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GLASS CERAMIC MATERIALS ON THE BASIS OF BASALT RAW MATERIALS OF UZBEKISTAN

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Absract:
Basalt rocks from the Karakiya deposit in the Jizzakh region of Uzbekistan was investigated to obtain of glass ceramics for construction purposes. X-ray analysis showed that the crystalline phases of basalt of Karakiya deposit are represented by calcite, augite, chlorite, anorthite, small amounts of magnetite and albite. To obtain acid- and heat-resistant glass ceramics materials, composition was calculated to obtain of structure of anorthite. Synthesized glass ceramics have high compressive strength up to 670 MPa, high chemical resistance to acids and alkalis.

Keywords: basalt rocks, Karakiya deposit, glass ceramics, solid waste, sustainable, construction, synthesis, anorthite.

INTRODUCTION

Basalt rocks have been identified as a valuable resource for the production of building materials in Uzbekistan. Basalt-based building materials are energy-saving, have lower vibration resistance, and can withstand high temperatures. This makes them an excellent choice for construction in various conditions.

In addition, the availability of these rocks in Uzbekistan provides a local and sustainable source of raw materials, which could lead to economic benefits and contribute to the local industry's growth. Research of the specific properties of these rocks to make them suitable for building materials, the processes involved in transforming them into usable forms, and the potential environmental impact of their extraction and use is indeed very relevant and timely.

For example, the study [1] compared the use of basalt raw materials with the requirements of the world's leading basalt processing enterprises and the acid modulus and chemical composition using data from the Berkuttau, Madaniyat, and Aktash basalt rocks sites found in the territory of the Republic of Uzbekistan.

Moreover, a plant for the manufacture of continuous basalt fiber is being built in the city of Jizzakh [2]. The planned capacity of this plant, which is based on Mega Invest Industrial Company, is 2.5 thousand tons of continuous basalt fibers per year. Nowadays this company is implementing a project on creating a production complex for deep processing of basalt stone, production of basalt fiber, and basalt-composite reinforcement that can be used in the construction of roads, bridges, low-rise buildings, swimming pools, greenhouses, foundations, monoblocks, lighting poles, and many other sites [3].

These initiatives indicate a promising future for the use of basalt rocks in the production of building materials in Uzbekistan. The local availability of these rocks not only provides a sustainable source of raw materials but also contributes to the growth of the local economy.

There are many researches worldwide on possibilities of use of basalt rocks in the production of building materials, but investigation showed few challenges in using basalt rocks for construction: at first, it is the shaping difficulty. Basalt has a high compressive strength ranging from 200 MPa to 350MPa, which makes it very difficult to shape or dress into tiny slabs [4]. Therefore we need to develop a method for shaping products from basalt or melt it before shaping and forming. On the other side, there is an inconsistency reported in the literature with respect to the behavior of basalt fiber reinforced composites [5].

Volcanic rock masses like basalt exhibit temporal and spatial variability, even at the scale and duration of engineering projects [6]. Because of this variability we need to carefully mass characterization of rock, ranging from mm to dm scale. Laboratory experiments must be carefully planned and undertaken to characterize as many of the anticipated lithology as possible since empirical and published values cannot capture this variability [7-8].

Despite these challenges, basalt's benefits such as its high modulus of elasticity, high elastic strength, corrosion resistance, high-temperature resistance, extended operating temperature range, and ease of handling make it a promising material for construction.

MATERIALS AND METHODS

In the conditions of Uzbekistan, to provide raw materials in the production of building materials, a promising direction is the use of widespread rocks (basalts, diabases) from deposits located on the territory of our republic. Building materials based on basalt rocks are rightfully energy-saving. Due to the special properties of basalt, building materials produced on its basis have lower vibration resistance, do not burn and are not damaged at high temperatures.

Uzbekistan have large reserves of basalt, which is unique as an additional building material. A promising basalt deposit is the Arvaten-Karakia occurrence, located 12 km west of the city of Jizzakh, 1.5 km south of the Jizzakh-Yangikishlak highway.

Glass ceramics and products made from them are produced mainly using glass and ceramic technology, sometimes using a chemical method. The most common is the so-called glass technology, which includes melting glass from a batch, molding products (pressing, rolling, centrifugal casting) and heat treatment. The last stage ensures the crystallization of glass due to the introduction of special initiators into the glass mass - catalytic additives - oxides of Ti, Cr, Ni, Fe, fluorides, sulfides, platinum group metals, as well as due to the tendency of glasses to segregation, which promotes the formation of an interface and brings the chemical composition closer microregions to the composition of future crystals. Heat treatment is usually carried out in a two-stage mode; the temperature of the first stage lies in the region of the softening temperature of glass and corresponds to the maximum rate of nucleation of crystallization centers; at the temperature of the second stage, crystals of the leading phase are released, which determines the basic properties of glass ceramics.

Modern physical chemical methods as crystal-optical, x-ray diffraction, differential thermal analysis, as well as classical methods of glass and glass ceramics technology were used in the experiments. The phase composition of the studied raw materials and experimental masses was determined by x-ray diffraction on Bruker AXS D8 Advance diffractometer, Bruker, Germany. Conditions - Cu-Kα - cathode, step - 0.05, speed 2 deg/min. The Match! program package was used to interpret the radiographs (Crystal Impact GbR, Bonn, Germany). In the calculations and identification of phases, tables and reference books were used, as well as an Internet file of minerals at www.mindat.org [8-9].

RESULTS AND DISCUSSION

Chemical composition of basalt from the Karakiya deposit is as follows: SiO_2 -38.88; Fe_2O_3 total - 10.84; incl. Fe_2O_3-2.94; FeO-7.11; Al_2O_3-10.93; CaO-15.14; MnO-0.10;

K_2O- 0.50; Na2O-3.08; P_2O_5 -0.40; SO_3 sulfate -<0.10; SO_3 total - <0.10; SO_3 sulfide-<0.10; H_2O-0.49; MgO-4.84; TiO_2-2.36; LOI-12.94.

Calculation of the acidity coefficient of basalt is determined using the formula:

$$K = (SiO_2+Al_2O_3+TiO_2) / (CaO+MgO+FeO+Fe_2O_3+Na_2O+K_2O)$$

$$K_{(Karakiya\ basalt)} = 56.54 / 43.46 = 1.3$$

The most suitable for the production of stone casting and glass-ceramics are rocks with a Coefficient in the range of 1.3-1.8; at values of $K > 1.8$-1.9 and at $K< 1.3$, mixing should be carried out with more basic and more acidic materials, respectively.

Basalt stone casting refers to materials and products obtained from molten rocks - basalts, diabases, etc. by casting. Stone casting consists of crystalline formations 5-800 microns in size and an amorphous glassy mass. Depending on the main material-forming mineral, it is divided into pyroxene, melilite, mullite, corundum, etc. For the production of building materials, pyroxene (basalt, diabase, basalt-dolomite, etc.) conglomerates of black, greenish, light yellow and almost white colors are usually used.

Basalt stone casting is characterized by the following properties: density – 2800-3000 kg/m^3; compressive strength - 100-500 MPa, bending strength - 10 - 30 MPa; hardness on the Moos scale for pyroxene casting - up to 7.5, for corundum casting - up to 9; abrasion losses – 1-1,4 kg/m^2; porosity – up to 0.2%; water absorption – 0.1-0.2%. The advantages of stone casting include high chemical resistance, heat and wear resistance, significant mechanical strength, and hardness. It is not subject to corrosion and aging, which compares favorably with metals and polymers [10-12].

Basalts can also be used to produce glass-ceramics, which are widely used in our lives. Sitalls or glass-ceramic materials are inorganic materials obtained by the directional crystallization of various glasses during their heat treatment [13-14]. They consist of one or more crystalline phases. In glass ceramics, finely dispersed crystals (up to 200 nm) are evenly distributed in a glassy matrix. The amount of crystalline phases in glass ceramics can be 20-95% (by volume). By changing the composition of the glass, the type of crystallization initiator (catalyst) and the heat treatment mode, glass ceramics with different crystalline phases and specified properties are obtained [15]. Sitalls were first made in the 50s of the 20th century. Materials similar to glass ceramics are also called pyroceram, devitroceram, and glass ceramic.

Glass-ceramics have very high strength, hardness, wear resistance, low thermal expansion, chemical and thermal stability, gas and moisture impermeability. According to their purpose they can be divided into technical and construction

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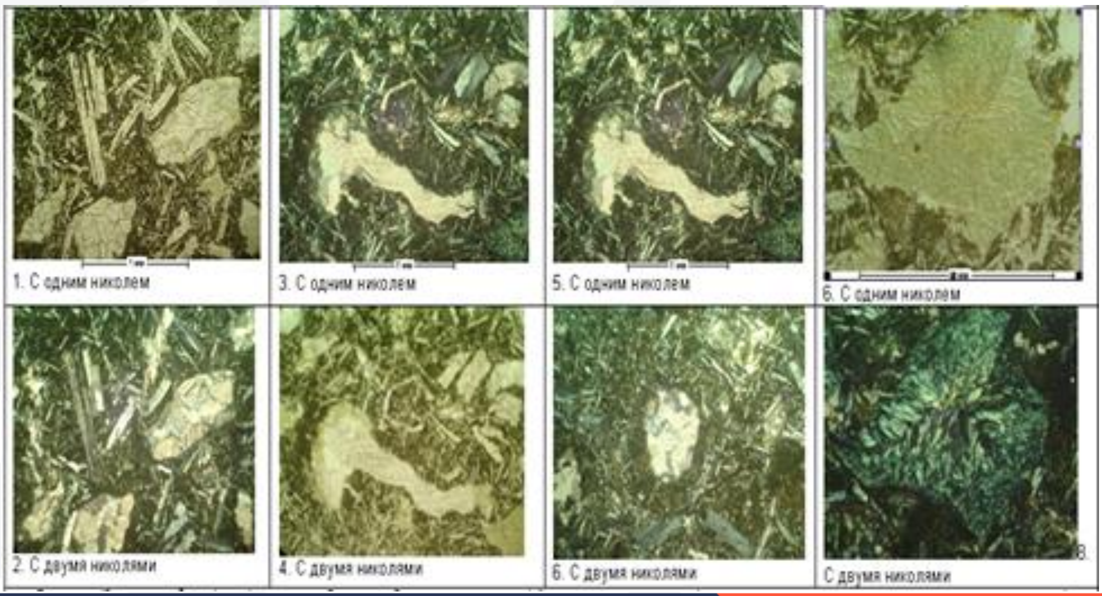
materials. Technical glass ceramics are produced on the basis of the systems: Li_2O-Al_2O_3-SiO_2, MO- Al_2O_3-SiO_2, Li_2O-MO- Al_2O_3-SiO_2, where M is Mg, Ca, Zn, Ba, Sr, etc.; MgO- Al_2O_3-SiO_2-K_2O-F; MO-B_2O_3- Al_2O_3 (where M-Ca, Sr, Pb, Zn); PbO-ZnO-B_2O_3- Al_2O_3-SiO_2, etc. According to the main property and purpose, they are divided into high-strength, radio-transparent chemically resistant, transparent heat-resistant, wear-resistant and chemically resistant, photositalls, mica-sitalls, biositalls [16], glass-ceramic cements, sital-enamels, glass-ceramics with special optical or electrical properties [17-18].

Glass-ceramics is characterized by increased mechanical strength, higher wear and chemical resistance compared by stone casting products [19]. These advantages of glass ceramics are explained by their composition and more advanced dense structure, which makes it possible to more fully use the capabilities of the crystalline structure in many areas of our life [20-22].

Microscopy and X-ray analysis results represented on Figure 1, showed that the crystalline phases of basalt of Karakiya deposit are represented by minerals of calcite, augite, chlorite, anorthite, small amounts of magnetite and albite. To obtain acid- and heat-resistant materials, the glass ceramics composition was calculated to obtain of composition of anorthite [23].

Anorthite is calcium-rich member of the plagioclase group of minerals, with chemical formula of $CaAl_2Si_2O_8$. High chemical and mechanical propersties such a hardness of 6 on Moos scale, specific gravity of 2.7-2.8, melting temperature of 1553^{o}C makes it promising component in the production of glass-ceramics. To obtain the composition of anorthite in glass-ceramics basalt melt should be enriched by one or more components such as CaO, MgO and SiO_2, to achieve needed ratio of oxides in the batch.



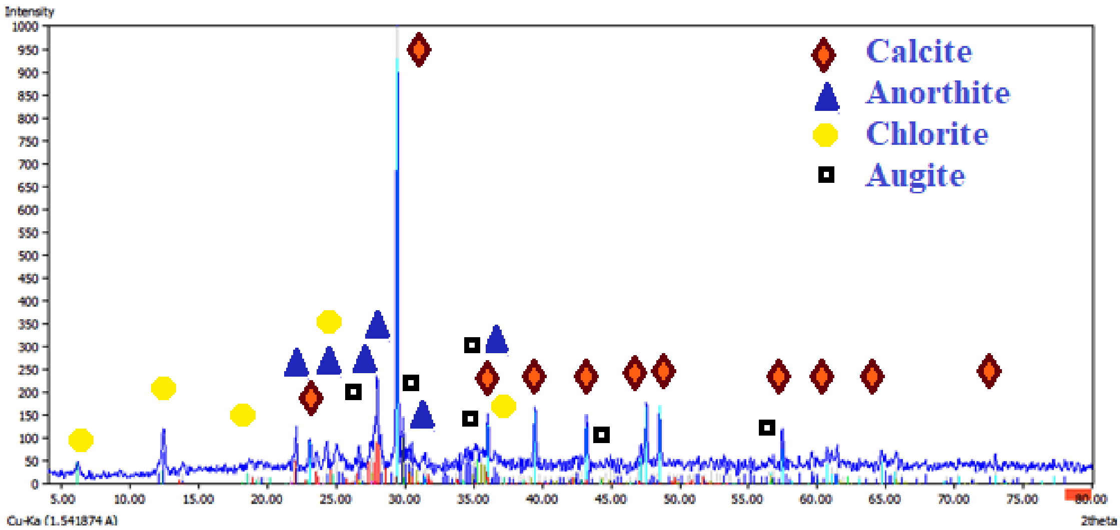


Fig.1. Optical microscopy and X-ray diffraction analysis of basalt.

Glass melting and crystallization

As a main raw materials was used local raw materials and industry wastes of Uzbekistan. For the production of glass-ceramics of with anorthite structure, a composition was calculated, in wt. %: Basalt of Karakiya (Uzbekistan) - 68; Primary enriched kaolin of Agren deposit (Uzbekistan) – 20; Alumina containing waste from Shurtan GCC – 12.

Glass was melted in an electric furnace with carborundum heaters at a temperature of 1450°C (holding time 1 h.), obtained black color glass was poured onto a heated metal plate.

Glass crystallization was carried out in a laboratory muffle furnace. The glass samples were heat-treated at different temperatures - from 700 to 1000°C (temperature rise at a rate of 40 °C/min) with holding at the final temperature for 3 h. Glass-crystalline samples of black and dark violet-black colors were obtained.

As a result of the studies, the optimal temperature of two-stage crystallization for the formation of a finely dispersed structure of anorthite glass ceramics was chosen as 800 °C (1 h.) and 1000 ° C (1 h.).

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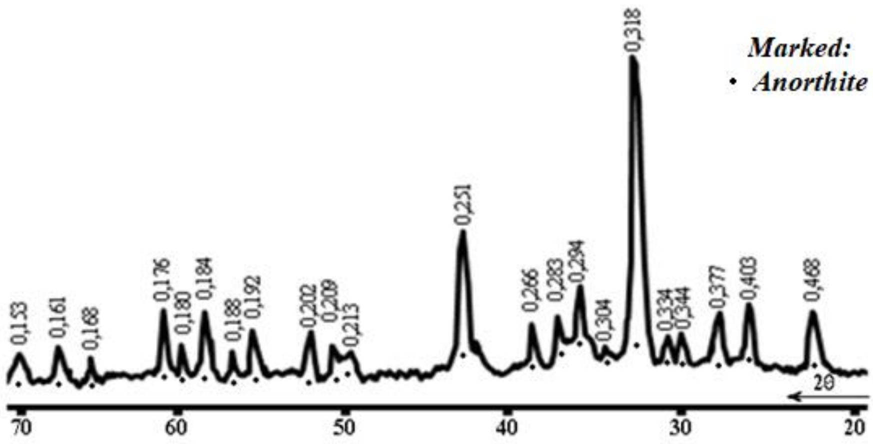

Fig. 2. Diffraction pattern of a sample crystallized under optimal conditions.

The physicochemical properties of glasses and glass ceramics synthesized on the basis of Karakiya basalt are given in Table 1.

Table 1 The physicochemical properties of glasses and glass ceramics synthesized on the basis of Karakiya basalt

Property	**Glass**	**Glass-ceramic**
Density, kg/m^3	2700	3100
Ultimate compressive strength, MPa	250	670
Chemical resistance, %		
to 35% NaOH	95,0	99,8
to HCl (conc)	99,0	99,9
to H_2SO_4 (conc)	99,1	99,9
Crystallization temperature, ^oC		
Lower limit	800	
Upper limit	1000	
TCLE, $\alpha{*}10^{-7}$ degree^{-1}	60	55
$T_{melting}$, ^oC	1400	

The technological scheme for the production of glass-ceramic tiles based on basalts from the Karakiya deposit consists of the following technological stages: preparation of raw materials, preparation of the glass batch, glass melting, rolling molding, crystallization, cutting into sheets and tiles, sorting and packaging of finished products.

1. The process of preparing raw materials includes: drying, grinding and sifting:
a) Preparation of basalt.
b) Preparation of kaolin.
c) Preparation of alumina-containing solid waste.
2. Glass melting in furnace at 1450 ^{o}C.
3. The glass strip is formed using the continuous rolling method. The welded glass melt comes from the working part of the furnace bath and is captured by the upper and lower rolls rotating in different directions [24].
4. Crystallization of the glass strip is carried out in an electric roller furnace. The maximum heat treatment temperature is 1000°C; when passing through a zone with a temperature of 800°C in the furnace, it is held for 2 hours.

Crystallized sheets and slabs are products made from glass-crystalline material obtained from basalt, can be used to make rolled sheets and slabs, as well as pressed slabs of white and gray colors, painted in the mass or with a surface painted with ceramic paints [25].

CONCLUSION

Synthesized glass ceramics has high compressive strength (670 MPa), high resistance to alkalis and acids. Knowledge of the laws of isomorphism made it possible to design and synthesize glass-ceramic from basalt, kaolin and industrial solid waste, where the crystalline phase is mineral anorthite, one of the main representatives of feldspars. Most likely we have in glass ceramics a solid solution of feldspar crystal structure. The calcium ion positions include the calcium ion itself, the doubly charged iron ion, the doubly charged manganese ion, the magnesium ion, the potassium ion, and the sodium ion. The second position includes elements such as aluminum and iron (III). The silicon position may contain titanium (IV) ions. Synthesized glass ceramics recommended for production of wear and acid resistant grey and black colored tiles.

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