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STUDY OF MINERAL FORMATION PROCESSES DURING FIRING OF CERAMIC MASSES CONTAINING MUD VOLCANO ERUPTION PRODUCT

Yasin Khalilov[1], Sevinj Akbarova[2*], Vasif Shahmarov[2]

[1]Baku Engineering University, Baku, Azerbaijan
[2]Azerbaijan University of Architecture and Construction, Baku, Azerbaijan

Abstract. As a result of the research, the mineralogical compositions of the eruption products of the mud volcanoes (EPMV) of Azerbaijan Keyreki, Sangachal and Kobu and the products of their firing were established. X-ray phase analysis showed that despite the remoteness of their deposits, the phase compositions of all three eruption products are close and are represented by quartz, feldspar, montmorillonite, kaolinite, illite, calcite, hematite and an amorphous phase. As a result of the studies, the mechanisms of mineral formation in EPMV-containing systems that differ in raw material composition and firing temperatures were established. The research results showed that the introduction of NaF into masses containing Kobu EPMV leads to a decrease in α-quartz and an increase in diopside, and the introduction into lime-faience masses with Sangachal EPMV leads to a sharp increase in the diopside content and a decrease in the glass phase content. The introduction of NaF into masses with Keyreki EPMV contributes to a decrease in the α-quartz content of the glass phase and an increase in feldspar and diopside. It has been established that NaF has a more significant effect on the process of mineral formation in mixtures with Keyreki EPMV, which may be due to its high dispersity and the optimal ratio of components in the mixture. The data obtained show that the effect of the NaF mineralizer in an amount of up to 3% on the process of mineral formation during firing of stone ceramic masses containing EPMV is insignificant. Preliminary studies have also shown the possibility of using volcanic eruption products in the production of building ceramic materials.

Keywords: *Mud volcano, X-ray phase analysis, mineral formation, firing temperature, mineralizers.*

Corresponding Author: *Sevinj Akbarova, Azerbaijan University of Architecture and Construction, Baku, Azerbaijan, e-mail: sevinjakbarova16@gmail.com*

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1. Introduction

About half of the world's mud volcanoes are located in Azerbaijan. Distinctive features of mud volcano eruption products (EPMV) are their high dispersion and homogeneity, deep thermal history, complex composition and structure. In our opinion, huge reserves of EPMV can be a good raw material base for the ceramic industry of the Republic of Azerbaijan in the context of the growing need of the industry for high-quality raw materials.

The physicochemical processes occurring during clay firing have been studied in sufficient depth. Phase transformations, the nature of the obtained minerals, the kinetics

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of mineral formation processes in complex multicomponent systems are determined by the composition, structure and ratio of the initial components, the dispersion of materials, the firing and cooling mode (temperature and firing rate). In turn, the phase composition of the shard largely determines the most important operational and consumer properties of finished products. In our opinion, the uniqueness of these materials predetermines their prospects for use in the production of building materials. In order to expand the raw material base of the building materials industry, it is necessary to conduct deep experimental and theoretical studies on the mechanism of physical and chemical processes, phase transformations and structural changes occurring during firing of raw mix containing EPMV.

Currently, research is being conducted on the use of volcanic ash and mud volcano eruption products in complex multi-component mixtures, in particular in ceramic compositions. Of interest are also works devoted to studying the nature of the processes occurring during the firing of these mixtures (Khalilov *et al*., 2024; Ermolin *et al*., 2023; Vergunov *et al*., 2024; Belfiore *et al*., 2024; Candamano *et al*., 2023; Alraddadi, 2024).

Analysis of literary sources (Levitsky & Klimov, 2005; Golovanov *et al*., 2004; Livandovskaya *et al*., 1988; Chernyak *et al*., 1980; Orlova *et al*., 1989; Maslennikova & Koneshova, 1987; Chaudhuri, 1974; Oyamada & Sumi, 1982; Kiselev & Dutkina, 1977). shows that not enough attention has been paid to the study of the process of mineral formation in raw mixes of different compositions during firing using EPMV. This is apparently due to their limited geographical distribution in the world. Therefore, the relevance of these studies is beyond doubt and the results obtained are of great theoretical and applied importance.

2. Research methodology

At the beginning of the study, the chemical and mineralogical compositions of the EPMV were studied (Tables 1, 2).

Table 1. Chemical composition of EPMV

Name of sample	Na_2O	MgO	Al_2O_3	SiO_2	P_2O_5	SO_3	K_2O	CaO	TiO_2	MnO	Fe_2O_3	BaO	SrO	CL-	L.O.I
Kobu	1,40	2,37	15,15	49,94	0,13	3,84	3,92	2,01	0,76	0,10	8,25	0,05	0,03	0,07	11,97
Sangachal	2,48	2,15	12,80	52,30	0,10	3,00	3,04	4,00	0,73	0,13	6,60	0,009	0,03	0,50	12,11
Keyreki	2,17	2,16	13,34	47,51	0,14	1,40	2,95	8,06	0,81	0,11	6,97	0,05	0,05	0,85	13,40

Table 2. Mineralogical composition of EPMV

Name of sample	SiO_2-(α-quartz)	$CaCO_3$ (calcite)	Feldspar	Gypsum	Illite	Montmorillonite	Kaolinite	Fe_2O_3 (hematite)	FeS_2	Amorph
Kobu	16	-	8	3	12	33	6	3	2	15
Sangachal	19	5	9	-	12	27	8	3	2	15
Keyreki	19	8	15	-	7	26	5	4	1	15

Subsequently, the features of the mineral formation process in raw mixtures with EPMV during firing and without it were studied in the following sequence. At the first stage of the research, the phase transformations of EPMV Keyreki, Sangachal and Kobu were studied after firing at a temperature of 1050°C in the following mode: temperature increase for 8 hours, holding at the maximum temperature for 30 minutes. At the second stage, the mineral formation process was studied using raw mixes of different compositions containing EPMV (Table 3) after firing at a temperature of 1050^{o}C (in the mode: temperature increase for 8 hours, holding at the maximum temperature for 30 minutes) and after firing at a temperature of 1150^{o}C (in the mode: temperature increase for 10 hours, holding at the maximum temperature for 30 minutes). The basic compositions and firing temperatures were adopted in the research based on the data of the Nargizporcelain plant, which produces decorative ceramic products.

At the third stage of the research, the effect of the mineralizer on the mineral formation process was studied. It is known that the intensity of solid-phase reactions increases with the increase in the content of the liquid phase formed during firing, largely due to fluxes. With an increase in the proportion of fluxes in the composition of the ceramic mass, the content of the glassy phase in the composition of the shard increases, as does the rate of mineral formation, but at the same time, thermal resistance and mechanical strength decrease, especially to impact and the tendency to deformation of fired products increases.

Table 3. Compositions of raw mixes

No	Name of raw materials	Lime-faience mass (1), mass %:	Stone-ceramic mass (2), mass %:
1	EPMV	24	24
2	Kaolin	24	24
3	Quartz sand	19,2	4
4	Dolomite	2,3	2
5	Calcite	17,5	-
6	Na - feldspar	6,5	46
7	K - feldspar	6,5	-

To prevent these negative consequences, intensification of mineral formation is most often achieved by introducing mineralizers. NaF was used as a mineralizer, the amount of which introduced into the raw mix was 1, 2 and 3% over 100 mass parts. The choice and amount of NaF is due to its high mineralizing capacity in silicate systems in the specified amounts (Kiselev & Dutkina, 1977; Nikiforova *et al.*, 2013).

For each recipe, after the appropriate preparation of the source materials using well-known technology, slips were prepared in ball mills to achieve the most uniform mass in composition. Then the slip humidity was reduced to 18-22%, prismatic samples were molded, dried and fired at 1050 and 1150^{o}C. Then the fired products were subjected to X-ray phase analysis to identify the mechanism of mineral formation. The mineralogical composition of the roasting products was studied using a Miniflex 600 X-ray diffractometer from the Japanese company Rigako (with a copper anode) and the chemical composition was studied using an S8 TIGER X-ray spectrometer from the German company Bruker. The mineralogical composition was assessed qualitatively and quantitatively (Table 4, Figures 1-6) (Shishakina & Palamarchuk, 2019). The samples of EPMV taken from the Keyreki, Sangachal and Kobu deposits were studied.

3. Results of the research and their discussion

As noted above, the operational properties of ceramic materials are determined, first of all, by the phase composition, the nature and ratio of the phases formed at high firing temperatures, the structures and forms of crystalline neoplasms, the number and ratio of crystalline, amorphous and gas phases. The properties of materials and products are controlled by optimizing the raw material composition, the technological parameters of the preparation of the raw mixture and the firing mode. Phase transformations and the process of structure formation during the firing of ceramic masses, including EPMV and ordinary low-melting clays may differ. This is due to the fact that EPMV have a more complex mineral composition, high homogeneity and dispersion, a certain thermal history. Therefore, the study of mineral formation in masses including eruption products after their firing under the above temperature conditions and using a mineralizer is an urgent scientific and applied task. The results of the studies (Table 4, Figures 1-6) showed that the mineralogical compositions of the calcined pure volcanic eruption products are identical and are represented mainly by α-quartz, feldspar, diopside, hematite and an amorphous phase. The content of α-quartz in the products of calcination of samples from the Kobu, Sangachal and Keyreki volcanoes at a temperature of 950^{o}C (samples No.3, 6, 9, Table 4) is, respectively, 22, 23 and 16%, feldspar - 20, 30, 25%, diopside - 5, 10, 12%, hematite - 6, 7, 5% and the amorphous phase - 45, 30, 40%. As can be seen from the results, there is a high content of feldspar, diopside and amorphous phase in the sample from the Keyreki volcano with the lowest amount of free α-quartz, which indicates high prospects for the material for use in the ceramic industry. Good physical and mechanical properties of products based on the products of the Keyreki eruption can be expected with a properly selected firing mode. The analysis of the phase compositions of lime-faience masses, including EPMV fired at 1050^{o}C, shows a significant difference in their quantities. At the same time, the nature of phase transformations for different samples is not the same. Thus, in all three samples fired at 1050^{o}C, a sharp increase in the content of α-quartz (up to 2 times) is observed, apparently due to the crystallization of some part of the amorphous phase during cooling (samples No.1, 5, 8, Table 4).

At the same time, different patterns are observed in the change in the amount of feldspar. Thus, if for the compositions containing Kobu and Keyreki EPMV an increase in the feldspar content is observed, then in the case of Sangachal, on the contrary, we record a decrease in the feldspar content. This is apparently due to the fact that the high content of the glass phase in the original Kobu and Keyreki EPMV, compared to the composition of the original Sangachal EPMV, contributes to the formation of a larger amount of liquid phase during the firing of lime-faience masses, which in turn creates favorable conditions for the formation of the crystalline structure of feldspar. There is also a general trend in increasing the amounts of diopside in EPMV containing lime-faience masses, compared to the fired samples from pure EPMV. At the same time, the greatest crystallization of diopside is observed in the sample with the product of the Kobu volcano eruption. This is also explained by the creation of more favorable thermodynamic conditions for the recrystallization of feldspar into diopside due to the appearance of its melt in a relatively larger amount during firing.

The results of the studies show that the effect of introducing the NaF mineralizer in an amount of 3% into lime-faience masses on the mineral formation process is not the same (Table 4, Figures 1-3). Thus, the introduction of NaF into masses containing Kobu EPMV leads to a decrease in the content of α-quartz and an increase in the diopside content by 1%. In the case of firing the lime-faience mass with Sangachal EPMV, a sharp increase in the diopside content from 14 to 21% (samples No.4 and 5) and a decrease in the glass phase content (from 15 to 10%) are observed. When analyzing the results of phase compositions of fired samples with Keyreki EPMV with and without a mineralizer (samples No.7 and 8), we observe a more complex and different picture.

Table 4. Study of the influence of temperature, composition and mineralizer on the phase composition

Sample No	Sample composition	Mineralogical composition, %					
		SiO_2 (α-quartz)	Feldspar	Diopside	FeS_2 (pyrite)	Fe_2O_3 (hematite)	Amorphous part
1	(1)+Kobu	40	30	15	-	-	15
2	(1)+Kobu+3%NaF	39	30	16	-	-	15
3	Kobu - 950°C	22	20	5	2	6	45
4	(1)+Sangachal+3% NaF	43	25	20	-	2	10
5	(1)+Sangachal	44	25	14	-	2	15
6	Sangachal - 950°C	23	30	10	-	7	30
7	(1)+Keyreki+3%NaF	39	35	16	-	-	10
8	(1)+Keyreki	40	30	15	-	-	15
9	Keyreki - 950°C	16	25	12	2	5	40
10	(2) + Keyreki	33	30	10	-	2	25
11	(2)+Keyreki+3%NaF	31	32	10	-	2	25
12	(2) + Sangachal	32	31	10	-	2	25
13	(2)+Sangachal+3% NaF	30	33	10	-	2	25
14	(2) + Kobu	32	31	10	-	2	25
15	(2)+Kobu+3% NaF	30	33	10	-	2	25

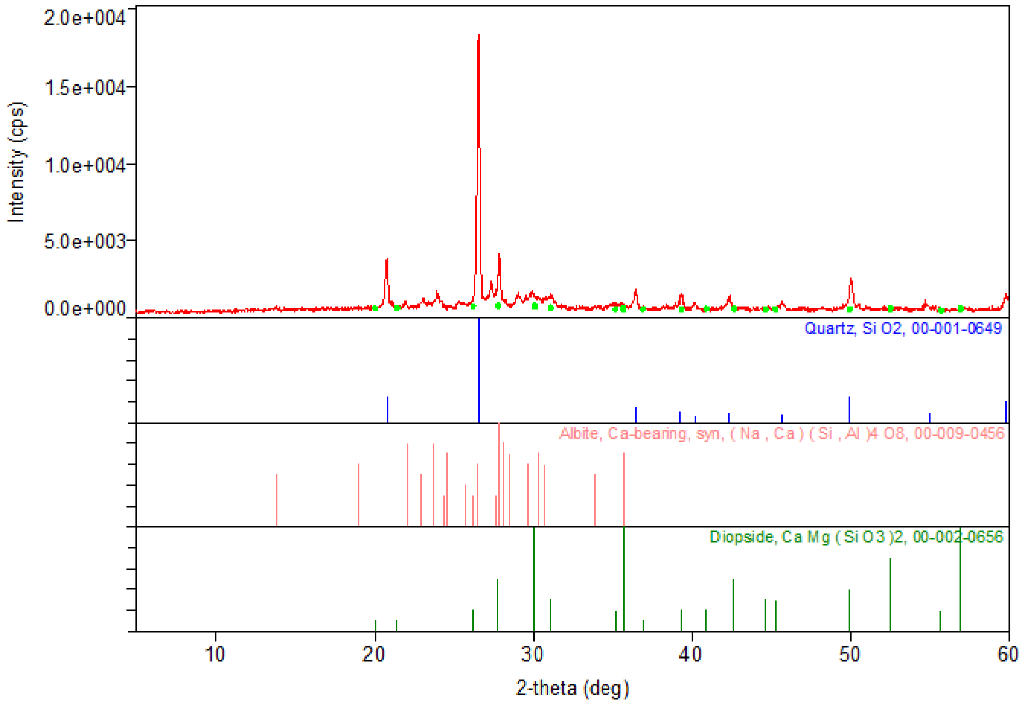

Figure 1. X-ray diffraction pattern of a lime-faience composition containing Kobu EPMV and NaF mineralizer in an amount of 3% (No.2)

Thus, the introduction of NaF contributes to a decrease in the content of α-quartz (from 40 to 39%), an increase in the content of feldspar (from 30 to 35%), diopside (from 15 to 16%) and a decrease in the content of glass phase from 15 to 10%). Thus, NaF has a more significant effect on the process of mineral formation in mixtures with Keyreki EPMV, which is possibly due to its high dispersion and the optimal ratio of components in the mixture, as well as the fact that fluorine causes the destruction of the silicate network due to the rupture of Si-O-Si bonds and the appearance of weakened local Si-F bonds, which, in turn, leads to a decrease in the melting temperature and viscosity and thereby intensifies the crystallization process (Rusakov, 1977; Tikhi, 1988; Pavlov, 1977).

The study of mineral formation in stone ceramic masses, including EPMV, after firing shows a very insignificant difference in their mineralogical compositions (samples No.10, 12, 14).

Compared to pure EPMV Kobu, the mineralogical composition of the fired stone ceramic mass with EPMV Kobu is characterized by a reduced content of glass phase and a higher content of free α-quartz, feldspar and diopside. Apparently, high-temperature firing leads to a decrease in the viscosity of the melt, from which crystals of α-quartz, diopside and feldspar are relatively easily released upon cooling.

Analysis of the results shows that, unlike lime-faience masses, hematite is released during firing of stone ceramic compositions including material from the Kobu volcano. The mineralogical composition of the firing product is characterized by a reduced content of diopside and free α-quartz and a slightly increased content of glass phase (up to 30%, samples No.1 and 14, Table 4) with a virtually unchanged amount of feldspar. In our opinion, this is due to the fact that at a temperature of 1150°C, favorable conditions are created for reactions to occur with the production of a glass melt of complex composition, possessing high viscosity and at the same time, the release of quartz and diopside crystals.

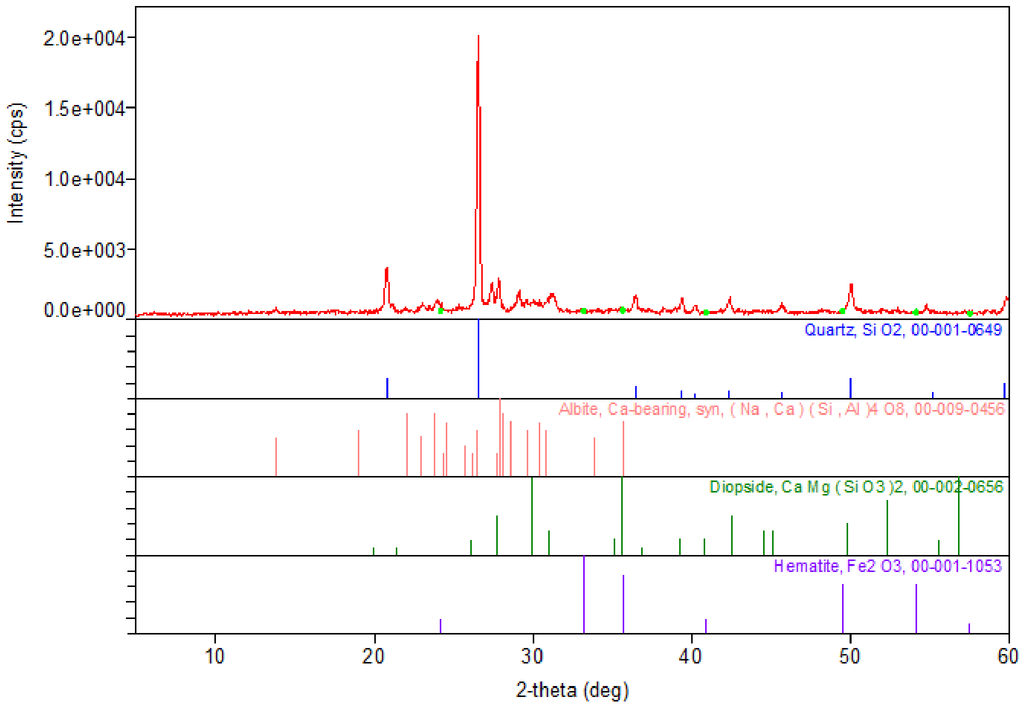

Figure 2. X-ray diffraction pattern of limestone-faience composition containing Sangachal EPMV and NaF mineralizer in an amount of 3% (No.4)

In stone ceramic mixtures including EPMV Keyreki, in comparison with the product of firing of the initial raw material, the content of free α-quartz and feldspar increases with a decrease in the content of diopside and glass phase. In comparison with the lime-faience composition, a decrease in the content of α-quartz and diopside and an increase in the content of glass phase with an unchanged value of the content of feldspar are observed.

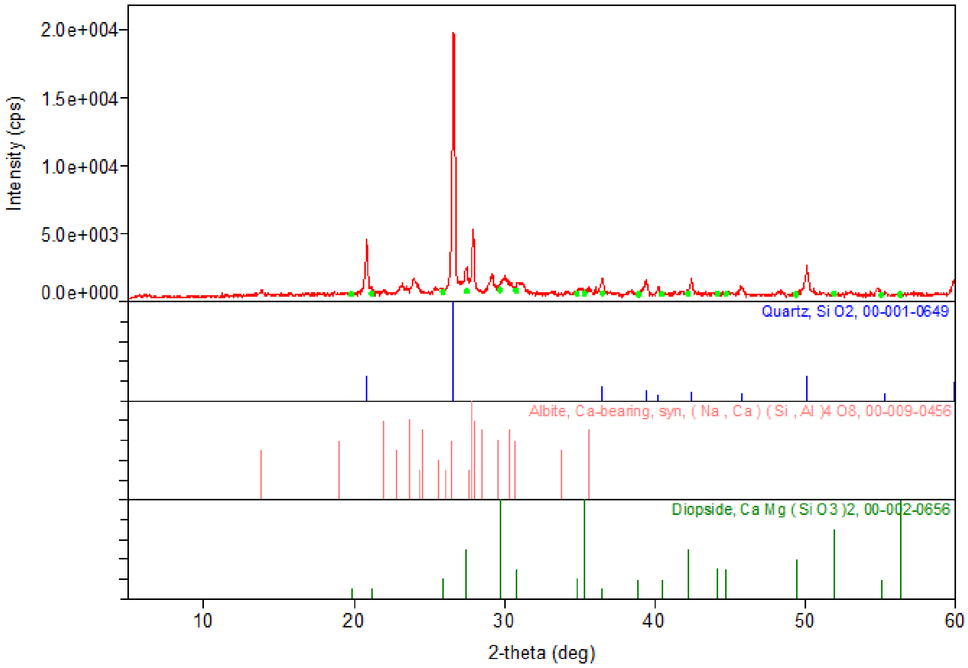

Figure 3. X-ray diffraction pattern of lime-faience composition containing EPMV Keyreki mineralizer NaF in the amount of 3% (No.7)

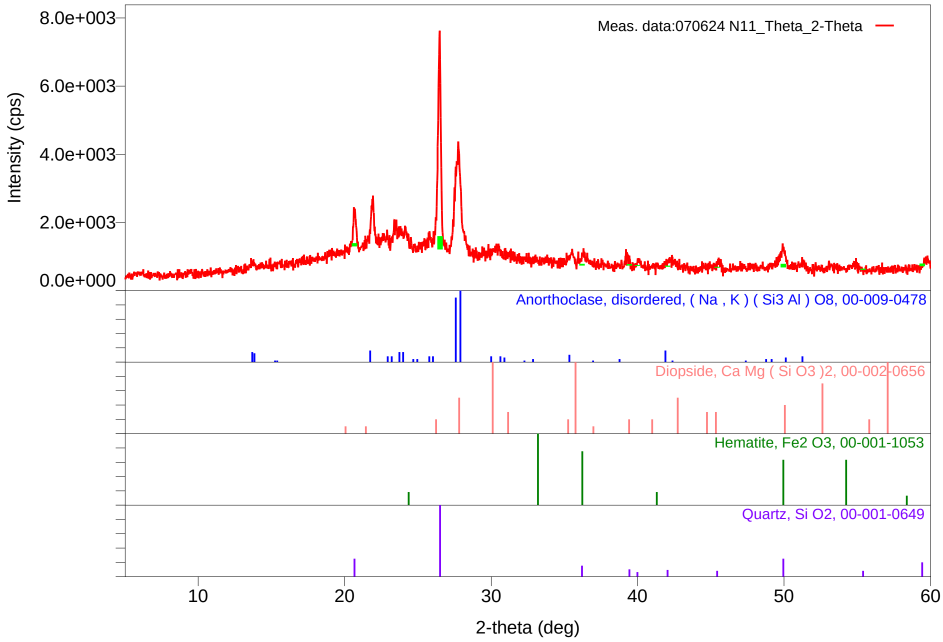

Figure 4. X-ray diffraction pattern of a stone ceramic composition containing Keyreki EPMV and NaF mineralizer in an amount of 3% (No.11)

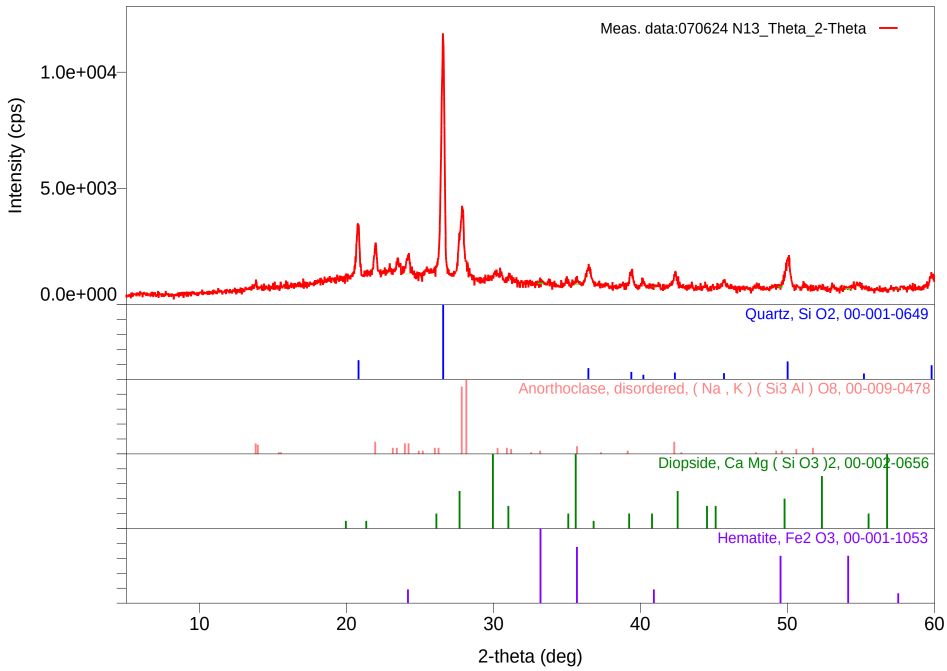

Figure 5. X-ray diffraction pattern of a stone ceramic composition containing Sangachal EPMV and NaF mineralizer in an amount of 3% (No.13)

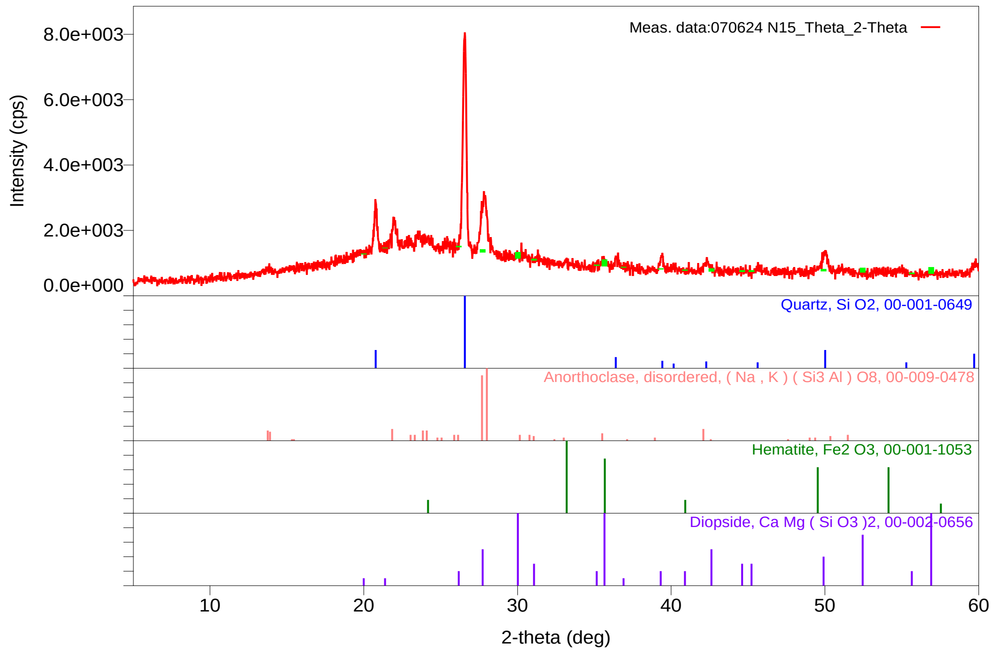

Figure 6. X-ray diffraction pattern of a stone ceramic composition containing Kobu EPMV and NaF mineralizer in an amount of 3% (No.15)

Fired stone ceramic masses with Sangachal EPMV are characterized by a higher content of free α-quartz and feldspar, a lower amount of glass phase with an unchanged content of diopside compared to the original composition. In comparison with the lime-faience composition, a decrease in the content of α-quartz and diopside, an increase in the amount of feldspar and glass phase is observed.

The effect of the NaF mineralizer in an amount of up to 3% on the process of mineral formation during the firing of stone ceramic masses containing EPMV is identical and insignificant (Table 4 and Figures 4-6).

Thus, in all three cases, a slight decrease in the content of free α-quartz and a slight increase in feldspar are observed. This is due to the fact that at a firing temperature of 1150^{o}C, even in the absence of a mineralizer, viscosity is significantly reduced and therefore, the intensity of the mineral formation process and its nature do not change.

4. Conclusions

As a result of the conducted studies, the mechanisms of mineral formation in EPMV-containing systems differing in raw material composition and firing temperature were established. The introduction of NaF into masses containing Kobu EPMV leads to a decrease in the content of α-quartz and an increase in the content of diopside in the firing product and the introduction of lime-faience masses with Sangachal EPMV leads to a sharp increase in the content of diopside and a decrease in the content of quartz. The introduction of NaF into masses with Keyreki EPMV contributes to a decrease in the content of α-quartz, an increase in the content of feldspar, diopside and a decrease in the content of glass phase. It was found that NaF has a more significant effect on the process of mineral formation in mixtures with Keyreki EPMV. This may be due to their high dispersion and the optimal ratio of components in the mixture, as well as the fact that fluorine causes destruction of the silicate network due to the rupture of Si-O-Si bonds and the appearance of weakened local Si-F bonds, which in turn leads to a decrease in the melting point and viscosity and thereby intensifies the crystallization process. The data obtained show that when firing stone ceramic masses containing EPMV, the effect of the NaF mineralizer in an amount of up to 3% on the mineral formation process is identical and insignificant.

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