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Glass-Ceramics Produced by Vitrification of Coal Fly Ash

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ABSTRACT: Glass-ceramics based on CAS (CaO-Al2O3-SiO2) system was produced by controlled crystallization of vitrified fly ash. Fly ash was pre-treated by magnetic separation and nonmagnetic part of fly ash (NFA) was used. Maximal crystallization of parent glass occurs in the temperature region from 900 oC to 1160 oC. Glass-ceramics was produced by consolidation of parent glass i.e. pressing (45 MPa) and sintering at 950, 1000, 1050 and 1100 oC, and isothermal time at the final temperature of 30, 60, 120 minutes. The dominant crystalline phase was calcium aluminum silicate (anorthite). The obtained glass-ceramics could be potentially used in construction applications.

Keywords: coal fly ash, parent glass, quenching, vitrification, glass-ceramics.

INTRODUCTION

Fly ash generated as by-product from the thermal power plants is mainly used in the cement industry [Hwang & Cortés, (2021); Cavusoglu et al., (2021); Qin et al., (2019)] mostly as supplementary cementitious materials. However the utilization rate is much smaller than production rate (ECOBA, 2020) and the rest of the ash disposed in a landfill causes huge environmental problem. There are many existing applications of fly ash as construction materials, but also green transformation is foreseen in the future (Gollakota, et al*.,* 2019). One of the possibilities fly ash to be used in construction is the production of glass-ceramics. It is characterized with attractive appearance, excellent mechanical properties, good chemical resistance *etc.* [Zhu et al., (2016); Rzepa et al., (2020)]. The useage of fly ash for the production of glass-ceramics achieves savings in the exploitation of natural resources, and on the other hand, waste from one industry can be used as raw material in another industry, which is in line with the principles of circular economy [Bielecka and Kulczycka, (2020)]. The significant content of SiO_2, Al_2O_3 and CaO in fly ash is essential for production glass-ceramics in the CaO-Al_2O_3-SiO_2 (CAS) system. There are numerous papers and methodologies for modifying the composition of fly ash in order to obtain glass with the desired properties [Zong et al., (2015), Zhang et al., (2019), Baowei et al., (2013), Angjusheva et al., (2011), etc.] .

Production of glass-ceramics involves controlled nucleation and crystallization of glasses through specific temperature treatments. Dense, fine grained microstructure with excellent physical and mechanical properties can be obtained. Zhang et al., (2020) reported the production of low cost additive free glass-ceramic from coal fly ash and municipal bottom ash. By variation of the content of fly ash and the temperature they obtained anorthite and anortite-diopside glass-ceramics with density 2.55 g/cm^3, water absorption 0.1 % and compressive strength 299 MPa. Binhussain et al*.,* (2014) reported the production of glass by the vitrification mechanism, and transformation into low cost glass-ceramics. By combining direct sintering of waste mixture and sintering of waste derived glasses they create layered hybrid glass-ceramic with good mechanical properties and homogeneous microstructure that could be used in building facades as lightweight tiles.

The aim of this paper was to produce glass-ceramics from fly ash originated form the largest power plant in the Republic of North Macedonia – REK Bitola. Anorthite glass-ceramics were prepared by vitrifi-

cation of fly ash and sintering of parent glass in defined thermal treatment. Physical and mechanical properties in relation to the microstructure have been studied.

MATERIALS AND METHODS

Raw fly ash (RFA) used in the investigation was from the thermal power plant REK Bitola, Republic of North Macedonia. In order to decrease iron content and to increase the content of glass formers, such as SiO_2 and Al_2O_3, pre-treated fly ash was used to synthesize glass composition. Namely, nonmagnetic fly ash (NMA) was obtained by dry magnetic separation using magnetic separator Frantz, Model L-1, with a front slope of 20^o and a lateral slope of 30^o with a magnetic field of 0.07*T*.

Chemical analysis of the NFA was obtained using X-ray fluorescence spectroscopy (XRF; model ARL 9900). Loss of ignition (LOI) was determined on a dried sample heated for two hours at 900 ^{o}C. To investigate the phase composition of raw material and crystalline phases formed during heat treatment, powder and heat treated samples were analyzed using X-ray diffractometry (Philips X-ray diffraction unit, Model PV 105-1) operating at CuKα - radiation at an accelerating voltage of 40 kV and current of 40 mA.

The granulometric composition of the NFA was determined by sieving analyses (Retsch AS200). The specific gravity of the NFA was obtained by the pycnometer method. The morphology of the fly ash was followed by a scanning electron microscope (Leica S 440I).

The glass was obtained by melting the NFA at 1450-1500 ^{o}C/ 120 min in the graphite molds using the electrically heated furnace. The melt was quenched into water. The obtained glass was crushed and milled in the ball mill for 30 min. Glass granulation of less than 0.063 mm was used. The glass transition (Tg), crystallization (Tp) and melting temperatures (Tm) were determined using differential thermal analysis (DTA) (NETZSCH STA 409PC/PG) at heating rate of 10 ^{o}C/min in dry air.

Prior to the sintering parent glass powder was pressed using a binder (5% distillate water) by uniaxial pressing at P= 45 MPa (Weber Pressen KIP 100). Sintering was realized in the chamber furnace at sintering temperatures: 950, 1000, 1050, 1100 ^{o}C using heating rate of 10 ^{o}/min. The isothermal period at the final temperatures was 30, 60 and 120 min. The glass-ceramics was coded as NFA-T-time of isothermal treatment.

Bulk density was determined from the ratio of weight and volume of the sintered glass-ceramics. The porosity of the glass-ceramics was calculated from the relative density. Shrinkage (%) was estimated from the differences of the green and fired sample's length.

Mechanical properties (bending strength and E-modulus) were determined by three point bending tester (Netzsch 401/3) with a 30 mm span and 0.5 mm/min loading rate. Five specimens with dimensions 50 mm × 4 mm × 4 mm were used for the investigation and the average values were presented. Microstructure of the final glass-ceramics was followed by scanning electron microscope (SEM, Leica S440I) and energy dispersive analysis (EDS, JSM - 6460LV, JEOL).

RESULTS AND DISCUSSION

Table 1 presents the granulometric composition of the fly ash (NFA). Around 40 wt.% of fly ash particles are with dimensions less than 63μm.

Table 1. Granulometric composition of FA

Sieve diameter [mm]	NFA [wt.%]
+ 1.0	0.58
- 1.0 + 0.5	1.59
- 0.5 + 0.25	7.19
- 0.25 + 0.125	21.97
- 0.125 + 0.063	28.15
- 0.063 + 0.045	40.51
Σ	99.99

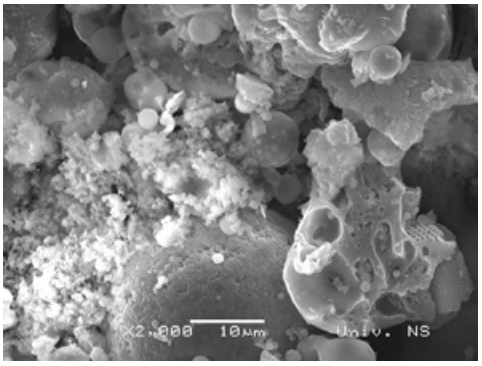


Figure 1. Morphology of raw fly ash, bar 10μm;

SEM analysis shows the presence of small spherical particles with diameter 1-10 μm, hollow particles and larger particles with undefined geometry and dimensions between 20-150 μm. Agglomerations of the small particles is evident. Specific gravity of the NFA was 2.095 g/cm^3.

Table **2***. Chemical composition of the NFA*

Oxide	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	Na_2O	K_2O	SO_3	LOI	Σ
NFA[wt.%]	56.56	18.63	5.77	8.11	6.06	0.78	1.52	0.83	1.15	99.41

Fly ash belongs to class F according to ASTM (SiO_2+Al_2O_3+Fe_2O_3 >70 wt.%). The major components of NFA are SiO_2 (56.56 wt.%) and Al_2O_3 (18.63 wt.%) contributing around 75 wt.% of NFA (Table 2). As far as nonmagnetic part of fly ash was used in the investigation, Fe_2O_3 (5.77 %) was still present in fly ash. Its presence can be prescribed to the agglomerates and unburned porous coal particles, both composed of magnetic and nonmagnetic particles (Shoumkova, 2010). The basicity of fly ash is defined based on the CaO/SiO_2 ratio, and for the investigated fly ash it is 0.14. This is important factor for the phase transformations during sintering (Tabit et al., 2020).

The mineralogical composition of NFA was quartz, anorthite, albite, hematite, anhydrite and amorphous phase.

Glass-ceramic formation

Differential thermal analysis (DTA) carried out on parent glass to determine the nucleation and crystallization temperatures for production of glass-ceramic is presented in Figure 2. The results indicate that the NFA glass is in accordance to the typical events of vitreous materials that transform into glass-ceramics.

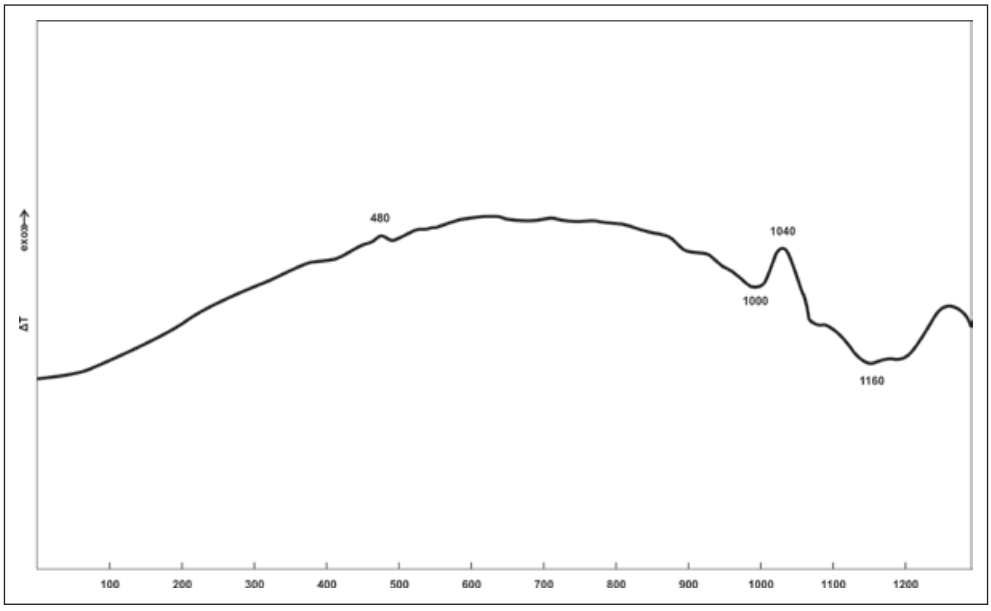
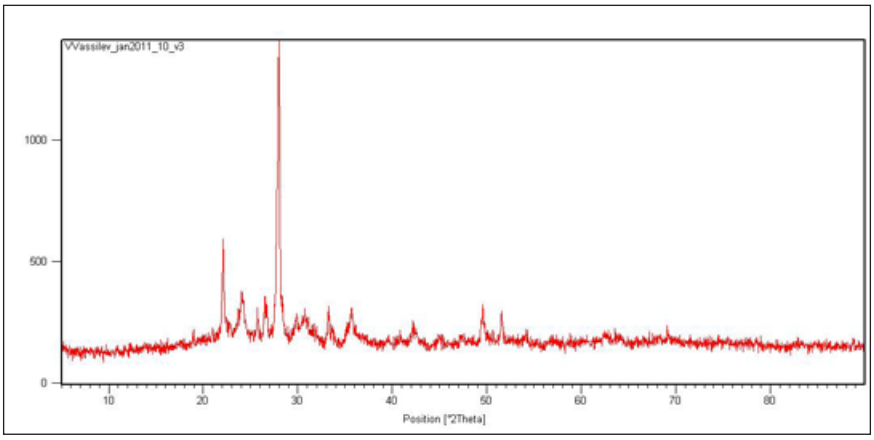


Figure 2. DTA curve of glass sample at heating rate of 10 °C/min

DTA curve indicates that glass transformation temperature (Tg) is at 480 °C and the exo peak of crystallization (Tp) occurs at 1040 °C, suggesting that the crystallization process is intense at the temperature region of 900-1050 °C. Glass transition, crystallization and melting temperatures generally decrease by increasing the content of alkaline oxides. (Vu et al., 2012). Endo effect refers to glass melting (Tm) appears at 1160 °C. Based on the above results, the maximal crystallization of glass obtained by NFA melting occurs in the temperature region from 900 °C to 1160 °C.

Mineralogical composition of glass-ceramics

Fig. 3 presents the XRD pattern of glass-ceramics sintered at 1050 °C/60 min. The main crystalline phase in glass matrix is anorthite ($CaSi_2Al_2O_8$). Tabit et al., (2020), reports that CaO/SiO_2 ratio ranging from 0.12 to 0.38 promotes the high content formation of anorthite. The content of anortite (68 wt.%) in the present study proves Tabit's reports based on the CaO/SiO2 ratio in NFA of 0.14.



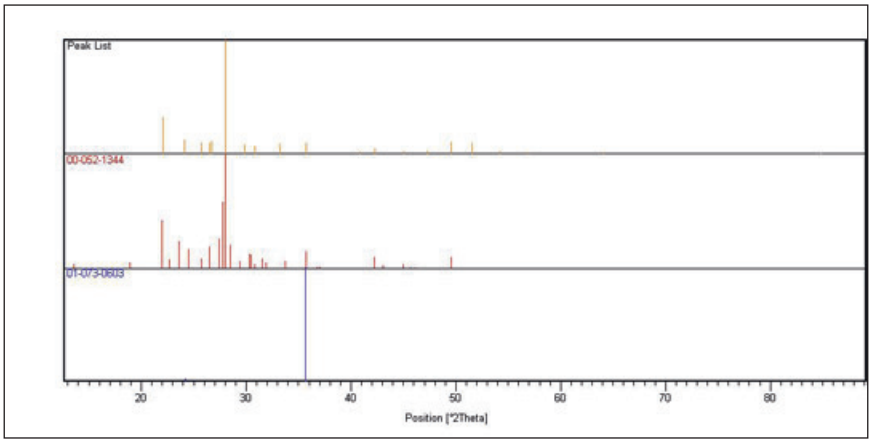
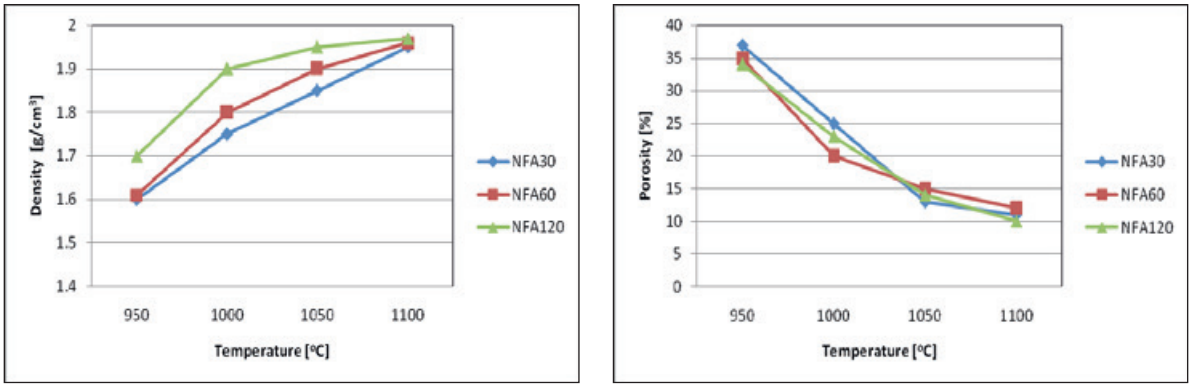


Figure 3. XRD patterns of glass-ceramics of NFA sintered at 1050 °C/60', Phase 1: Calcium Aluminum Silicate 00-052-1344; Phase 2: Iron oxide (III) reference ICSD. 01-073-0603

Physical and mechanical properties of glass-ceramics

Density and porosity of glass-ceramics are the typical parameters to evaluate the degree of sintering of glass-ceramics. The sintered density and porosity of glass-ceramic as function of temperature are plotted in Figure 4 with respect of different time of isothermal sintering. The density increases with the rise of the sintering temperature (from 1.60 to 1.98 g/cm^3), and consequently porosity decreased (from 37 % to 10 %). As far as sintering conditions act as an important parameter, also careful control of basicity (CaO/SiO_2 ratio) is required to optimized the properties of glass-ceramics (Zhang, 2020, Tabit, 2020).



(a) (b)

Figure 4. Physical properties of glass-ceramics sintered at different temperatures, (a) Density [g/cm^3]; (b) Porosity [%]

In addition to bulk density, sintering behavior of glass-ceramics was further described by linear shrinkage, Figure 5. The linear shrinkage rate of glass-ceramics varied evidently from 950 to 1050 °C, but above this temperature glass-ceramics were over-burning and entered the expansion process (Montodo, 2009). However, the linear shrinkage of glass-ceramics did not change significantly. Maximal shrinkage (12%) of glass-ceramics was achieved at 1050°C/60 min which is in accordance to the reported values (13-15%) from Ikeda et al., (2007).

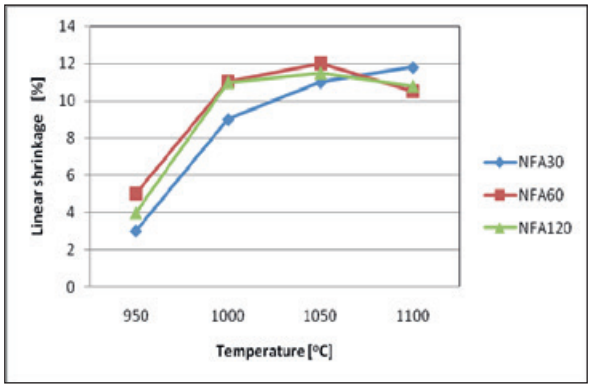
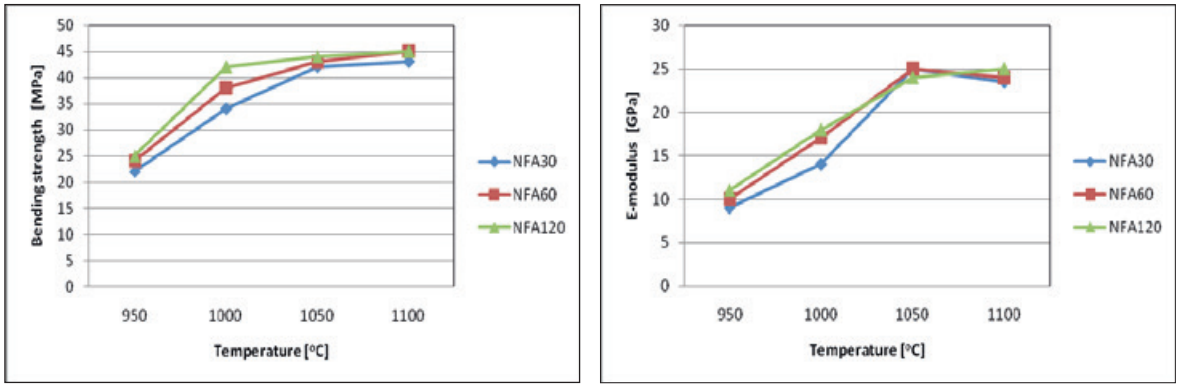


Figure 5. Linear shrinkage of glass-ceramics after exposure on defined temperature treatments

Figure 6 shows the bending strength and E-modulus of glass-ceramics sintered at 950- 1100 °C. Regardless the isothermal treatment of sintering, the bending strength and E-modulus of sintered glass-ceramics increases with the rise of sintering temperature. Mechanical properties of glass-ceramics sintered at 1050-1100 °C are much higher not only due to the densification and crystallization (anorthite has good mechanical properties) (Bernardo, 2008), but also to the lower porosity. Also, basicity i.e CaO/SiO_2, rather than the sintering temperature, has a more important impact in changing crystallinity of glass-ceramics (Zhang, 2020). The isothermal sintering is less influential on the mechanical properties of glass-ceramics. The maximal values for bending strength (45 MPa) and E-modulus (25 GPa) are comparable to the values reported in the literature. (Savvilotidou et al., 2019)

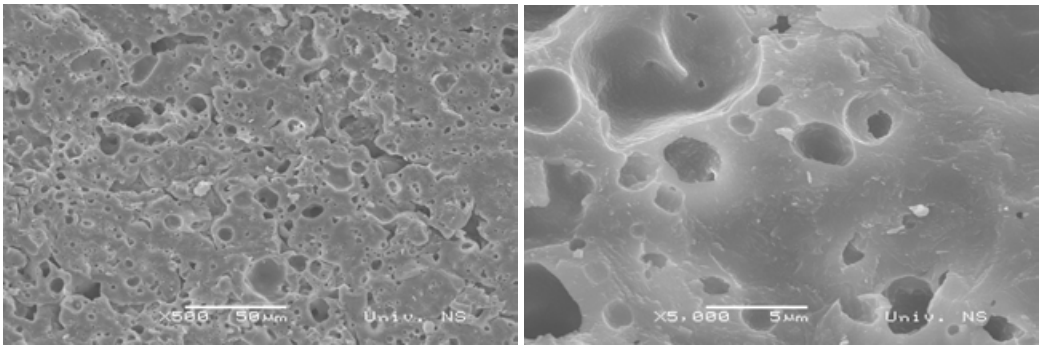


(a) (b)

Figure 6. Mechanical properties of glass-ceramics after exposure on defined thermal treatments, a) bending strength (MPa); b) E-modulus (GPa)

Microstructure of the glass-ceramics

The microstructure development of the glass-ceramics sintered at 1050/60 min is presented in Figure 7.



(a), x500 (bar 50µm) (b), x5000 (bar 5µm)

Figure 7. SEM micrographs of fractured glass-ceramic sample from NFA, sintered at 1050/60 min

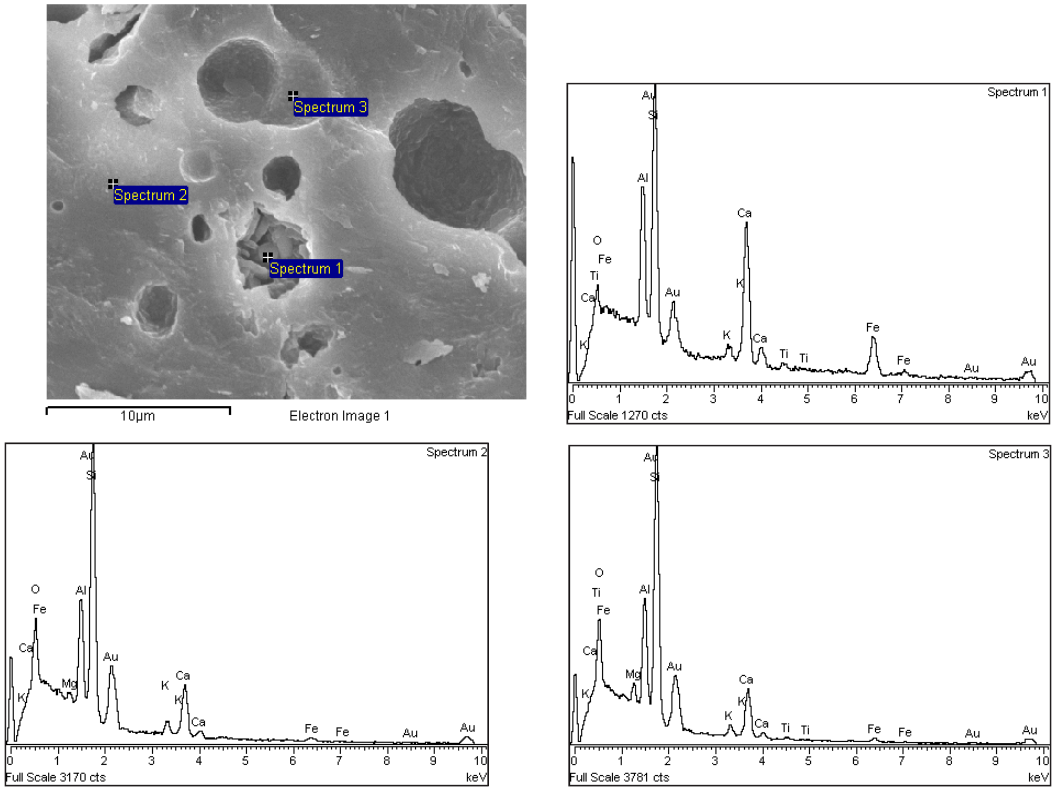


Figure 8. EDS analysis of glass-ceramic sample from NFA, sintered at 1050/60 min

Figures 7 (a) and (b) show that the fractured surface is homogeneous and crystal phases are well incorporated in the glassy matrix. Also, the presence of closed unconnected pores with dimensions between 2 and 20 mm is evident. The presence of small pores in the microstructure is reported to be usually formed around the anorthite phase. (Zhang et al., 2020). From EDS analysis (Fig.8) it is evident presence of detected predominant phase of calcium aluminum silicate (spectar 2 and 3) while inside the pores (spectrum 1) is iron oxide incorporated in the silicate matrix.

CONCLUSION

Anorthite-based glass-ceramics was produced without any additives from coal fly ash. Nonmagnetic fraction of fly ash was vitrified and glass-ceramics were obtained by controlled crystallization of parent glass.

The crystallization behavior of the parent glass revealed the glass transition temperature (Tg=480 °C), peak temperature (Tp=1040 °C) and melting temperature (Tm=1160 °C). Glass-ceramics with optimal

properties (density 1.98 g/cm^3; porosity 11 %; bending strength 45 MPa and E-modulus 25 GPa) was produced at 1050 ^{o}C/60 min. Calcium aluminum silicate (anorthite) as dominant crystalline phase (68 %) was homogeneously dispersed in the glass matrix. The obtained glass-ceramics can be potentially used as a substitute for traditional materials in construction, such as tiles, panels, bricks and other products.

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