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SYNTHESIS OF DIFFERENT STRUCTURAL TYPES OF ZEOLITES IN THE HALLOYSITE-DOLOMITE-OBSIDIAN SYSTEM

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Abstract. Gismondine, laumontite and levyne type zeolites have been synthesized based on the natural minerals of Nakhchivan and the optimal crystallization conditions have been established. The influence of temperature, alkaline solution concentration, ratio of starting components and time of processing on the synthesis process has been studied. The mineral resources of Nakhchivan − halloysite deposits of Pirigel, dolomite deposits of Negram and obsidian deposits of Zangezur served as samples. The initial components and the reaction products have been examined by X-ray diffraction, thermogravimetric and elemental analysis. The optimal conditions for the synthesis of gismondine zeolite with a 100% crystallinity are as follows: temperature of 200°C, alkaline solution of 2 N NaOH, ratio of the initial components of halloysite (H):dolomite (D):obsidian (O)= 1:1:1, processing time of 50 hours. The optimal conditions for laumontite synthesis are: temperature of 220°C, alkaline solution of NaOH of 1 N, H:D:O= 1:3:1, processing time of 75 hours. The optimal conditions for levyne are: temperature of 200°C, alkaline solution of KOH of 4 N, H:D:O= 2:1:2, processing time of 100 hours. It was found that changes in the temperature, alkalinity, ratio of starting components and time of processing of the reaction have different effects on the rate of formation of products, on their degree of crystallinity and on the phase purity of the obtained zeolite.

Keywords: hydrothermal synthesis, zeolite, gismondine, laumontite, levyne.

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Introduction

The synthesis of zeolites can be carried out on the basis of a wide range of starting components. The synthesis, study of physicochemical properties and applications of zeolites, as well as their implementation based on the local natural resources are currently a promising and relevant field in modern chemistry.

In the zeolites synthesis, diverse materials are used as a source of silicon and aluminum: clay [1-4], natural and synthetic glasses [5,6], diatoms [7], natural aluminosilicates [8-10], halloysite [11], including feldspars [12,13], zeolite-bearing rocks [14-16], industrial fly ash [17,18], *etc*. These starting materials mainly differ from each other in structural and chemical characteristics. As a cost-effective alternative for the synthesis of zeolites, is the use of natural mineral resources instead of chemical raw materials. In this work, halloysite deposits of Pirigel, dolomite deposits of Negram and obsidian deposits of Zangezur were used as initial local materials for the synthesis of different structural types of zeolites.

Due to their structural features, zeolites such as gismondine, laumontite and levyne are important for their use in catalysis and ion exchange. According to the literature data, gismondine was used in water purification from cations of strontium, barium, magnesium, and also, as a highly active and selective catalyst for the production of biofuels [19,20]. Laumontite was used as an adsorbent, an ion exchanger in catalytic systems, and a raw material for producing nanomaterials [21].

The gismondine framework topology consists of two sets of intersecting, doubly connected 4-membered rings linked into double crankshaft chains [22,23]. The laumontite framework exhibits two different types of four-membered rings, those where SiO_4 and AlO_4 alternate and those formed only by SiO_4 tetrahedra [24]. The crystal structure of levyne is built up of layers of single and double six-membered rings of $(Si,Al)O_4$ tetrahedra and cations are all disposed along the symmetry axis inside the levyne cage [25].

The purpose of this research work is the rational use of local natural resources of the Nakhchivan Autonomous Republic for the synthesis of gismondine, laumontite and levyne zeolites; identification of the optimal conditions; evaluation of the influence of temperature and alkalinity on the crystallization process.

Experimental

Materials

The mineral resources of Nakhchivan Autonomous Republic − halloysite deposits of Pirigel, dolomite deposits of Negram and obsidian deposits of Zangezur served as samples.

Sodium and potassium hydroxides (flake, 99% purity, Alfa Aesar GmbH & Co KG, Germany) have been used as received without further purification.

Synthesis

Hydrothermal synthesis of gismondine, laumontite and levyne has been carried out in Morey autoclaves made of 45MNFT stainless steel. The synthesis has been studied in the temperature range from 100 to 250°C, the concentration of the alkaline solution varied from 0.5 to 5 N, the autoclaving time varied from 10 to 200 hours and the fullness degree was of 70-75%. Solid-liquid ratio was 1:10. After crystallization was completed, the final material was separated from the initial solution, washed with distilled water from excess alkali, and dried at 70–80°C. NaOH and KOH have been used as alkaline solutions.

Characterization techniques

The *X-ray diffraction* measurements were performed using the X-ray analyser 2D PHASER "Bruker" (Cu K_α radiation, $2\theta = 5-50°$), using of NaCl, SiO_2 (quartz) and pure zeolites in internal and external standards. Samples have been placed on a front mounted plastic sample holder. The measuring conditions have been as follows: step size of 0.15 s/step, nickel filter as incident beam, slit aperture of 0.3°.

The *thermogravimetric analysis* of the samples has been carried out on a "Derivatograph-Q 1500-D" of the Hungarian company MOM in the dynamic mode in the temperature range 20-1000°C. Shooting mode: heating rate of 20°/min; paper speed of 2.5 mm/min; the sensitivity of DTA, DTG and TG was 500 mv; ceramic crucibles with Al_2O_3 as standard.

Elemental analysis of the starting materials and their obtained products has been carried out on a Launch of Trition XL dilution refrigerator "Oxford instrument" multichannel X-ray spectrometer. Measurement mode: Pd - anode, voltage 25 kW, current strength 70 MA, exposure time 100 s, sensitivity limit of 10^{-2}. Samples have been prepared as follows: the analyte has been diluted with $Li_2B_4O_7$ flux (ratio 1:10) at a temperature of 1250°C. The resulting glass has been crushed and pressed under the pressure of 20 t/cm^2 with a holding time of 1 min.

Results and discussion

General characterization of the starting materials

An analysis of the scientific literature showed that numerous works have been done on the synthesis of gismondine [26-28], laumontite [29], levyne [30-33]. The difference of this work in relation to the above is in the use of natural mineral resources of the country, as well as in the conditions of synthesis.

The initial components and the reaction products have been examined by X-ray diffraction, thermogravimetric and elemental analysis. The chemical composition of the collected mineral resources samples is presented in Tables 1-3, showing that the local mineral resources of Nakhchivan are distinguished by phase purity, thus making possible their use as starting materials in the synthesis of zeolites.

Table 1

Chemical analysis of major elements (wt.%) of the halloysite deposit of Pirigel.

Element	*Weight*	*Amount of oxide*	*Formula*
Si	29.37	44.52	SiO_2
Al	20.54	32.78	Al_2O_3
Ca	1.17	2.33	CaO
Na	0.63	0.78	Na_2O
K	0.79	0.93	K_2O
Mg	2.23	3.15	MgO
Fe	0.98	1.47	Fe_2O_3
Fe	0.73	0.87	FeO
Ti	0.12	0.24	TiO_2
O	43.44		
		12.93	H_2O
Total	100.00		

Table 2

Chemical analysis of major elements (wt.%) of the dolomite deposit of Negram.

Element	*Weight*	*Amount of oxide*	*Formula*
Ca	26.38	31.34	CaO
Mg	17.43	23.44	MgO
Na	0.77	0.93	Na_2O
K	0.65	0.82	K_2O
Si	3.93	7.43	SiO_2
Fe	0.98	1.07	FeO
C	15.03	34.97	CO_2
O	34.83		
Total	100.00		

Table 3

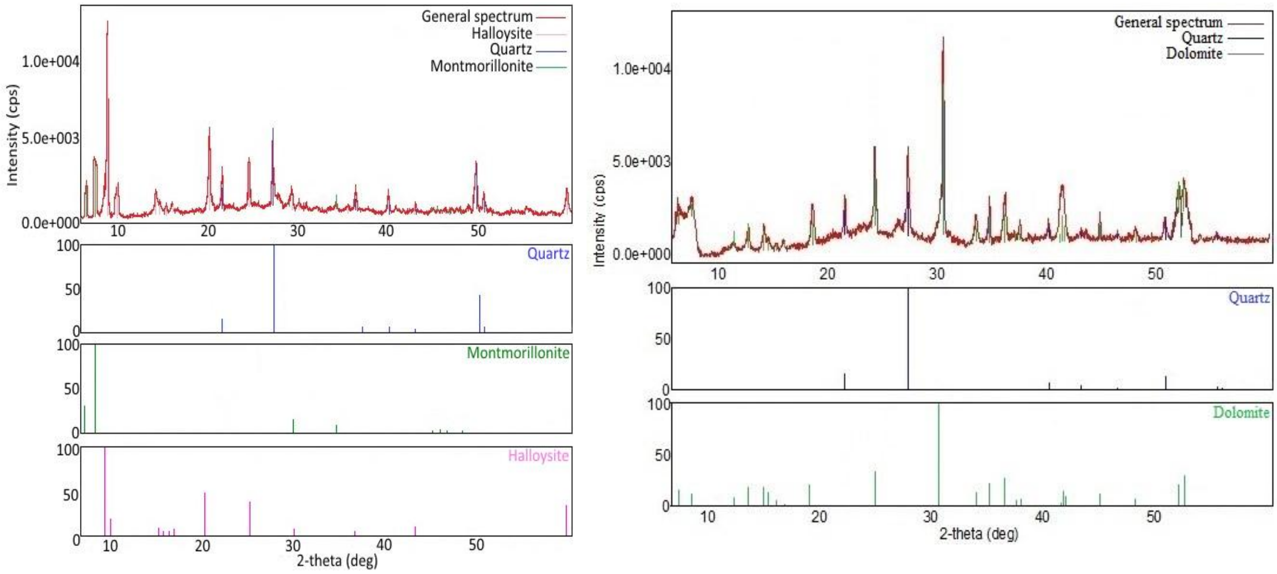
Chemical analysis of major elements (wt.%) of the obsidian deposit of Zangezur.

Element	*Weight*	*Amount of oxide*	*Formula*
Si	29.37	44.42	SiO_2
Al	20.54	32.68	Al_2O_3
Ca	1.17	2.33	CaO
Na	0.63	0.78	Na_2O
K	0.79	0.93	K_2O
Mg	2.23	3.15	MgO
Fe	0.98	1.47	Fe_2O_3
Fe	0.73	0.87	FeO
Ti	0.12	0.24	TiO_2
Mg	0.10	0.20	MgO
O	43.34		
		12.93	H_2O
Total	100.00		

X-ray diffraction patterns of the initial mineral resources − halloysite and dolomite of Nakhchivan are shown in Figure 1. Since obsidian is amorphous, its diffraction pattern is not presented. The comparison of X-ray experimental data with the known literature [34] showed that the test sample is the halloysite clay mineral (Figure 1*(a)*). In the X-ray diffraction pattern, the interplanar spacing is 10.48; 9.77; 4.41; 3.62; 1.48 Å being characteristic for halloysite, which is dominant in the sample. Values of interplanar distances (*d*) are equal to 15.3; 11.5; 4.50; 3.07; 2.62 Å and suggest the presence of montmorilonite in the sample. According to the diffraction pattern, quartz is also present in the sample (*d*= 4.24; 3.34; 2.45; 2.28; 1.81 Å). In the natural mineral - dolomite, besides the main mineral (*d*= 3.70; 3.34; 2.88; 2.19; 1.78 Å), in the composition of the sample also can be detected quartz in a small amount (*d*= 4.24; 3.34; 2.45; 2.28; 1.81 Å) (Figure 1*(b)*). X-ray diffraction patterns and thermograms of the synthesized gismondine, laumontite and levyne zeolites are presented in Figures 2 and 3, respectively.

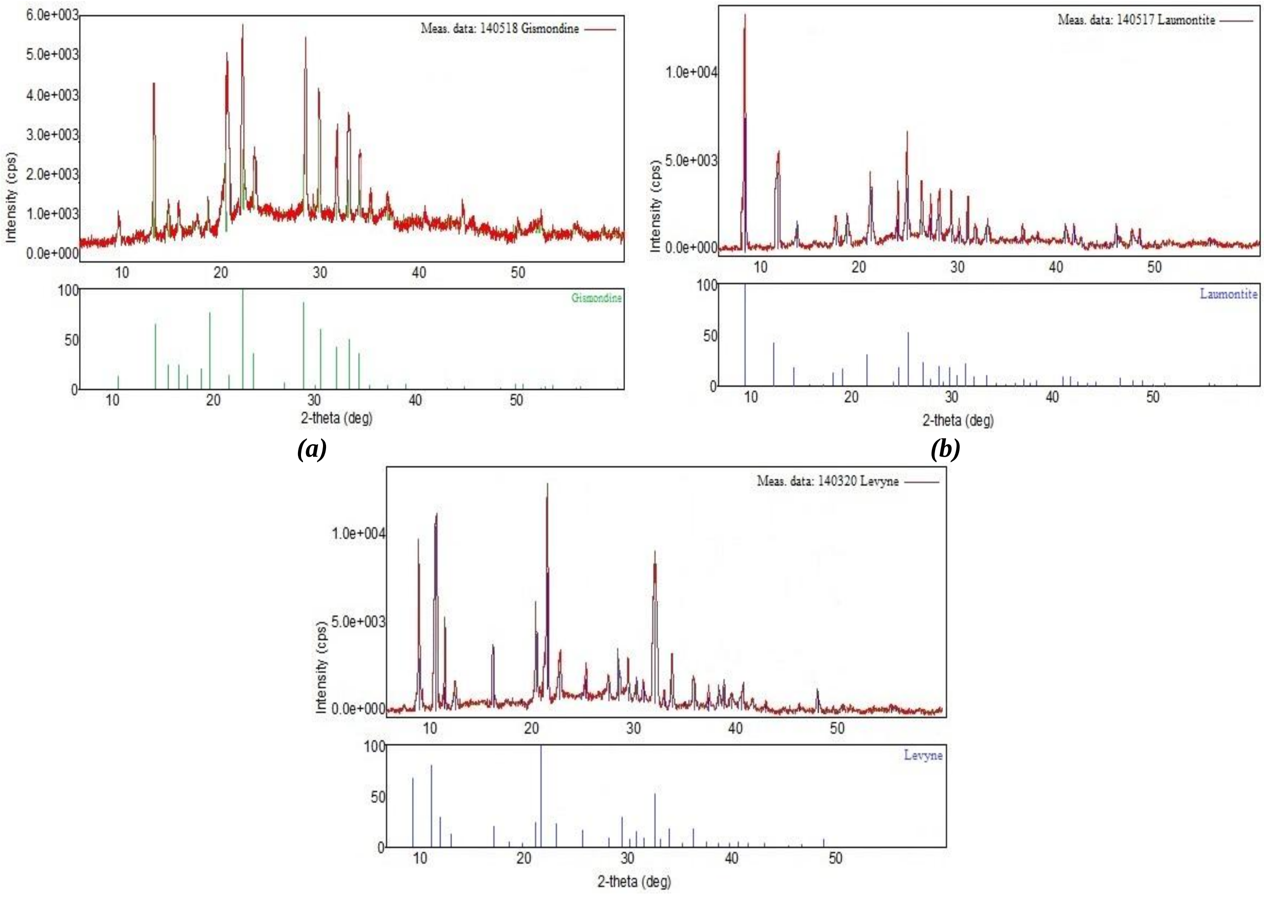
According to results presented in Figure 2, the obtained zeolites are characterized by a high degree of crystallinity demonstrated by phase purity. Comparison of the experimental values of interplanar spacings (*d*, Å) with theoretical and calculated ones has shown that the obtained diffraction patterns indicate the obtaining of phase-pure gismondine, laumontite and levyne zeolites. In the presented diffraction patterns, peaks with a relative intensity of 100% characterize the baseline of the synthesized zeolites. For gismondine, a baseline with 100% relative intensity is characterized by a value of *d*= 4.27; 3.18 Å, for laumontite of 9.57 Å and for levyne of 8.15; 4.08 Å, which is in good agreement with the literature data [34]. According to the X-ray phase analysis, gismondine crystallizes in the monoclinic crystal system $P112_1/a$ with the unit cell parameters a= 9.84 Å; b= 10.02 Å; c= 10.62 Å, β= 92°25´; laumontite in the monoclinic crystal system $C12/m1$ with a= 14.90 Å; b= 13.17 Å; c= 7.50 Å, β= 111°30'; levyne – in the rhombohedral crystal system $R\bar{3}m$ with a= 10.75 Å, α= 76°25', which also is in good agreement with the reference data [34].

Using the thermogravimetric analysis, the region of dehydration and thermostability of the synthesized zeolites has been established (Figure 3). The DTA curve presented in Figure 3*(a)*, in the case of gismondine zeolite is characterized by one endothermic and one exothermic effect.



(a) ***(b)***

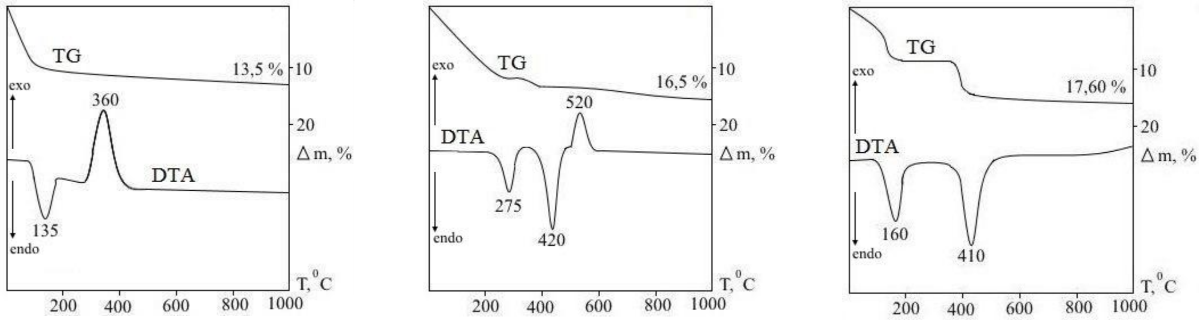
Figure 1. X-ray diffraction patterns of the starting components: halloysite *(a)* and dolomite *(b)*.



(a) *(b)*

(c)

Figure 2. X-ray diffraction patterns of the synthesized zeolites obtained under optimal conditions with a 100% degree of crystallinity: gismondine *(a)*, laumontite *(b)* and levyne *(c)*.



(a) *(b)* *(c)*

Figure 3. Thermograms of the zeolites obtained under optimal conditions: gismondine *(a)*, laumontite *(b)* and levyne *(c)*.

The endothermic effect corresponds to the dehydration of the sample with a maximum of 135°C, at which the weight loss along the TG curve is 13.5%. The exothermic effect, detected at a temperature with a maximum of 360°C, according to X-ray diffraction analysis, refers to the formation of fieldspar - anorthite. The DTA curve of laumontite (Figure 3*(b)*) is characterized by two endothermic and one exothermic effect. The first two endothermic effects relate to dehydration of the sample, which occurs in stages with maxima at 275 and 420°C, with a 16.5% weight loss along the TG curve. The exothermic effect detected at a temperature of 520°C, according to X-ray diffraction analysis, refers to the formation of anorthite. For levyne the DTA curve (Figure 3*(c)*) is characterized by two endo-effects thus the dehydration occurs in two stages in a wide temperature range from 100 (max. 160°C) to 500°C (max. 410°C) with 17.60% weight loss. As shown by X-ray diffraction analysis, the structure of levyne is stable at 1000°C.

Zeolites are very sensitive to changes in synthesis conditions, namely temperature, alkalinity and processing time [35]. The effect of temperature, alkaline solution concentration, the ratio of the starting components and processing time on the crystallization process of the synthesized zeolites has been studied. Figures 4, 6 and 8 show the kinetic curves of crystallization process of the synthesized zeolites.

Gismondine synthesis

The crystallization process of gismondine has been studied at temperatures of 180°C, 200°C and 240°C (Figure 4). Studies have shown that the optimum crystallization temperature of gismondine with a high degree of crystallinity is 200°C.

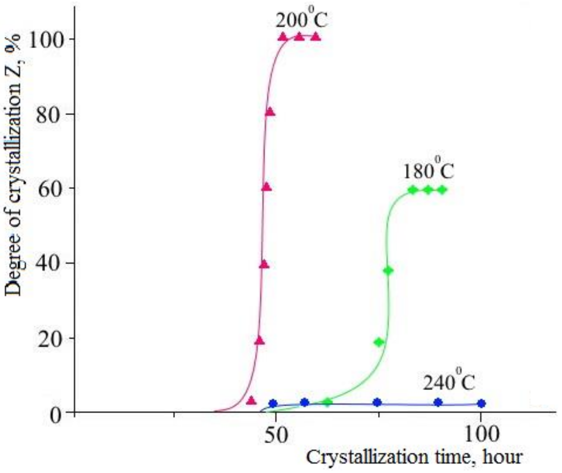
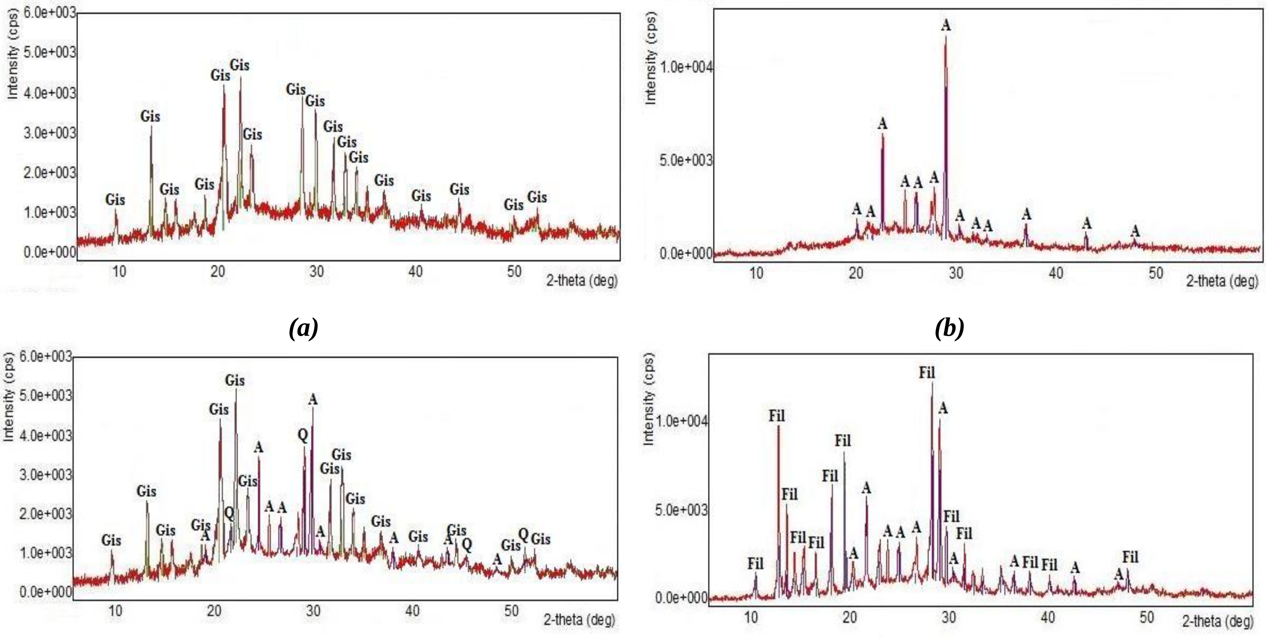


Figure 4. Kinetic curves of crystallization process of gismondine.

At a temperature of 180°C, the crystallization process is not completed, and gismondine is obtained with a low degree of crystallinity. At a temperature of 240°C, the product of synthesis is anorthite.

The studies conducted at various concentrations of alkaline solution (NaOH, 1.0–3.0 N) showed that, in addition to gismondine, quartz and anorthite are present in the reaction product at 1.0 N NaOH. At a concentration of alkaline solution of 3.0 N, the structure of gismondine is destroyed and phillipsite and anorthite crystallize. The optimal concentration of NaOH to obtain gismondine with high crystallinity is 2.0 N. The effect of the ratio of the starting components on the crystallization of gismondine has showed that, the halloysite increase leads to crystallization of phillipsite and anorthite in addition to gismondine, and an increase of dolomite to the synthesis of anorthite. The increasing of the obsidian content promotes crystallization of phillipsite and quartz. The optimal ratio of the starting components is H:D:O= 1:1:1. The optimal crystallization time of gismondine is 50 hours. Less than 50 hours of processing time (starting from 10 hours) contributes to the formation of gismondine with a low degree of crystallinity, while increasing the processing time to 100 hours promotes the transition of gismondine into phillipsite and anorthite. X-ray diffraction patterns of crystallization products in the case of gismondine are presented in Figure 5.



(a) *(b)*

(c) *(d)*

Figure 5. X-ray diffraction patterns of the products in the case of gismondine at synthesis conditions: 180°C *(a)*; 240°C *(b)*; 1.0 N NaOH *(c)*; 3.0 N NaOH *(d)* (Gis – gismondine, A – anorthite, Q – quartz, Fil – phillipsite).

Laumontite synthesis

The synthesis of laumontite has been studied at temperatures of 180°C, 200°C, 220°C and 240°C (Figure 6). A study of the temperature influence has shown that, at 180°C, clinoptilolite, quartz and anorthite have been obtained; at 200°C, clinoptilolite, laumontite with low crystallinity and quartz, and at 240°C, wairakite with a high degree of crystallinity have been obtained. The temperature of 220°C is optimal for the synthesis of laumontite with a high degree of crystallinity. The study of the influence of the concentration of NaOH solution (in the range of 0.5–2.5 N) has showed that at 0.5 N, clinoptilolite and quartz are obtained; at 2.0 N, clinoptilolite and wairakite and at 2.5 N, wairakite crystallize. The optimal NaOH concentration for the synthesis of laumontite with a high degree of crystallinity is 1.0 N.

The study of influence of the ratio of starting components has showed that, the increase of halloysite content leads to crystallization of wairakite and quartz in addition to laumontite (Figure 7). An increase of dolomite content leads to the synthesis of clinoptilolite and increase of obsidian to wairakite synthesis. The optimal ratio in obtaining highly crystallized laumontite is H:D:O= 1:3:1.

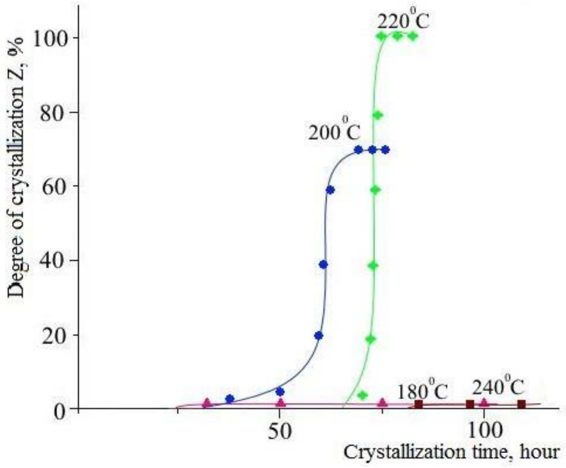
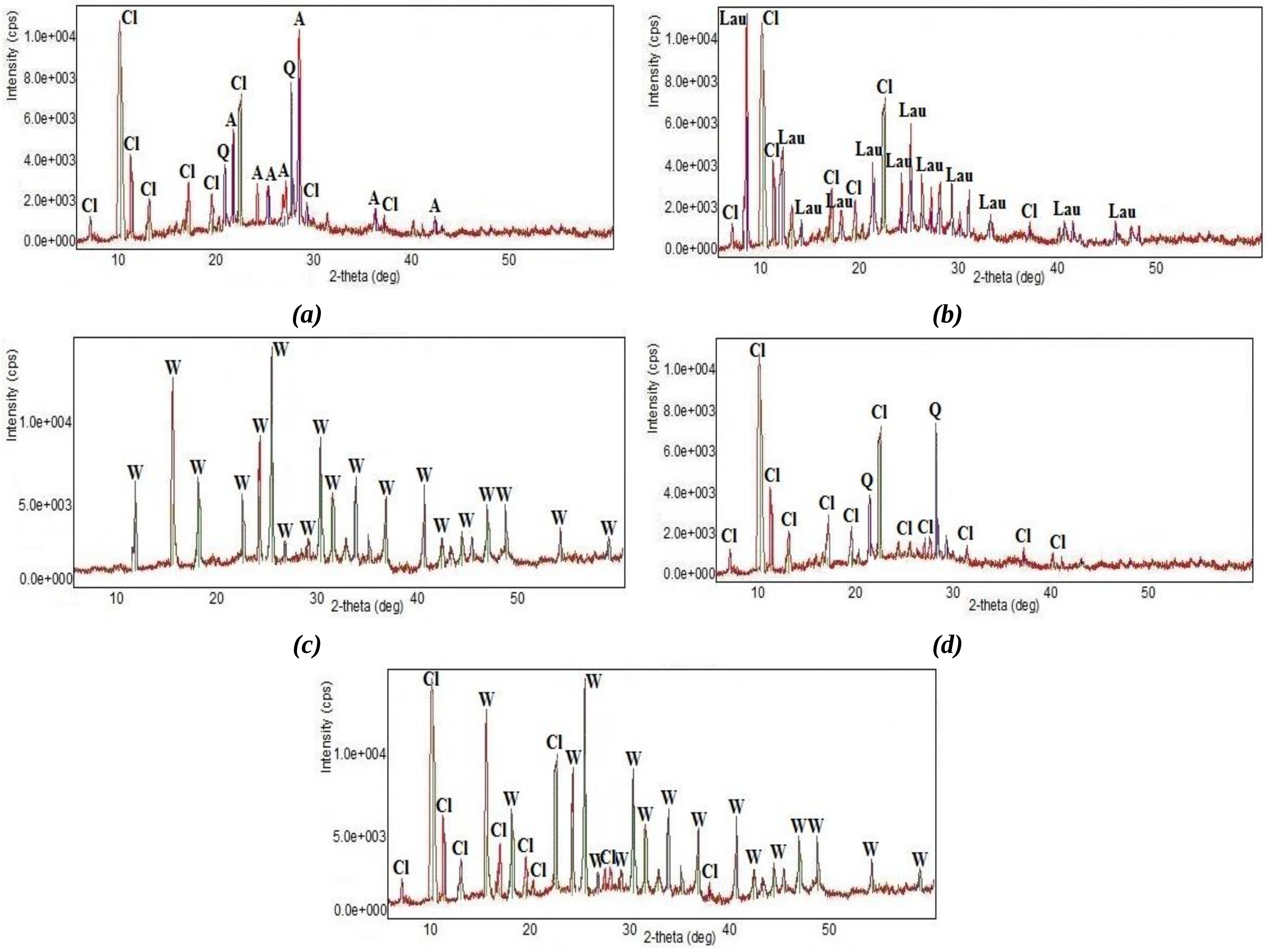


Figure 6. Kinetic curves of crystallization process of laumontite.



(a)

(b)

(c)

(d)

(e)

Figure 7. X-ray diffraction patterns of the products in the case of laumontite at synthesis conditions: 180°C *(a)*; 200°C *(b)*; 240°C and 2.5 N NaOH *(c)*; 0.5 N NaOH *(d)*; 2.0 N NaOH *(e)* (Cl – clinoptilolite, A – anorthite, Q – quartz, Lau – laumontite, W – wairakite).

Processing for 50 hours leads to the formation of laumontite with a low degree of crystallinity, and when the processing time is increased to 100 hours, laumontite transition into wairakite. The optimal processing time was established at 75 hours. X-ray diffraction patterns of crystallization products in the case of laumontite are presented in Figure 7.

Levyne synthesis

The crystallization kinetics of levyne zeolite has been studied at temperatures of 180°C, 200°C and 210°C (Figure 8). The obtained results (Figures 8 and 9) show that levyne zeolite does not form at 180°C, its formation occurs at 210°C, but the product with 100% degree of crystallinity is not obtained. At a temperature, above 210°C, hydrothermal crystallization changes its direction and zeolite-levyne recrystallizes into zeolite-phillipsite. The crystallization of zeolite at 200°C is very intense and the zeolite-levyne with a high degree of crystallization is obtained. Analysis of the hydrothermal reaction products has shown that crystallization reaches a maximum within 100 hours.

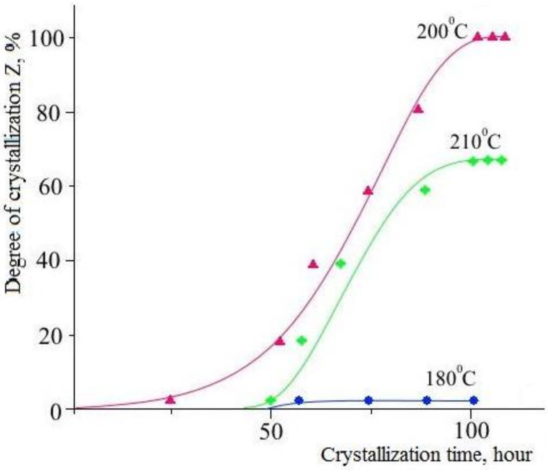
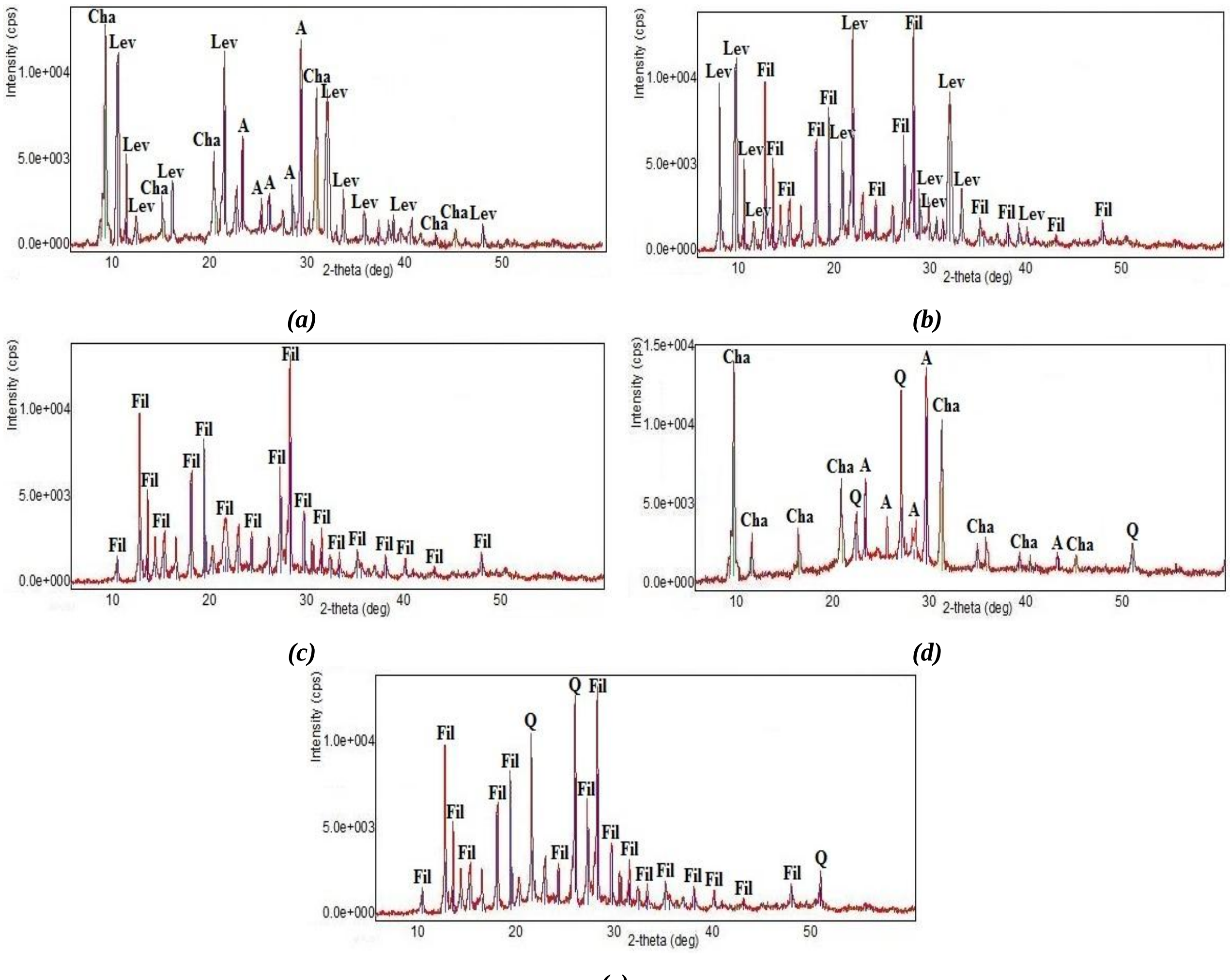


Figure 8. Kinetic curves of crystallization process of levyne.



(a)

(b)

(c)

(d)

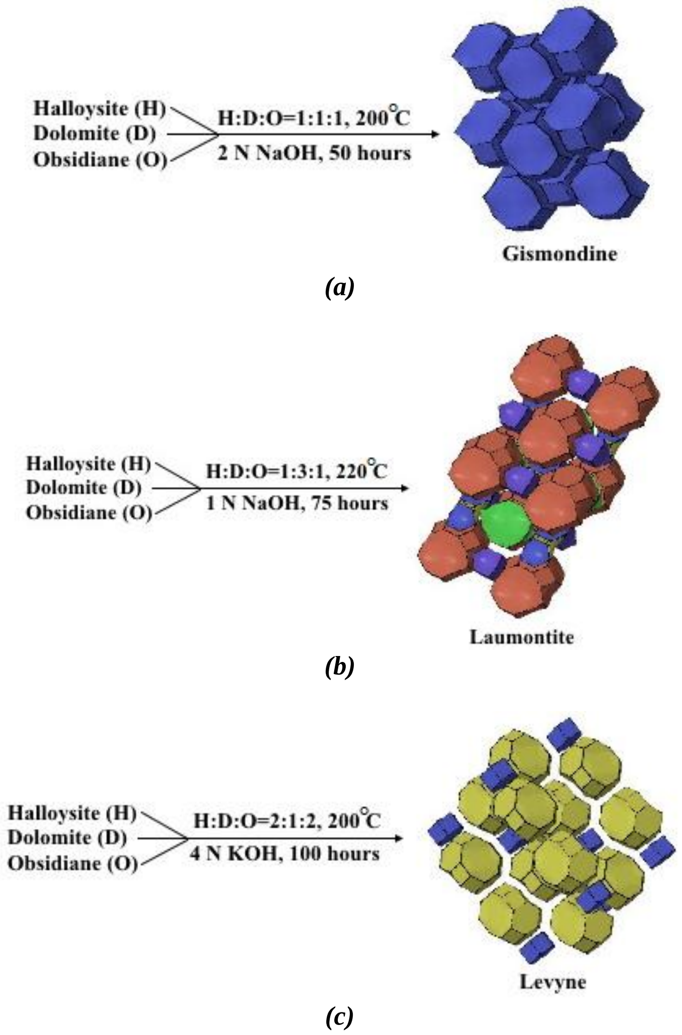
(e)

Figure 9. X-ray diffraction patterns of the products in the case of levyne at synthesis conditions: 180°C *(a)*; 210°C *(b)*; > 210°C *(c)*; 2.0-3.5 N KOH *(d)*; 4.5-5.0 N KOH *(e)* (Lev – levyne, Cha – chabazite, A – anorthite, Fil – phillipsite, Q – quartz).

The influence of the concentration of the KOH solution has been studied in the range 2.5–5.0 N. The optimal concentration of the alkaline solution for the synthesis of levyne with a high degree of crystallinity is 4.0 N. At a concentration of the alkaline solution below 4.0 N, in the range 2.0–3.5 N, chabazite, anorthite, and quartz have been identified in the crystallization products. Increasing the concentration above 4.0 N, 4.5–5.0 N, leads to crystallization of phillipsite and quartz. The optimal ratio of the starting components in the crystallization of levyne with a high degree of crystallinity is H:D:O= 2:1:2. A decrease of halloysite or obsidian in the content contributes to the formation of levyne with a low degree of crystallinity. An increase of dolomite leads crystallization of phillipsite, chabazite and quartz. Processing for 50 hours leads to the formation of chabazite with a low degree of crystallinity and quartz, and when the crystallization time is increased to 150 hours, levyne transition to phillipsite. The optimal processing time is 100 hours. X-ray diffraction patterns of crystallization products in the case of levyne are presented in Figure 9.

Optimal synthesis conditions

Gismondine, laumontite and levyne with a 100% degree of crystallinity have been obtained under the following optimal conditions: temperature of 200°C, solvent concentration of 2.0 N NaOH, ratio of the initial components of halloysite (H):dolomite (D):obsidian (O)= 1:1:1, processing time of 50 hours; temperature of 220°C, solvent concentration of NaOH of 1.0 N, H:D:O= 1:3:1, processing time of 75 hours; temperature of 200°C, solvent concentration of 4.0 N KOH, H:D:O= 2:1:2, processing time of 100 hours, respectively. A representation of the optimal synthesis process of zeolites of gismondine, laumontite and levyne with a 100% degree of crystallinity is shown in Scheme 1.



Scheme 1. The optimal conditions of the process for the synthesis of zeolites with a 100% crystallinity: gismondine *(a)*, laumontite *(b)* and levyne *(c)*.

The use of KOH, instead of NaOH, in the case of levyne, as an alkaline solution, is explained by the fact that the synthesis in KOH solutions lead to the formation of levyne with a 100% degree of crystallinity. Most likely, in the case of crystallization of levyne in a solution of NaOH, Na^+ cations interfere to obtain the product with a 100% degree of crystallinity. For this reason, KOH solutions have been used and allowed to obtain positive results.

Conclusions

The natural mineral resources of Nakhchivan have been used for the synthesis of zeolites such as gismondine, laumontite and levyne.

Crystallization kinetics and the effect of temperature, alkaline solution concentration, processing time, the ratio of the starting components on the speed, direction and crystallinity of zeolites have been studied. Gismondine with a 100% degree of crystallinity has been obtained at temperature of 200°C, alkaline solution concentration of 2 N NaOH, ratio of the initial components of halloysite (H):dolomite (D):obsidian (O)= 1:1:1, processing time of 50 hours. The optimal conditions for the synthesis of laumontite with a 100% degree of crystallinity are temperature 220°C, alkaline solution concentration of 1 N NaOH, H:D:O= 1:3:1, crystallization time of 75 hours. In the case of levyne, the optimal conditions included temperature of 200°C, alkaline solution concentration of 4 N KOH, H:D:O= 2:1:2, synthesis time of 100 hours.

According to the obtained experimental data, even small changes in the synthesis conditions lead to obtain various products. It has been found that changes in temperature, alkaline solution concentration, processing time and the ratio of the starting components differently affect the rate of formation of products, their degree of crystallinity, the phase purity of the obtained zeolite. According to X-ray phase analysis, it has been found that, under the selected optimal conditions, the synthesized zeolites are characterized by a high degree of crystallinity.

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