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# Glass-Ceramics Obtained by the Crystallization of Basalt

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***Abstract:***
*The possibility to obtain glass-ceramics from basalt from the locality on Vrelo (Kopaonik mt.) is shown in this paper. The parent rock was ground to fraction -0.4 +0.1 mm, and then melted at 1250 - 1300°C. The crystallization melted bazaltic glass at 950 °C during the time interval of 3 hours caused synthesis of a glass-ceramic material with a microstructure that has excellent mechanical properties according to the determined dynamic modulus of elasticity and uniaxial compresive strength. The phase composition of the obtained glass ceramic material was determined by XRPD using Rietveld refinement and SEM. Two phases were found: pyroxene which corresponds to omphacite of the composition* $(Na_{0.199} K_{0.180} Ca_{0.471} Mg_{0.249})_{1.1}(Mg_{0.271}Fe_{0.299}Al_{0.430})_{1.0}(Si_{1.704}Ti_{0.046}Al_{0.250})_{2.0}O_6$ *and glass with an approximate relationship 69:31.*
***Keywords:*** *Basalt, Glass-ceramics, phase composition, microstructure, mechanical properties.*

## 1. Introduction

The glass material rich in iron, which is considered the forerunner of glass-ceramics was developed before World War II in a French company „Generale du Basalte" by smelting rock – petrurgy [1-4]. The resulting materials have great application in construction of footpath/pavements/sidewalk/landingplace tiles, pipes, insulation, etc. as well as in other industries. First, the magmatic rocks (basalts, diabases, gabros) were smelted and in more recent times the metamorphous and sedimentary rocks as well as industrial slag from ferrous and non-ferrous metalurgy as well. In the last 20 years, great development was made in obtaining glass ceramics from industrial raw materials which have a pyroxene phase [5, 6]. Due to the high chemical durability and high resistance to abrasion and corrosion, natural basalts are cheap raw materials that are present in significant quantities and are the main raw material for petrurgy [7-9]. Also glass-ceramic materials with basalt and iron-rich glass similar basalt compositions have been developed for nuclear waste disposal [10, 11] and for vitrification industrial wastes which are environmental pollutants [12-20].

Many research papers deal with the study of melting and crystallization of igneous rocks [21-25].

Directing the process of crystallization and cooling can result in the formation of glass-ceramics, which is characterized by much better properties than normal ceramics. The main advantage is that it is possible that the final ceramic product can be given any desired

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shape, which can be achieved by recycling glass. Changing of the conditions of heat processing can produce a material with predefined characteristics [1, 26].

The Vrelo locality was geologically explored extensively and physical, mechanical and technological characteristics of basalt were analysed. The reserves of this rock as a raw material have been found to be at a little over a million tons [27].

The aim of this research paper is examination of the phase composition and mechanical properties of the glass- ceramic material produced by thermal procesing basalt glass at 950°C during 3 hours.

## 2. Experimental work

The basic raw material basalt is crushed and then ground until grain size under 0.4 mm was reached. The ground up material was melted without any additives in a chammote ladle, in a gas furnace at the temperature 1250 – 1300°C. A completely clear melt which is characterized by low viscosity, crystallized in the owen at a temperature of 950°C for the duration of 3 hours and was gradually cooled.

The mineral composition of the obtained glass-ceramic material as well as the starting basalt was determined by X-ray diffraction analysis (XRPD), polarising and scanning electronic microscope (SEM). The chemical composition of the phases of the glass ceramic material was determined on a SEM Phillips XL30 equipped with an EDAX DX4 Energy Dispersive Spectrometer (EDS).

The XRPD data was collected using a Siemens diffractometer with Cu $K_{\alpha}$ radiation in the range of 10 to120° 2θ with a 2θ step of 0.02° and counting time of 15 seconds.

The dynamic modulus of elasticity of the obtained glass ceramic material was determined from propagation velocities of ultrasound waves using the Sonic viewer equipment model 5210 in accordance to the procedure of the standard JUS.D.B8.121. The uniaxial compressive strength was determined on a hydraulic press type „MS-2000“.

## 3. Results and discussion

### 3.1 Starting material

The basalt from Vrelo on Kopaonik is a rock with rare and macroscopic barely visible and recognisable olivine and pyroxene [27]. The microstructure of basalt from Vrelo consists of phenocryst pyroxene, olivine, plagioclase and groundmass (Fig.1) Accessory minerals present in relatively minor amounts include magnetite and rarely biotite.

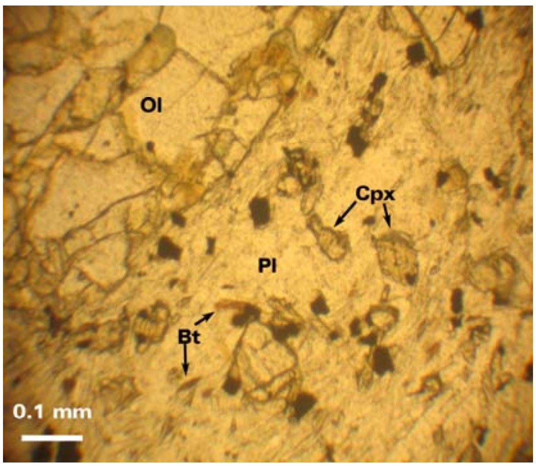


**Fig. 1.** Microstructure of basalt (polarising microscope Nik II) Pl-plagioclase, Cpx-clinopyroxene, Ol-Olivine, Bt-biotite.

The XRPD of the raw basalt found out that the basic plagioclase is andesine and pyroxenes are represented by diopside which is dominant and hypersthene.

Thanks to its mineral composition basalt melts at relatively low temperatures of 1140 – 1160°C during which a homogenous melt is obtained which loses it's gaseous phase in a short time [9].

## 3.2 Chemical composition

The chemical composition of the phases of the synthesised glass ceramic material is presented on Tab. I. The X-ray energy spectra were colected by SEM EDAX from the entire area then from the omphacite and the matrix particularly.

**Tab. I.** The chemical composition of phases found in basalt glass-ceramic (SEM)

| | Average analisys (%) | Matrix(%) | Omphacite (%) | Elements distribution (%) | |
|---|---|---|---|---|---|
| | | | | Omphacite | Matrix |
| $SiO_2$ | 47.92 | 50.43 | 46.88 | 33.15 | 14.77 |
| $Al_2O_3$ | 16.84 | 19.23 | 15.89 | 11.34 | 5.51 |
| $TiO_2$ | 1.46 | 1.17 | 1.7 | 0.94 | 0.52 |
| FeO | 9.54 | 9.1 | 9.83 | 5.98 | 3.56 |
| MgO | 8.01 | 4.61 | 9.59 | 6.54 | 1.47 |
| CaO | 11.31 | 8.75 | 12.1 | 9.24 | 2.07 |
| $Na_2O$ | 2.08 | 2.34 | 1.78 | 0.82 | 1.26 |
| $K_2O$ | 3.18 | 4.48 | 2.27 | 1.34 | 1.85 |
| Total | 100.35 | 100.11 | 100.04 | **69.35** | **31.00** |

The quantitative phases content was calculated using the average composition and particular analiysis of matrix and omphacite. The results show that the content of omphacite (dendrites) and of the glassy matrix is 69 % and 31%, respectively (tab.I).

## 3.3 Diffraction analysis

XRPD of the synthesised glass ceramic material shows the presence of one crystal phase which is appropriate to omphacite of the space group C 1 2/c 1 with latice parameters (nm): $a_o$=0.96903(6), $b_o$=0.88310(6) and $c_o$=0.52737 (3); $\beta_o$=106.940° (5).

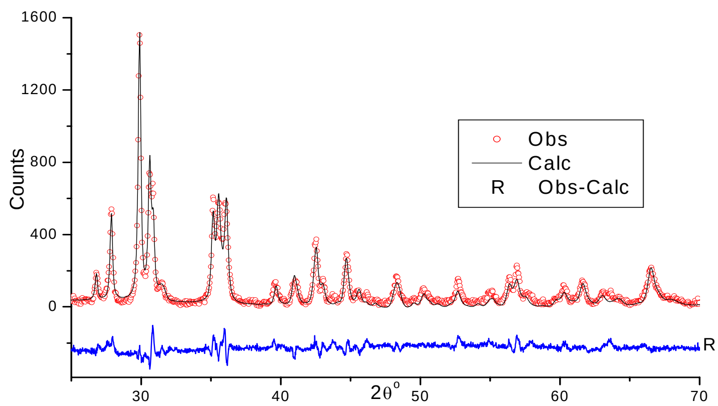


**Fig. 2.** Observed and calculated XRPD patterns of omphacite from basalt's glass-ceramic

The XRPD have been fitted according to the structural model of omphacite [28] by the Rietveld method using the FullProf program. The results of fitting indicate very good accordance of experimental data with the proposed model of omphacite structure (Fig.2). The R factor of diffraction points with Bragg's contribution are: $R_{Bragg}$=9.40, $R_p$=2.22, $R_{wp}$ = 2.96 i $R_{exp}$= 4.22. ($\chi^2$ = 0.491).

The obtained omphacite is of the calcium-rich type with cation distribution between octahedral sites (M1 and M2) which follow the stoichiometric priorities [29] . The unit cell has 4 cations, but in the obtained omphacite there is a cation surpluss of about 0.1 atoms per formula unit. So, the structural formula of omphacite is:

$$(Na_{0,199}K_{0,180}Ca_{0,471}Mg_{0,249})_{1,1}(Mg_{0,271}Fe_{0,299}Al_{0,430})_{1,0}(Si_{1,704}Ti_{0,046}Al_{0,250})_{2,0}O_6$$

Because of the largest cation oxygen distances, the M2 sites open up the uttermost possibility for unusual cation occupation. Therefore we have assigned the cation surplus to these sites. The presence of K is unusual in the omphacite structure as well as Mg in the M2 site. It can be a consequence of the structural disorder because we should have in mind that the crystallisation was quick and there wasn't enough time to establish a thermal equilibrium. As a result an insufficiently ordered structure forms (high $R_{Bragg}$), which offers the basis for further reexamination of the omphacite composition, especially from the viewpoint of thermodinamic conditions.

## 3.4 Description of microstructures

The SEM observations reveal that basalt glass crystallization at 950° C during three hours, produced a glass-ceramic material consisting of two phases (Fig.3a). The crystal phase has the form of dendrites and appears as a dense network of interlocking acicular branches. The interstices are filled with a compact amorphous phase – the glassy matrix or ground mass. The dendritic crystal habit is the consequence of quick crystallisation.

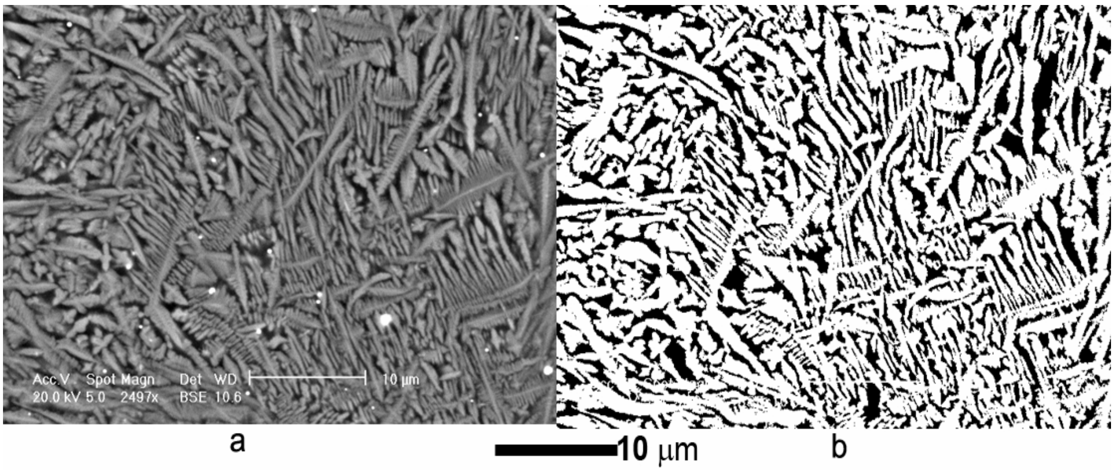


**Fig 3.** SEM: microstructure of glass-ceramics (a); computer simulation of microstructure (b)

When the crystal grows there is an exchange of its inner free energy with the melt. If the temperature gradient between the crystal and its surrounding is high enough, diffusion exchange of heat ceases to be operative. A convection appears as the mechanism of energy transfer. Because this kind of heat exchange needs a larger surface the interface between the melt and solid changes from a planar to a columnar shape, creating a dendritic structure [30]. Dendritic crystals in glass represent a kind of framework and improve general mechanical characteristic of glass ceramics such as elasticity, which is important because fragilty is its weak point.

The omphacite and ground mass content have been determined by digital image analisys. A computer simulation of the integrated surface is given on Fig. 3b. Omphacite dendrites (white) take 66 % of the total area. The reamainig 34 % belong to the glassy matrix which is in excellent accordance with previous chemical analysis results.

### 3.5 Mechanical characteristics

Measurement of ultrasound propagation velociteis points to the compactness of the glass-ceramics. The velocity of longidutinal waves was 5474 m/s and of transversal waves 2730 m/s. From these, a dynamic modulus of elasticity is 55 GPa which is in the agreement with Young's Modulus for glass ( 50 to 90 GPa, according to www.EngineeringToolBox.com). The uniaxial compressive strength is 550 MPa. This value is about ten times higher than the common value for glass (50 MPa) due to the omphacite dendritic framework in the glass-matrix.

## 4. Conclusion

By crystallising basalt glass at 950° C in the time interval of 3 hours A glass ceramic material was synthesised, made up of a crystal and glass phase. The crystal phase has a pyroxene structure which by its chemical composition corresponds to omphacite. Omphacite crystals appear in the shape of acicular dendrites, branching out through the glassy matrix as a unique framework which prevents the spreading of cracks. In this way a microstructure of glass-ceramics is built with crystals of omphacite (69%) as a framework and a glassy phase as the bonding agent (31%) which is characteriZed by excellent mechanical abilities. The obtained glass ceramics can be used for different industrial purposes where a high level of hardness and durability is necessary.

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***Садржај:*** *Могућност добијања стаклокерамике из базалта са локалитета Врело са Копаоника приказана је у овом раду. Изворна стена је самлевена у фракције -0,4+0,1 mm, а затим топљена на 1250-1300°C. Кристализацијом истопљеног базалтног стакла на 950℃ у временском интервалу од 3 сата синтетисан је стакло-керамички материјал са микроструктуром која има изванредне механичке особине у складу са одређеним динамичким модулом еластичности и притисном чврстоћом. Фазни састав добијеног стаклокерамичког материјала испитиван је хемијски, рендгенском дифракцијом, поларизационим и скенирајућим електронским микроскопом (SEM).*
*Резултати испитивања указују на присуство две фазе: пироксена који одговара омфациту састава* $(Na_{0.199}\ K_{0.180}\ Ca_{0.471}\ Mg_{0.249})_{1.1}(Mg_{0.271}Fe_{0.299}Al_{0.430})_{1.0}(Si_{1.704}Ti_{0.046}Al_{0.250})_{2.0}O_6$ *и стакла са приближним односом 69% : 31%.*
***Кључне речи:*** *базалт, стаклокерамика, фазни састав, микроструктура, механичке особине*