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Production and Characterization of Glass-Ceramics From Waste Materials

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Abstract: The fly ash, produced by power plant in Republic of Macedonia have been milled and sintered with addition of waste glass to obtain glass-ceramics. The physical, chemical and mechanical properties of fly ash and waste glass were determined. Through adequate sintering time and temperature, the glass-ceramic materials were manufactured. Chemical, physical and mechanical properties of the obtained composites were defined. The optimal composition of the composite was fly ash with the addition of 40% waste glass. Optimal sintering condition was 1000°C with 1h isothermal time at final temperature and heating rate of 10°/min. The addition of 40%wt of waste glass in the fly ashes increased the E-modulus from 4.24±1 to 30.55±2 GPa and increased the bending strength from 9.93±1 to 63.18±4 MPa Porosity of the compacts decreased from 44.34±3 to 14.32±2%. Investigation of durability of the produced systems did not show presence of any harmful elements in the obtained solution.

Owning to combination of the macroscopic appearance, microstructure, mechanical and thermal properties developed, dense materials could be used in the civil engineering.

Key words: ceramics, glass-ceramics, composites, coal fly ash

Introduction

Disposal of industrial waste in landfill sites is not a proper solution from economic and environmental consideration. This is related to coal fly ash obtained through combustion of coal and trapped within the power plant by an electrostatic precipitator. Fly ash available as a fine powder presents a valuable source of minerals containing SiO_2, Al_2O_3, Fe_2O_3, CaO, MgO, Na_2O and other oxides. A number of methodologies of treatment and recycling have been developed to minimize the harmful effects in the environment caused by the landfill disposal [1-3]. According to [4] the highest utilization of coal fly ahs is in the construction industry either as addition in concrete or supplement in cement. There are several reports for various application of fly ash in ceramic and glass-ceramic materials [5-7]. Rozenstrauha et al. [8] investigates the influence of various addition on a microstructure and mechanical properties of glass-ceramics obtained from silicate waste. The most commonly used procedure for treatment of industrial waste is vitrification [9, 10], but one of the main disadvantages of the process is the high cost involved, since it is an energy intensive process. The aim of this paper is to demonstrate the possibility of obtaining a dense glass-ceramic composite using high percentage of industrial waste and waste glass with reducing the sintering temperature due to the presence of liquid phase. Furthermore, by using waste glass ecologically, hazardous components are fixed at the molecular level in the silicate phase and inserted additionally in the matrix based on waste material.

The principle of this procedure was presented as a multibarier-concept by Ondracek [11] and basically investigated for various waste combinations. The new glass-ceramic composites possess significantly higher mechanical properties and lower leaching behavior. Dense glass-ceramic materials can be used as building materials.

Materials and methods

The raw materials, fly ash, were taken from thermal power station from Republic of Macedonia (REK Bitola), in further text coded FA and laboratory waste glass mark Pyrex coded WG. Chemical analysis of the fly ash was carried out by X-ray Fluoroscence, model ARL 9900XP. Chemical composition of the waste glass was declared from the manufacturer Pyrex [12]. XRD studies of the samples were realized by using a Philips X-ray diffraction unit (Model PV 105-1) operating at CuK_{α} - radiation. Scanning electron microscopy (SEM) investigations were conducted in JSM - 6460LV, JEOL, using standard metallographic techniques for preparation of the specimens followed by coating of the samples with a thin layer of gold in instrument BAL – TEC SCD 005.

The raw materials were ground in the planetary mill (Fritsch pulverisette 5) during 120 min and screened through a 63 μm screen.

Pressing of the samples was performed by uniaxial press (Weber Pressen KIP 100) at P=45 MPa using PVA as a plastificator.

Sintering of the compacted samples was realized in the chamber furnace in the air atmosphere at temperatures 900, 1000, 1050, 1100^{0}C, using heating rate of 10^{0}C/min and isothermal treatment at the final temperature of 60 min. Bulk density of the sintered samples was determined by water displacement method according to EN-993. The value of theoretical density of the compacts was calculated based on the composition of the initial mixture and known densities of the FA and WG.

Measurements of the mechanical properties (E-modulus and bending strength) of the dense specimens were made on three point bending tester (Netzsch 401/3), where a 30 mm span and 0,5 mm/min crosshead speed were used . Sample shrinkage (%) was determined from the differences in green and fired samples length. Porosity of the samples was calculated from the relative density.

Thermal investigations were perform on the dilatometer Netzsch 402E in the air atmosphere and temperature interval RT-650-RT, with heating rate of 5^{0}C/min. Technical coefficient of thermal expansion of the waste glass was declared from the manufacturer Pyrex [12]. Durability of the obtained materials was tested using the standard methods for glass-ceramics materials. The durability was determinated as a mass loss in 0.1mol/dm^3 HCl, 0.1 mol/dm^3 Na_2CO_3 solutions and in distilled water.

Results and discussion

The chemical composition of the investigated waste materials is given in Table 1.

Table 1. Chemical composition of the industrial waste

Oxide	FA [wt%]	WG [wt%]
SiO_2	50.33	83.34
Al_2O_3	18.59	1.33
Fe_2O_3	7.71	/
CaO	13.76	0.03
MgO	3.05	/
Na_2O	1.07	4.08
K_2O	1.41	0.04
SO_3	1.41	/
B_2O_3	/	11.19
Weight loss	2.60	/
Σ	99.96	100

Investigated fly ash consists highly amount of SiO_2, Al_2O_3 and Fe_2O_3, significant levels of MgO and other alkali metal oxides. It also possesses relatively high level of CaO and belongs to a class C which is in accordance with the literature [13]. XRD analyses of the FA is shown in Table 2.

Table 2. XRD analysis of the fly ash

Material	Composition
FA	quartz, anorthite, albite, hematite anhydrite and amorphous phase

Fig. 1 shows morphology of the FA particles and Fig. 2 presents particles of WG. Fig. 1 confirms that the size of the particles has a diameter of the FA ranging from 5 to 100 μm. Larger particles have irregular shape and size, spherical and partially spherical particles are smaller. The particles of WG have irregular geometry and dimensions between 10-60 μm. (Fig. 2)

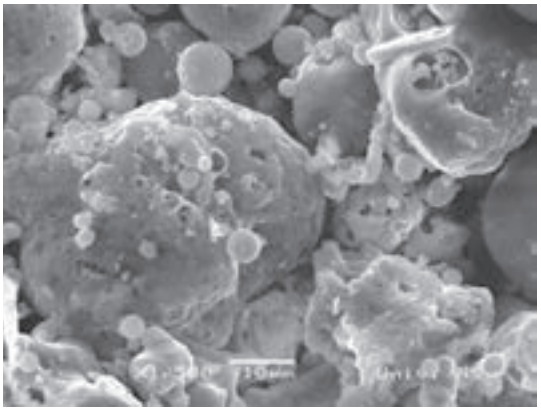


Fig 1. SEM micrograph of the FA, (1.500 χ, bar10 mm)

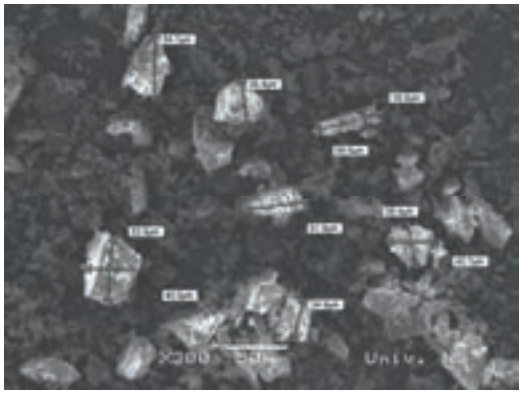


Fig 2. SEM micrograph of the WG, (300χ, bar 50 mm)

Investigations of the sintering studies, for compacts produced from FA point, show that relative density of 90% was achieved at 1100^{0}C and holding time of maximal temperature of 1h. The relative density of 85% was achieved for compacts obtained from WG sintered at 700^{o}C and holding time of maximal temperature of 1h. Density, bending strength, E –modulus, porosity and linear shrinkage of the compacts are shown in Table 3.

Table 3. Sintering temperature, Density, bending strength, E –modulus, porosity, linear shrinkage and technical coefficient of thermal expansion (a_{tech}) of the investigated materials

Compacts	Sinter.temp./ Time [^{0}C/h]	ρ [g/cm^3]	σ [MPa]	E [GPa]	Θ [%]	ΔL/L [%]	α_{tech} 10^{-6}/^{0}C
FA	900/1h	1.411	6.22	3.29	45.25	1.14	/
FA	1000/1h	1.453	9.93	4.24	44.34	1.80	7.3
FA	1050/1h	1.482	16.50	6.76	42.48	2.96	/
FA	1100/1h	2.340	60.98	30.53	10.01	16.00	/
WG	700/1h	2.233	69.08	27.31	14.43	15.77	3.3

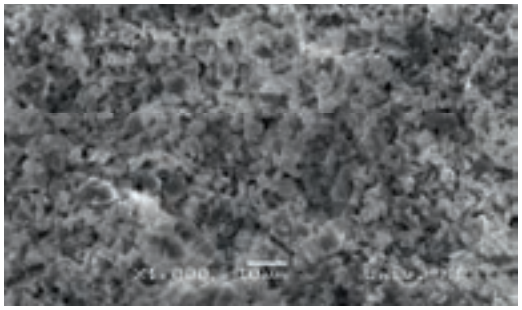
Glass-ceramics composites were obtained by adding the WG in quantity of 10-50% wt. into fly ash. One of the reasons for this was to increase mechanical properties and to decrease sintering temperature, and secondly, to encapsulate the particles of industrial waste into matrix. Dense composites with different densities were obtained by variation of the sintering temperature 900, 1000, 1050^{0}C. Sintering of the compacts FA50WG at 1000^{o}C and higher was not possible because it leads to a degasation and deformation of the compacts. Optimal composition of the composites obtained at optimized sintering temperature, their relative density, E-modulus and bending strength, porosity, and linear shrinkage of composites are shown in Table 4.

Table 4. Sintering temperature, Density, bending strength, E –modulus, porosity, and linear shrinkage of composites

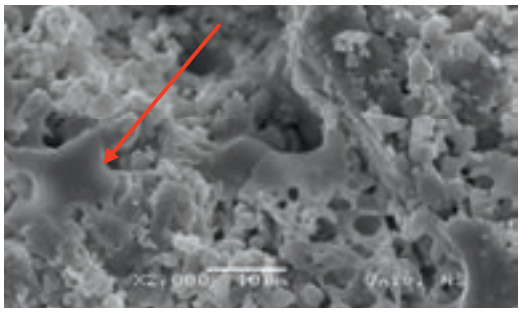
Compacts	Sinter.temp./Time, [^{0}C/h]	ρ [g/cm^3]	σ [MPa]	E [GPa]	Θ [%]	ΔL/L [%]
FA10WG	1000/1	1.568	30.56	10.87	39.94	4.32
FA40WG	1000/1	2.180	63.18	30.55	14.32	15.95

From the Table 3 and Table 4 it is evident that glass addition increases bending strength from 9.93±1 to 30.56±3MPa for FA10WG and 63.18±4 MPa for composite FA40WG, sintered at 1000^{o}C/1h. Increasing of E-modulus is also significant, ranging from 4.24±1 to 10.87±2 and 30.55±3GPa. Porosity of the compacts decreases from 44.34±3 for the compacts of FA to 14.32±2 for compacts FA40WG. Shrinkage of the samples increases from -1.8±0.5 for compacts of FA to -15.95±2 for compacts FA40WG.

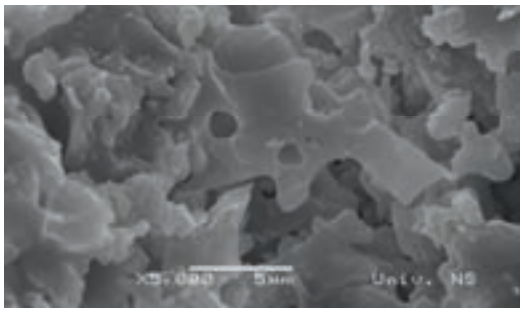
Fig. 3 presents microstructure of the fractured surface of the samples of FA10WG sintered at 1000, and with 1 h of holding at the final temperature and the heating rate of 10^0/min.



(a), bar 10μm



(b), bar 10μm



(c), bar 5μm

Fig. 3 SEM image for FA10WG, t=1000/1h (a-1000χ, b-2000 χ, c-5000 χ,)

Fig. 3 shows that the fractured surface of the sample is rough and granular. On some parts, the presence of the liquid glassy phase [arrow, Fig 3(b)] is evident, but the grains from the original morphology of the FA particles and WG are also recognisable. This confirmed EDS analysis (Fig. 4) on the fractured surface of the samples FA10WG sintered at 1000°C, and heating rate of 10^0/min. Spectrum 1 mainly consisting of SiO_2 points to a honey comb particle from diatomei originated from the fly ash. Point 2 corresponding to the composition of the FA and the point3 could be characterized as the region of the glassy phase.

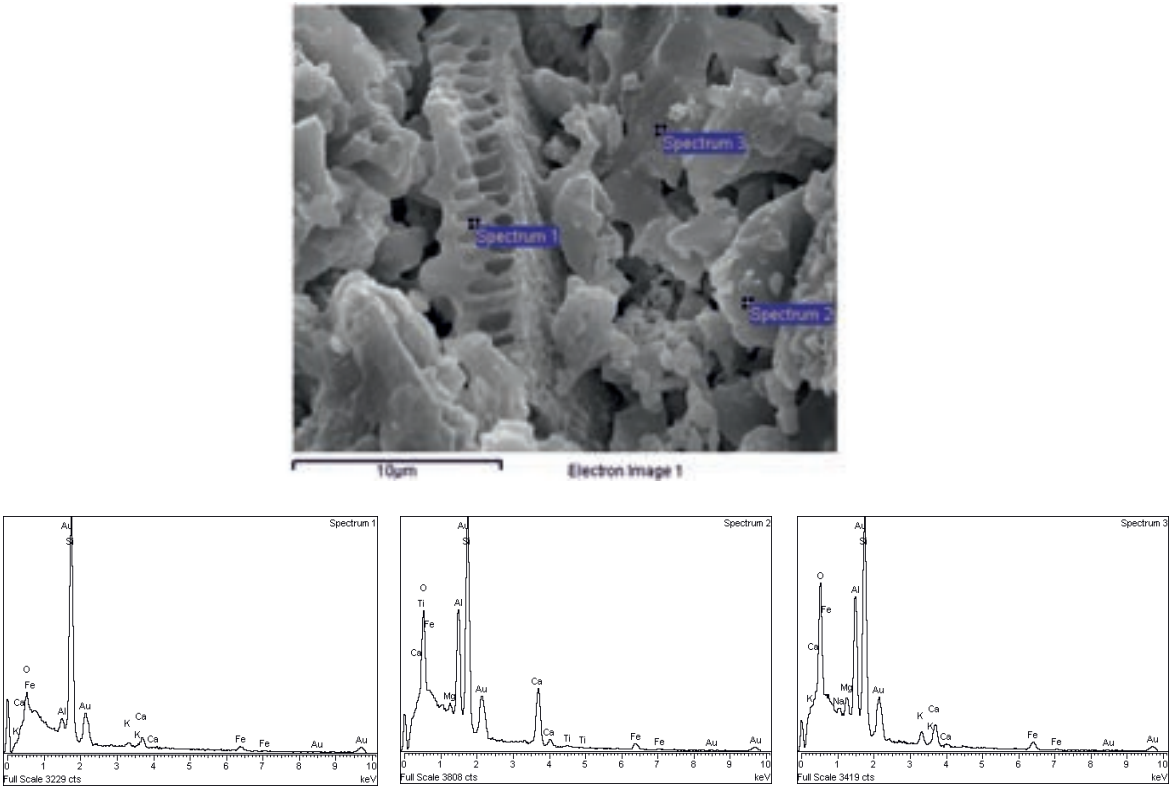
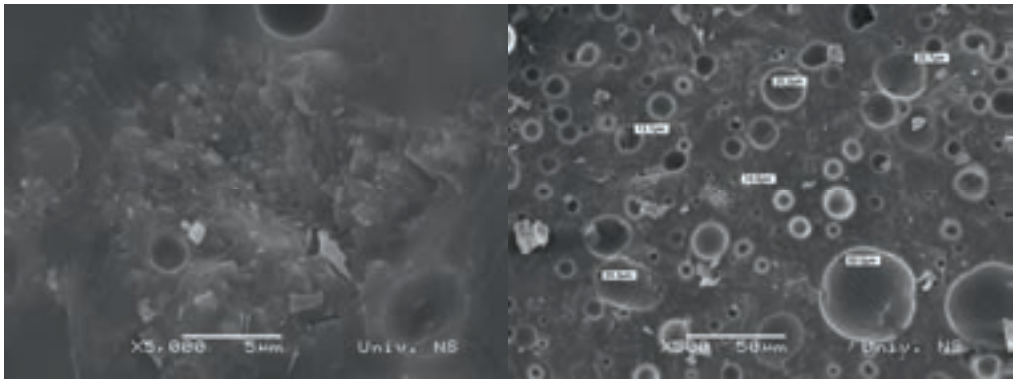
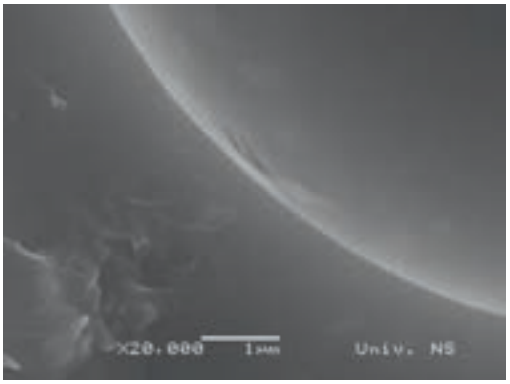


Fig. 4 SEM micrograph and EDS spectrums (1-3) of composites FA10WG, t=1000°C, (bar 10μm)



(a), bar 50 μm (b), bar 5 μm



(c), bar 1 μm

Fig. 5 SEM image for FA40WG, t=1000/1h(a-500 χ, b- 5000 χ, c- 20000 χ,)

Fig 5 shows the microstructure of the composites FA40WG, sintered at 1000^{o}C and at the heating rate of 10^{o}/min.

Fig 5 shows that the microstructure of the fractured surface of the ceramic samples obtained from FA40WG and sintered at 1000 ^{o}C is homogeneous and smoother compared to the FA10WG [Fig 3] sintered at the same temperature. There are no recognisable grains from the FA and they are well incorporated in the silica matrix. There is a significant formation of unconnected spherical pores with dimensions between 5-50μm. According to [13], formation of the spherical pores is connected with softening of the glassy phase and evolution of gas. They pointed that similar pyroplastic effects have been observed in other materials where the gas generation is reported to be due to the decomposition of alkaline metal salts. Fig 6 shows the EDS analysis of the compacts of FA10WG sintered at 1000^{o}C, and at the heating rate of 10^{0}/min. Point 1 is region mainly consisting of silica from the WG. Point 2 could be characterized as the region where FA particles are well embedded in the glassy matrix.

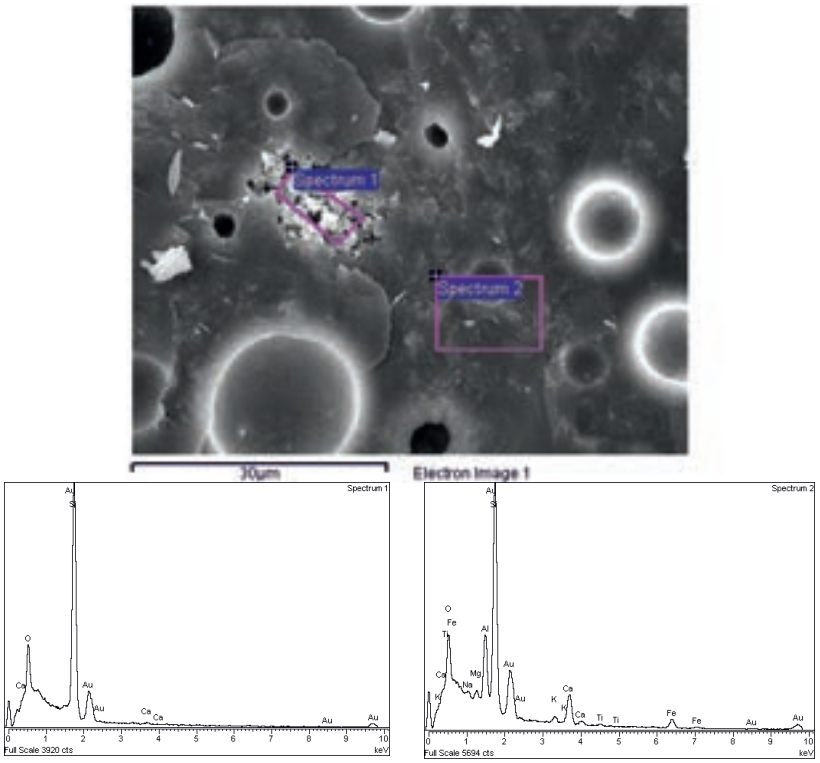


Fig. 6 SEM micrograph and EDS spectrums (1-2) of composites FA40WG, t=1000°C, (bar 30µm)

Temperature variation of the physical coefficient of thermal expansion presented as a second order polynomial form, and values of the technical coefficient of thermal expansion are shown in Table 5.

Table 5. Temperature variation of the physical coefficient of the thermal expansion and technical coefficient of thermal expansion (α_{tech})

Composite	$\vartheta(\Delta L/L_o)/\vartheta T=f(T)$	α_{tech} $10^{-6}/^0C$
FA10WG	$-0.0004+6\cdot10^{-5}T-6\cdot10^{-8}T^2$	6.40
FA40WG	$-0.0003+4\cdot10^{-5}T-6\cdot10^{-8}T^2$	5.91

Obtained values for technical coefficient of thermal expansion correspond to the value for technical coefficient reported in the literature [14].

Durability (mass loss after 30 days) of the compacts FA10WG, FA40WG was 4.5% and 2.3% in 0.1M HCl while 0.45% and 0.3% in 0.1M Na_2CO_3 respectively. Atomic absorption spectroscopy did not show presence of any harmful elements in the obtained solution.

Conclusions

- Glass-ceramics materials can be obtained from fly ash and waste glass;
- Optimal sintering condition was 1000°C with 1h isothermal time at final temperature and heating rate of 10°/min;
- The composite produced with addition of 40% wt WG and fly ash shows density of 2.180 g/cm^3;

- The addition of 40 %wt WG glass to FA increased the bending strength from 9.93±3 to 63.18±4 MPa and E-modulus from 4.23±2 to 30.55 ±3 GPa;
- Porosity of the composites is 14.32 ±2%;
- Linear shrinkage of the composite specimens is -15.77±2%;
- Dilatometer investigation has shown absence of the hysteresis effect, proving that the systems are in thermal equilibrium;
- Investigation of the durability on the glass-ceramics materials did not show presence of any harmful elements in the obtained solution;
- The chemical and physical properties of the dense materials make them suitable for a wide range of applications in the building industry.

References

[1] J. P. Wu, A.R. Boccaccini, P. D. Lee, M. J. Kershaw, R. D. Rawlings, (2006). Glass ceramic foams from coal ash and waste glass: production and characterization. Advances in Applied Ceramics, 105 (1), 32-9.

[2] J. Bossert, E. Fidancevska, B. Mangutova, B. Panova, D. Milosevki, M. Milosevski, (2004). Liquid phase sintereing of dence and porous glass-ceramics from coal fly ash and waste glass. Sciense of Sintering, 36, 87-92.

[3] R. Giere, L. E. Carleton, G. R. Lumpkin, American Mineralogist, (2003). Micro-and nanochemistry of the fly ash from a coal-fired power plant. 88, 1853-65.

[4] O. E. Manz, (1997). Worldwide production of coal fly ash and utilization in concrete and other products. Fuel, 76(8), 691-6.

[5] C. Leroy, M. C. Ferro, R. C. C. Monteiro, M. H. V. Fernandes. (2001). Production of glass-ceramics from coal ashes. Journal of European Ceramic Society 21,195-202.

[6] J. P. Wu, R. D. Rawlings, A. R. Boccaccini, I. Dlouhy, Z. Chlup. (2006). Waste Not, Want Not-An Inexpensive Glass-Ceramic from Waste. The Glass researcher, 15(2), 29-32.

[7] R. D. Rawlings, J. P. Wu, A. R. Boccaccini. (2006). Glass-ceramics: Their production from waste-Areview, Journal of Mater. Sci. 41, 733-61.

[8] I. Rozenstrauha, D. Bajare, R. Cimdins, L. Berzina, J. Bossert, A. R. Boccaccini. (2006). The influence of various additions on a glass-ceramic matrix composition based on industerial waste. Ceramics International, 32, 115-9.

[9] P. A. Bingham, R. J. Hand. (2006). Vitrification of toxic waste: a brief review. Advances in Applied Ceramics, 105(1), 21-31.

[10] I. A. Soboleb, S. A. Dimitriev, F. A. Lifanov, A. P. Kobelev, S. V. Stefanovsky. (2005). Glass Technol., 46 (1), 28-35.

[11] G. Ondracek. (1994). Waste treatment and recycling to remineralized products with multibarriers structure, Monatshefte, 7, 273.

[12] HYPERLINK "http://www.scilabware.com/Glass_technical/" www.scilabware.com/Glass_technical/, Accessed 15 June 2011.

[13] M. Ilic, C. Cheeseman, C. Sollars, J. Knight. (2003). Minerology and microstructure of sintered lignite coal fly ash. Fuel, 82 (30), 331-6.

[14] M. Erol, U. Demirler, S. Küçükbayrak, A. Ersoy – Meriçboyu, M. L. Öveçoğlu. (2003). Characterization investigation of glass-ceramic developed from Seyitomer thermal power plant fly ashes. Journal of the European Ceramic Society, 23, 757-63.

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