Study on the Production of Glass-Ceramics from Diabase Rocks: A case study of Uzbekistan

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Abstract. The article discusses the features of the chemical and phase composition of diabase rocks, including the rocks of Arvaten and Uzunbulak deposits of Uzbekistan. Glass materials based on diabase rocks have been obtained. The physicochemical properties and structural formation of glasses during crystallization were studied by X-ray analysis. Analysis of the chemical and mineralogical compositions of the diabases of the studied deposits indicates their multiphase character. IR spectroscopic, electron microscopic, microscopic and X-ray data show the presence in diabases of several main phases in the form of oligoclase with the formula (Ca,Na)$Al_2Si_2O_8$, orthoclase K($AlSi_3O_8$), iron-containing pyroxene solid solution of the augite type (Mg, Fe^{2+})[$Si_2O_6CaFe(AlSiO_6)$], calcite $CaCO_3$, chlorite (clinochlore) with the formula $Mg_{4.5}Al_{2.5}[OH]_8(Si_3AlO_{10})$, olivine $(MgFe)_2SiO_4$ and low contents of low-temperature quartz β-SiO_2.

1. Introduction

In recent years, the demand for traditional ceramic and glass products in various sectors of the national economy has been increasing in the world, while the increase in production volumes has led to an increase in the demand for raw materials. Therefore, many researches in the world related to the synthesis of glass crystal materials are to study raw materials (rocks and industrial waste) that replace traditional raw materials and to obtain glass crystal materials with high physical and mechanical properties based on them, and at the same time to further expand the fields of use due to the reduction of glass crystal materials production costs. aimed at expanding [1]. The ability of liquefaction of igneous rocks at low temperatures and rapid crystallization helps to reduce the cooking temperature and increase the strength if they are used to obtain ceramic products [2].

According to the analysis of scientific research conducted in the world on the creation of glass crystal materials, it was synthesized in the USA in the 50s of the last century by D. Stookey at the Koring company, and this new material was called "Pirokeram". In 1953, D. Stookey accidentally discovered a white glass-ceramic material by thermally heating glass samples to 450 °C (840 °F) in the Koring research and development department [3]. Since 1958, the production of household goods made on the basis of this material has been established and found its place in the consumer market of North America, Asia, Australia and other regions of the world. Glass-ceramic materials have become widely used in: daily life (e.g. on stoves) [4], industrial applications (e.g., abrasion-resistant tiles in industrial pipes), in the environment (e.g., waste recycling) [5,6], biomedical applications (eg prostheses for surgical implants) [7,8], architectural applications [9,10] and in more advanced technological applications (eg telescope mirrors, warheads and composite materials) [11].

Widespread rocks - basalt, diabase and gabbro in most literary sources are called basalt rocks. This is due to the similarity of their chemical compositions and volcanic origin. But various factors (temperature, pressure, etc.) and especially the processes occurring when they emerge in solid melts, with the same ions (molecules), lead to the formation of various compounds (minerals). For example, basalt rock, during a volcanic eruption in a liquid state, quickly cools under the influence of the external environment, as a result, it has a fine-grained structure and the glass phase is preserved in it. Diabase rocks, without pouring out of the crater of the volcano in the process of slow cooling, completely crystallize, the glass phase is absent and diabase differs from basalt in large crystal sizes. Gabbro at high temperatures and pressures, the non-erupted part of the lava cools at a very low rate, and is characterized by very large

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grain sizes of minerals. Therefore, basalt, diabase and gabbro, having similar chemical compositions, are considered different rocks.

2. Materials and Methods

In this article, the chemical, mineralogical and phase composition of diabase rocks is studied in order to obtain glasses and glass ceramics materials. X-ray, microscopic, IR-spectroscopic and differential analysis methods were used as research methods. Each method separately, as is known, provides information only about one side of the investigated solid, and therefore, for the reliability of the diagnosis of the material composition, the need arises for the complex application of various methods.

In Uzbekistan, such rocks are quite widespread. One of the promising objects is Arvaten diabase deposit, located in Jizzakh region, 9 km north-west of Jizzakh lime plant, 1.5 km from the village of Kuyabash. It is confined to the northeastern slopes of the mountains of the Northern Nurata. The asphalt road Jizzakh - Farishch runs along the village. The reserves are 95 million tons. Uzunbulak I deposit is located 22-23 km southeast of Gallyaaral district, 0.5 km north and northwest of the village Uzunbulak, on the southwestern slopes of the Malguzar mountains, in fact, being the beginning of the Malguzar mafic and ultramafic belt. The manifestation is connected with the nearest villages of Abdukarim, Aulye, Shatyrakatan by dirt roads. Stocks of diabase are 9.5 million tons. Uzunbulak II diabase deposit is located 22-23 km southeast of Gallyaaral district center, 12 km northeast of the village. Abdukarim, 2.0 km southeast of the village Uzunbulak and is located on the southwestern slopes of the Malguzar mountains. Reserves are 42 million tons.

The works used such research methods as electron microscopy, radiography, differential thermography, infrared spectroscopy, as well as instruments for determining physical, mechanical and chemical properties.

The chemical composition of the studied diabases is dominated by silica, alumina, oxides of calcium, magnesium, and iron (Tables 1). The study of samples of diabase deposits practically meet all the requirements for the quality of raw materials of the silicate industry. In accordance with the above tasks, the diabases of Arvaten and Uzunbulak deposits were first of all chosen as the objects of study, a comprehensive study of which allows us to establish their suitability in industries, the creation of which will avoid the importation of basalt (basalt, diabase and gabbro) products to the republic and even organize their export.

Table 1. The results of chemical analysis of samples of diabase rock of Arvaten deposit (wt%).

Oxides	Diabase rock of Arvaten deposit	Diabase rock of Uzunbulak I	Diabase rock of Uzunbulak II
SiO_2	47.98	48.64	42.20
Fe_2O_3	5.85	4.95	7.42
FeO	7.70	9.76	8.31
TiO_2	1.79	3.55	4.83
MnO	0.11	0.16	0.12
Al_2O_3	13.48	13.89	15.14
CaO	8.46	8.42	6.40
MgO	5.81	5.27	5.21
Na_2O	2.86	2.12	2.4
K_2O	1.28	1.64	0.81
L.O.I.	4.68	3.60	6.72

3. Results and Discussion

Based on the analysis of diffraction patterns (Fig.1), the presence in the composition of Arvaten rock of such minerals as oligoclase (d/n=0.259; 0.280; 0.318; 0.367; 0.401; 0.425; 0.644 nm), orthoclase (d/n=0.177; 0.190; 0.264; 0.283; 0.292; 0.318; 0.383 nm), augite (d/n=0.162; 0.212; 0.221; 0.252; 0.298 nm), chlorite (d/n=0.160; 0.186; 0.187; 0.199; 0.208; 0.238; 0.243; 0.353; 0.705; 1.420 nm) and calcite (d/n=0.156; 0.227; 0.302 nm).

The IR transmission spectra of the studied diabases, obtained by the traditional method, are shown in Fig. 2, and the IR transmission spectra of the studied diabases consist of absorption bands typical of silicate materials. The IR spectra of plagioclases in diabases are characterized by bands in the range of 900-1200 cm^{-1} and in the range of 500-700 cm^{-1}. The bands in the high-frequency region are due to antisymmetric stretching vibrations of the Si–O–Si(Al) bonds, the bands at 645 cm^{-1} and 585 cm^{-1} correspond to the bending vibrations of the O–Si(Al)–O bonds. The infrared spectra of pyroxene are characterized by bands in the region of 1100 and 950 cm-1. These bands are due to antisymmetric stretching vibrations of the Si–O–Si bridge bonds. The bands in the mid-frequency region of 500-550 cm^{-1} correspond to stretching vibrations of non-bridge Si–O bonds. The IR spectra (Fig. 2b, c) of olivine in diabases are characterized by bands at ~1060, 960, and 910 cm^{-1}. These bands are due to stretching vibrations of Si-O bonds in SiO4 tetrahedra. Bands in the region of 400-700 cm^{-1} are due to bending vibrations of O–Si–O bonds.

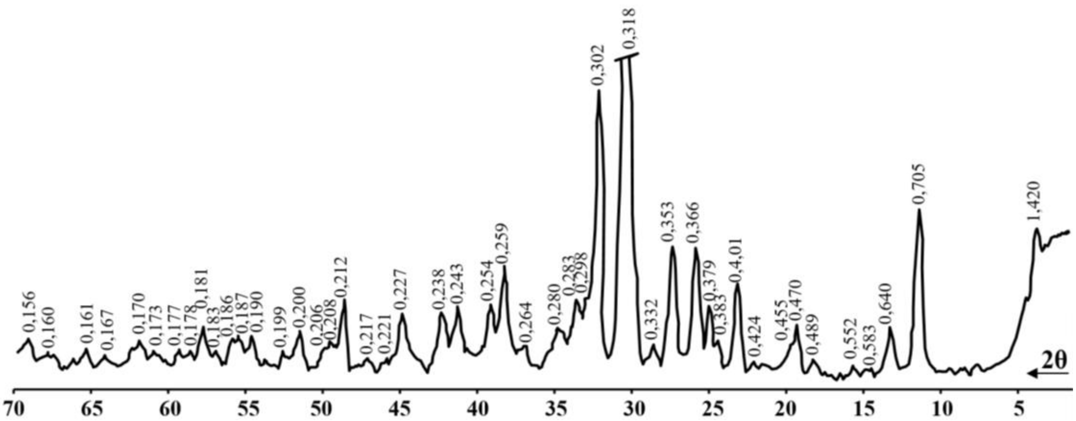


Fig. 1. X-ray patterns of initial samples of diabase deposits Arvaten.

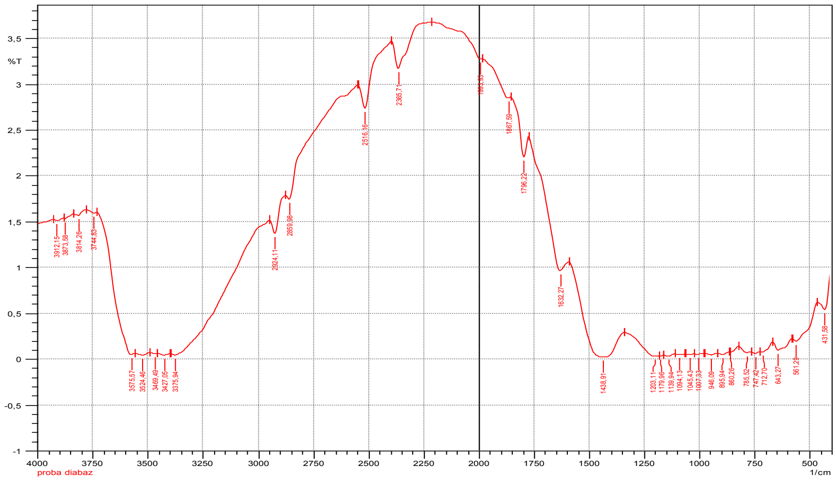
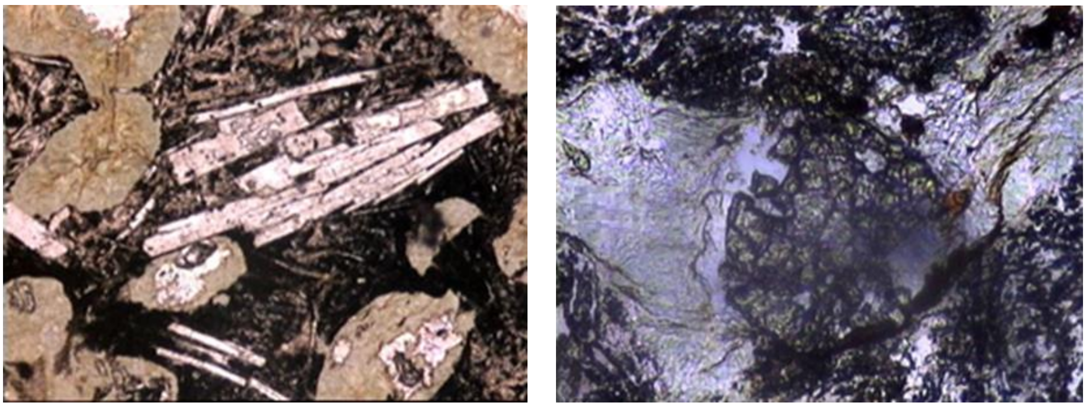


Fig. 2. IR spectra of the objects of the study Arvaten.

A microscopic study of transparent sections made from diabase rocks of the Arvaten deposit revealed its dolerite structure; against the background of the microdolerite structure, plagioclase crystals are observed in the form of tensile prisms with dimensions of 0.06x0.4 mm, 0.02x0.3 mm and 1.4x0.8 mm (Figure 3)a and at a 500-fold increase (Figure 3b) between plagioclase prisms, secondary minerals were revealed - chlorite, calcite and quartz, formed as a result of alteration of pyroxene.



a *b*

Fig. 3. Microscopic image of the diabase of the Arvaten deposit at 160x (a) and 500x (b) magnifications

The differential thermal analysis of the diabase of the Arvaten deposit shows (Fig. 4) that several exo- and endothermic effects are observed on the thermal curves, of which the endothermic effect manifested in the temperature range of 540-660ºC is characterized by the decomposition of water from the chlorite mineral $Mg_{4.5}Al_{2.5}[OH]_8(Si_3AlO_{10})$, the second endothermic effect, which is observed at 880ºC corresponds to the decomposition of the mineral calcite, above 900ºC against the background of horizontal DTG and TG lines, the endothermic effect on the DTA line shows the absorption of heat to form a liquid phase as a result of the beginning of sample melting.

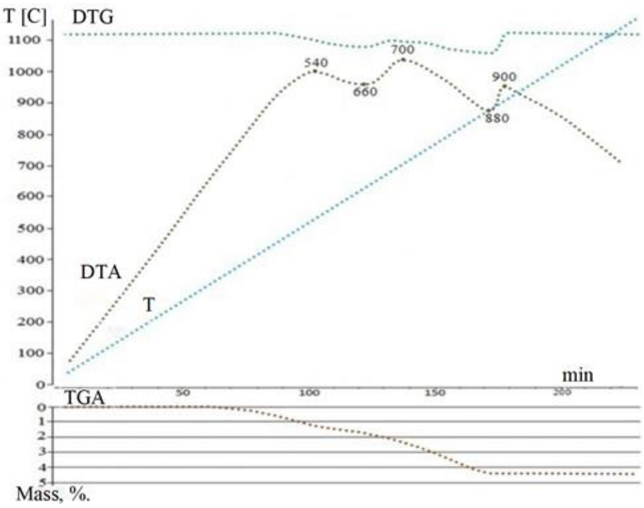


Fig. 4. The differential thermal an alysis of the diabase of the Arvaten deposit.

The chemical analysis of the rock and recalculation of the results of the analysis for the normative mineral composition (Table 2) show that the content of plagioclase is within 50%, judging by the ratio of anorthite and albite components, the composition of plagioclase is closer to oligoclase, the presence of a significant amount of the femic component. The latter, that is, primary minerals, in the real mineral composition are completely replaced by chlorite (pyroxene crystals), calcite, titanite (in the groundmass), etc. The high content of MgO = 5.81% is associated with the abundant development of chlorite aggregates in the groundmass, pseudomorphs along pyroxene, filling the crusts of numerous pores-tonsils of diabase amygdaloid. Numerous aggregates of titanite were formed during the decomposition of titanium-containing ore minerals, dark colours. Thus, plagioclase-oligoclase takes part in the mineral composition of the rock, chlorites are developed from dark colors - cryptogranular to large-scale aggregates in the form of pseudomorphs after pyroxenes, crusts and content of tonsils, pores are also filled with calcite, titanite, sometimes quartz, garnet. Relics of the primary dark-colored mineral (pyroxene) were not observed.

Table 2. The results of recalculation of the chemical analysis of diabases of Arvaten deposit for the normative mineral composition.

Oxides	Mass percent, %	Molecular Quantities	Minerals							
			Orthoclase	Albite	Anorthite	Pyroxene	Chlorite	Magnetite	Ilmenite	Quartz
SiO_2	47.98	798	84	276	144	158	112	-	-	24
TiO_2	1.79	25	-	-	-	-	-	-	25	-
Al_2O_3	13.48	132	14	46	72	-	-	-	-	-
Fe_2O_3	5.85	36	-	-	-	-	-	36	-	-
FeO	7.70	107	-	-	-	25	21	36	25	-
MnO	0.1	1	-	-	-	-	-	-	-	-
CaO	8.46	151	-	-	72	79	-	-	-	-
MgO	5.81	144	-	-	-	54	90	-	-	-
Na_2O	2.86	46	-	45	-	-	1	-	-	-
K_2O	1.28	14	14	-	-	-	-	-	-	-
Minerals %			7.7	25.3	19.8	21.7	15.5	5.0	3.4	1.6

Thus, the analysis of the material compositions of the diabases of Arvaten and Uzunbulak deposits indicates their multiphase nature. IR spectroscopic, electron microscopic, microscopic and X-ray data show the presence in diabases of several main phases in the form of oligoclase with the formula $(Ca,Na)Al_2Si_2O_8$, orthoclase $K(AlSi_3O_8)$, iron-containing pyroxene solid solution of the augite type $(Mg, Fe^{2+})[Si_2O_6*CaFe(AlSiO_6)]$, calcite $CaCO_3$, chlorite (clinochlore) with the formula $Mg_{4.5}Al_{2.5}[OH]_8(Si_3AlO_{10})$, with a low content of quartz β-SiO_2. Minor ore minerals are also present. The presence of olivine $(MgFe)_2SiO_4$ was found in the diabase of Uzunbulak deposit.

In order to study the changes in mineralogical compositions during heat treatment of diabase rock samples from Arvaten and Uzunbulak deposits, we subjected them to heat treatment until the rock melted. The products of heat treatment in order to determine the phase compositions at different temperatures were studied by X-ray diffraction.

Interpretations of X-ray patterns during heating of diabase rocks of Arvaten and Uzunbulak deposits at different temperatures are given. According to the results of X-ray analysis, it can be seen that the diabases of Arvaten and Uzunbulak deposits after heat treatment, at a temperature of 400 °C for 4 hours, retain the characteristic diffraction lines of the phases of the original minerals. A 4-hour heat treatment at a temperature of 800 °C shows the absence of characteristic phases of calcite and chlorite minerals, which indicates the destruction of their crystal lattices at this temperature. Thermal treatment of samples of Arvaten and Uzunbulak diabases for 1 hour at a temperature of 1200 °C causes the melting of crystalline phases - their transition to a liquid glass phase, upon cooling of which the X-ray patterns confirm the transition of the samples to an amorphous state.

Studies of the behavior of the diabase rock of Arvaten deposit have shown that the transition of the rock to the molten state begins at a relatively low temperature and ends at 1200 °C, which suggests the possibility of obtaining low-temperature glasses as the basis for the production of glass-ceramics.

According to the results of the study of diabase rocks of Arvaten and Uzunbulak deposits, it was found above that they melt at 1200 °C, but to obtain them in a glassy state, a temperature of the order of 1350-1400 °C is needed. Glass melting was carried out in electric furnaces with silicate heaters at temperatures of 1350-1400°C, the resulting melts were poured onto a metal plate. The obtained glasses were homogeneous, transparent and had various shades of black color.

The synthesized glasses were subjected to differential thermal analysis.

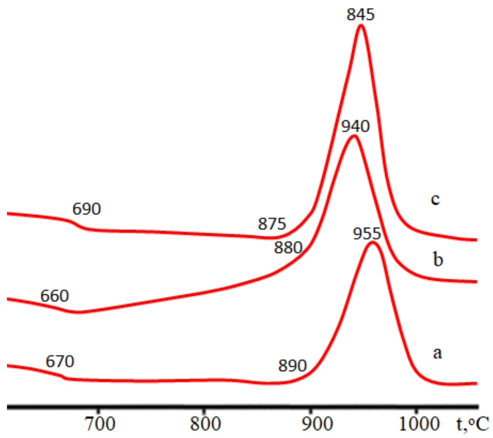


Fig. 5. DTA curves of glasses synthesized from diabase samples: a-Arvaten, b-Uzunbulak I and c-Uzunbulak II.

As can be seen from fig. 5., there is a similarity of the differential thermal curves of all three samples of diabase glasses. So, in the range of 660-730°C, weak endothermic effects are observed, obviously associated with the process of heat absorption, which is necessary for the formation of crystal nuclei in accordance with the existing theory of glass crystallization. Starting from temperatures of 875-890°C, the inflection of thermal curves begins, turning into intense exothermic effects associated with the growth of crystals of the precipitated crystalline phase. The maxima of exothermic effects are also in a fairly close temperature range of 940-955°C.

In order to study the formation of crystalline phases during heat treatment, samples of diabase glasses tempered on a metal plate were annealed at temperatures of 400, 500, 600, 700, 800, 900, 1000, 1100, 1200°C with an hourly exposure.

The obtained samples of heat-treated glasses were subjected to X-ray phase analysis using the powder method. It has been established that after heat treatment at 600°C there are no visible changes in glassy samples, X-ray patterns show an amorphous state. After annealing at 700°C, the glasses lose their transparency and luster, but the X-ray diffraction patterns also show an amorphous state. Samples after heat treatment at 800, 900, 1000 and 1100°C acquire crystalline structures, the X-ray patterns of which are shown in Figure 6.At a temperature of 1200°C, melting of the samples is observed, which is detected on the X-ray patterns by a sharp decrease in the intensity of the diffraction lines of the crystalline phases, passing into the amorphous glass phase. The results of interpretation of X-ray patterns of heat-treated glasses No. 1, 2 and 3.

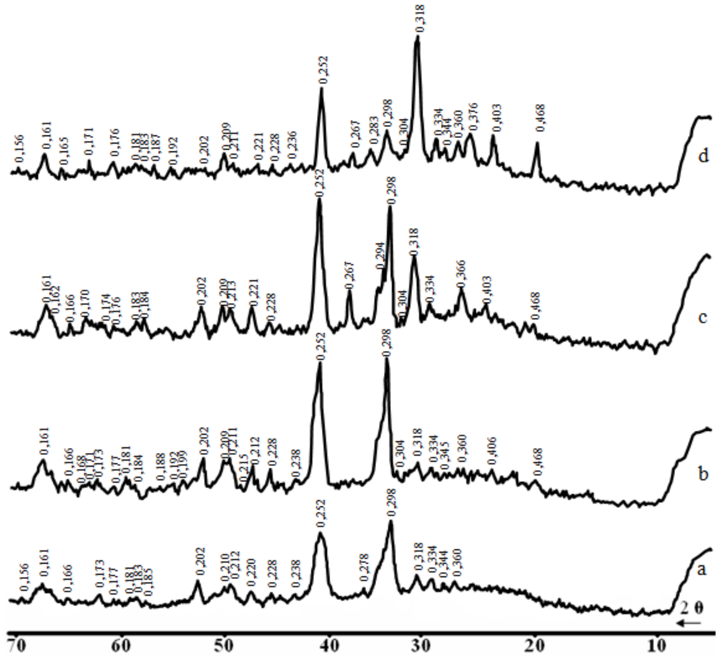


Fig. 6. X-ray patterns of glass samples crystallized at different temperatures from diabase samples of Arvaten deposit. Heat treatment of glasses at temperatures: a-800 °C, b-900°C, c-1000°C, d-1100°C.

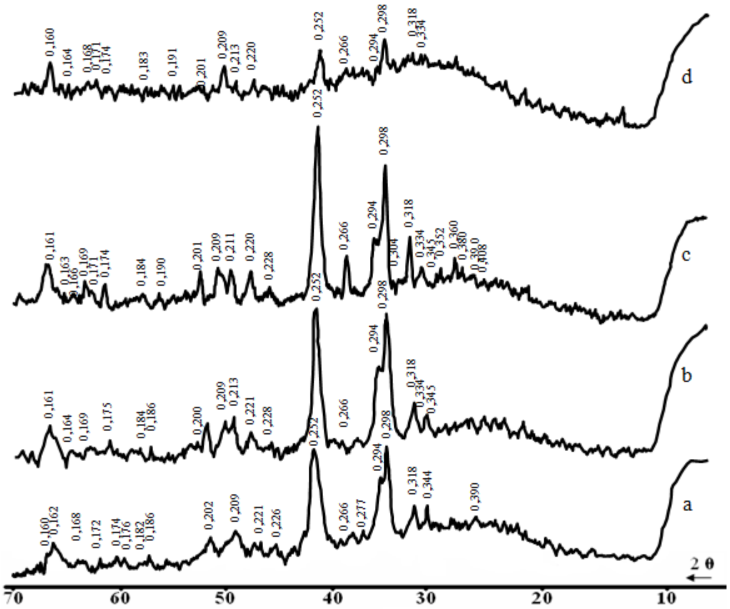


Fig. 7. X-ray patterns of glass samples crystallized at different temperatures from Uzunbulak I diabase samples. Heat treatment of glasses at temperatures: a-800 °C, b-900°C, c-1000°C, d-1100°C.

X-ray patterns of glass samples crystallized at different temperatures from the studied three samples of diabases are shown in Figs. 6-7. and the results of their interpretation show that in all three cases, the crystallization of two main phases occurs - a solid solution of iron-containing pyroxene - augite and anorthite.

X-ray diffraction patterns of samples of all three glasses after heat treatment at 800°C reveal signified diffraction lines of augite and only individual lines of anorthite. With an increase in temperature, the intensities of the lines of both

minerals increase, and for glasses of diabases Arvaten and Uzunbulak II, after annealing at 1100°C, the lines of oligoclase already predominate over the lines of augite, which indicates the sequence of phase separation.
On X-ray diffraction patterns of Uzunbulak I diabase glass samples, the intensity of anorthite lines remains low with increasing temperature, and at 1100°C, the intensity of all lines is sharply reduced, which indicates the beginning of sample melting.
The X-ray diffraction patterns of all samples contain a number of low-intensity diffraction lines related to impurity phases, which cannot be unambiguously identified due to their low contents.
Comparison of thermographic curves with X-ray diffraction data makes it possible to unambiguously characterize an important feature of the crystallization of the synthesized diabase glasses. The obtained results testify to the multiphase nature of the crystallized samples obtained after heat treatment of glasses. In this regard, in order to obtain monomineral glass-ceramic samples with high values of physicochemical and mechanical properties, it is necessary to batch the initial diabases.

4. Conclusion

The conducted research allowed to draw the following conclusions:
Based on the results of a comprehensive study of samples of diabases from Arvaten and Uzunbulak deposits, relatively low temperatures were established for the beginning of their melting - about 1200 °C, which showed the possibility of their melting at relatively low temperatures to obtain glasses.
Analysis of the chemical and mineralogical compositions of the diabases of the studied deposits indicates their multiphase character. IR spectroscopic, electron microscopic, microscopic and X-ray data show the presence in diabases of several main phases in the form of oligoclase with the formula $(Ca,Na)Al_2Si_2O_8$, orthoclase K(AlSi3O8), iron-containing pyroxene solid solution of the augite type $(Mg, Fe^{2+})[Si_2O_6*CaFe (AlSiO_6)]$, calcite $CaCO_3$, chlorite (clinochlore) with the formula $Mg_{4.5}Al_{2.5}[OH]_8(Si_3AlO_{10})$ and low contents of low-temperature quartz β-SiO_2. Minor ore minerals are also present. The presence of olivine $(MgFe)_2SiO_4$ was found in the diabase of Uzunbulak deposit.
Analysis of the mineralogical compositions of diabases of the studied deposits after heat treatment indicates the preservation of their multiphase character up to a temperature of 800°C. Using the methods of X-ray phase and differential thermal analysis, it was established that above 800 ° C, thermal decomposition of chlorite and calcite occurs, the residual crystalline phases are augite, oligoclase and orthoclase, as well as olivine in the samples of Uzunbulak diabases. Heat treatment at 1200°C and with a further increase in temperature leads to the transition to the melt of all the remaining minerals.
Experimental melting of diabase samples was carried out, homogeneous glasses were obtained, their physicochemical properties were studied, thermal analysis was carried out, and the similarity of the differential thermal curves of all three samples of diabase glasses was established.
Thermal treatment of samples of synthesized glasses was carried out in the temperature range of 400-1200°C, crystalline phases were identified by X-ray phase analysis. It has been established that after heat treatment at 800, 900, 1000 and 1100°C, in all three cases, crystallization of two main phases, augite and anorthite, occurs. At a temperature of 1200°C, melting of the samples is observed, which is detected on X-ray patterns by a sharp decrease in the intensity of the diffraction lines of crystalline phases.
It has been established that the crystallization of the investigated diabase glasses does not lead to the formation of glass-ceramic products with a monomineral crystalline phase suitable for the production of glass-ceramics. In this regard, to solve the problem of obtaining monomineral glass-ceramic, it is necessary to carry out their rational batching.

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