5. SEM of glass-ceramics

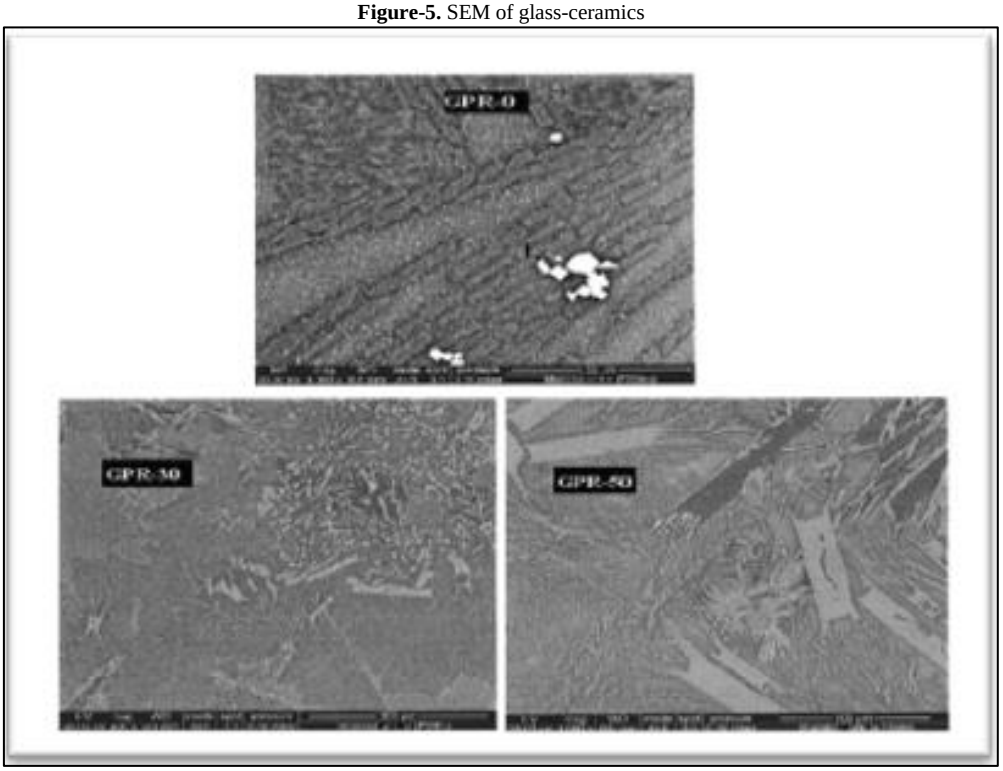
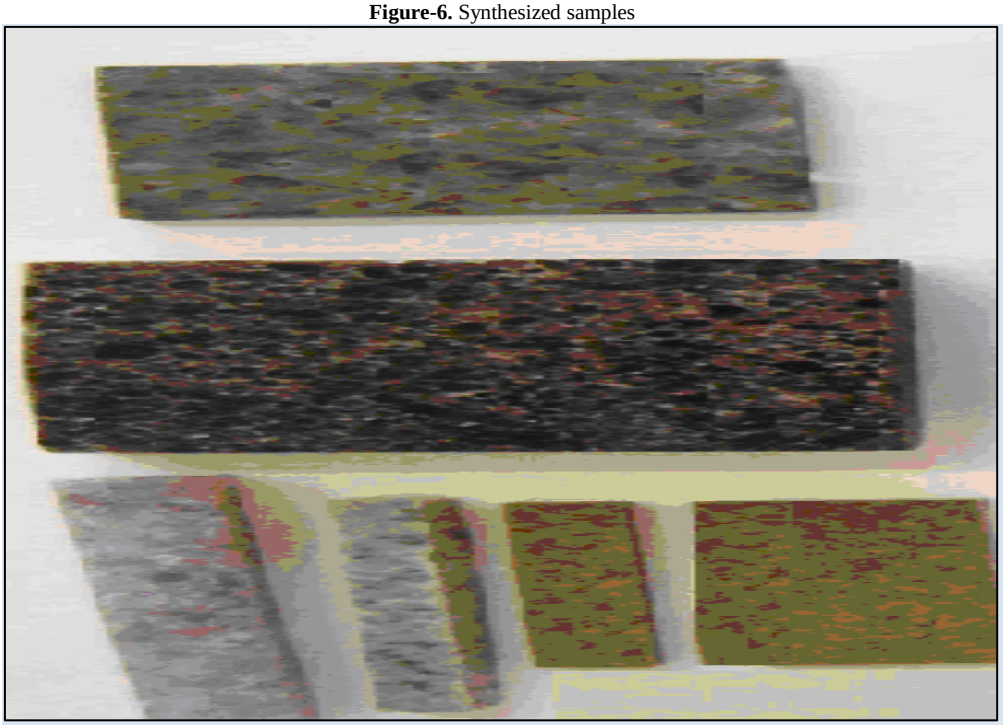


Figure-6. Synthesized samples



The total amount of crystalline phases formed, calculated by equation (4) in thermal glasses GPR-0, GPR-30 and GPR-50 is respectively 39, 46 and 51%. The amount of the forming crystal phase β-vollastonite defined by source [19] end for GPR-0, GPR-30 and GPR-50 is 37, 39 and 42%.

The samples obtained were studied for their main physicochemical properties - density, micro hardness, smoothing hardness, chemical resistance. The results obtained are presented in Table 3. Synthesized ceramic materials - cut and polished, resemble the natural appearance of marble and granite (Fig. 6)

Table-3. The properties of the glass-ceramics and natural products

Compo-sition	Density g /cm^3	Micro hardness, MPa	Smoothing hardness x10^3, kg/m^2 s	Chemical resistance	
				With 0,01 nHCl	With 0,01 nNaON
GPR-0	2.83	4620	8.96	1.25	0.41
GPR-30	2.84	5140	7.34	1.31	0.48
GPR-50	2.85	5790	2.95	1.86	0.52
Marble	2.58	2100	14.20	3.57	2.53
Granite	2.72	4800	10.62	3.26	2.11

4. Conclusion

Three kinds of glass compositions were developed for the synthesis of glass- ceramics, using natural products, as well as waste materials – coal ash from thermal power plants.

The introduction of ash from TPP to native glasses carry out to significant reduction of energy of crystallization by Ec=289 kJ/mol to Ec=221 kJ/mol.

The main crystalline phase in glass-ceramics is β-vollastonite in quantities 37 ÷ 42%. As secondary phases depending on the amount of ash have been identified - the anorthite, gehlenite and α-quartz. The phase composition, structures and some of the most important properties of the glass ceramic samples were determined. The obtained glass-ceramic materials have a marble-like effect. It was proved that marble – like surface of glass-ceramics is due to the residual glass-phase and the presence of needle-like crystals oriented to the inside surface of the glass. Those materials could be used as a wall-covering material in building.

References

[1] Holand, W. and Beall, G., 2002. *Glass-ceramic technology, the american ceramic society*. Westerville, OH, USA.

[2] Strnad, Z., 1986. *Glass-ceramic materials.* Amsterdam: Elsevier Science Publishers.

[3] Fredericci, C., Zanotto, E. D., and Ziemath, E. C., 2000. "Crystallization mechanism and properties of a blast furnace slag glass." *J. Non-Cryst. Sol.*, vol. 273, pp. 64–75.

[4] Barbieri, L., Ferrari, A. M., Lancellotti, I., and Leonelli, C., 2000. "Crystallization of (Na2O-MgO)- CaO-Al2O3-SiO2 glassy systems formulated from waste products." *J. Am. Ceram. Soc.*, vol. 83, pp. 2515–2520.

[5] Barbieri, L., Corradi, A., and Lancellotti, I., 2000. "Alkaline and alcaline-earth silicate glasses and glass-ceramics from municipal and industrial wastes." *J. Eur.Ceram. Soc.*, vol. 20, pp. 2477–2483.

[6] Ovecoglu, M. L., 1998. "Microstructural characterization and physical properties of a slag-based glass-ceramic crystallized at 950 and 1100oC." *J. Eur. Ceram. Soc.*, vol. 18, pp. 161–168.

[7] Prado, M. O. and Zanotto, E. D. "Glass sintering with concurrent crystallization." *C. R. Chimie.*, vol. 5, pp. 773–786.

[8] Clark, T. J. and Reed, J. S., 1986. "Kinetic processes involved in the sintering and crystallization of glass powders." *J. Am. Ceram. Soc.*, vol. 69, pp. 837–846.

[9] Muller, R., Zanotto, E. D., and Fokin, V. M., 2000. "Surface crystallization of silicate glasses: nucleation sites and kinetics." *J. Non-Cryst. Sol.*, vol. 274, pp. 208–231.

[10] Karamanov, A., Gutzow, I., Chomakov, I., Christov, J., and Kostov, L., 1994. "Synthesis of wall-covering glass-ceramics from waste raw materials." *Glastech. Ber. Glass Sci. Technol.*, vol. 67, pp. 227–230.

[11] Karamanov, A. and Pelino, M., 1999. "Evaluation of the degree of crystallisation in glass-ceramics by density measurements." *J. Eur. Ceram. Soc.*, vol. 19, pp. 649-654.

[12] Karamanov, A., Pisciella, P., Cantalini, C., and Pelino, M., 2000. "Influence of Fe3+/Fe2+ratio on the crystallization of iron-rich glasses made with industrial wastes." *J. Am. Ceram. Soc.*, vol. 83, pp. 3153–3157.

[13] Karamanov, A., Pelino, M., and Hreglich, S., 2003. "Sintered glass-ceramics from municipal solid waste-incinerator fly ashes-part I: the influence of the heating rate on the sinter-crystallization." *J. Eur. Ceram. Soc.*, vol. 23, pp. 827-832.

[14] Binhussain, M. and Abdulaziz, S., 2011. *Synthetic composition of marbleand method of production*. US Patent, p. 13214263.

[15] Binhussain, M., Alharbi, O., and Hamzawy, E. A., 2012. *Self - glazed ceramic/glass composite and method for manufacturing the same*. US Patent, p. 13726291.

[16] Uhlmann, D. and Uhlmann, E., 1992. *Crystal growth and melting in glass-forming system - a view from* vol. 30. In Ceram. Transact. Ser., Wiley.

[17] Karamanov, A., Taglieri, G., and Pelino, M., 1999. "Iron-rich sintered glass-ceramics from industrial wastes." *J. Am. Ceram. Soc.*, vol. 82, pp. 3012–3016.

[18] Gutzow, I. and Shmelzer, J., 1995. *The vitreous state-structure, thermodynamics, rheology and crystallisation*. Berlin, New York: Springer, Verlag.

[19] Hristov, J., Bogdanov, B., Chomakov, I., and Markovska, I., 2009. "Drawingstandard curve for quantitative determination of the crystalline phase in wollastonite glass-ceramics." *J. Balk. Tribolog. Assoc.*, vol. 15, pp. 347-354.