

*Physical Chemistry*

## Hydrothermal Transformation of Natural Analcime and Phillipsite

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**ABSTRACT.** The present paper studies hydrothermal transformation of natural zeolites analcime and phillipsite, widespread in Georgia, in order to obtain valuable products. It is found that phase-pure zeolite NaA with Si/Al~1 can be prepared in the form of cubic/rhombus crystallites with uniform micrometric (3-5  $\mu\text{m}$ ) dimensions by hydrothermal crystallization of aged at room temperature gel (4.5Na<sub>2</sub>O: 0.45Al<sub>2</sub>O<sub>3</sub>: 1SiO<sub>2</sub>: 178H<sub>2</sub>O) obtained from natural analcime, treated with hydrochloric acid before suspending in water and mixing with sodium hydroxide. Phase-pure zeolite NaX with Si/Al~1.5 can be prepared in the form of octahedral crystallites with uniform micrometric (2-7  $\mu\text{m}$ ) dimensions by hydrothermal crystallization of aged at room temperature gel (2.9Na<sub>2</sub>O: 0.26Al<sub>2</sub>O<sub>3</sub>: 1SiO<sub>2</sub>: 150H<sub>2</sub>O) obtained from water suspension of natural phillipsite, treated with hydrochloric acid and mixed with sodium hydroxide. Crystal structure of both zeolites is testified by X-ray diffraction patterns and infra-red spectra. Synthesized zeolite NaX is characterized by specific surface area of 589 m<sup>2</sup>/g and total pore volume of 0.578 cm<sup>3</sup>/g calculated by the Brunauer-Emmett-Teller method from the low-temperature nitrogen adsorption-desorption isotherms. Along with ordered homogeneous micropores, the obtained zeolite NaX has a developed system of cylindrical channels with an average diameter of 55 nm (calculated by the Barrett-Joyner-Halenda method), which opens up the prospect of its use in catalytic processes. © 2019 Bull. Georg. Natl. Acad. Sci.

**Key words:** analcime, phillipsite, hydrothermal transformation, zeolite A, zeolite X

Synthetic zeolites characterized by uniform and precise nano-scale porosity, molecular shape selectivity, ion-exchange capacity, strong Brønsted acidity and other beneficial properties, find the greatest practical application [1,2], and the hydrothermal zeolite synthesis through transformation of natural

silicates and industrial wastes has been used due to the search for cheap alumina and silica sources [3].

Among the zeolites known on the territory of Georgia the sedimentary and volcanic-sedimentary analcime is rather widespread, phillipsite-containing Eocene rocks were discovered firstly at

the northern fringe of the Akhaltsikhe depression, along with other zeolites, and then in the Gurian range [4], zeolite phase content in rocks differs in a range of 60-80% [5].

Compared with clinoptilolite, analcime and phillipsite are not widely used, there are only some considerations about their use for water and wastewater treatment [6], pollution control [7] and other environmental applications [8].

The aim of our work was to study the hydrothermal recrystallization of the Georgian analcime and phillipsite to obtain valuable zeolites in one step without application of crystallization seeds and organic templates. Analcime structure contains 4- and 6-member ring secondary building units [9] and may be suitable for the preparation of zeolite A (the crystal chemical formula  $[\text{Na}_{12}(\text{H}_2\text{O})_{27}]_8 [\text{Al}_{12}\text{Si}_{12}\text{O}_{48}]_8$ -LTA) widely used in detergents as a water-softening builder [10] and in ion exchange separation [11]. Phillipsite is structurally built up by layers of 4- and 8-member rings forming double crankshaft chains [9], it may be applied to obtain zeolite X ( $[(\text{Ca},\text{Mg},\text{Na}_2)_{29}(\text{H}_2\text{O})_{240}] [\text{Al}_{58}\text{Si}_{134}\text{O}_{384}]$ -FAU), having a very widespread use in catalysis [12].

## Materials and Methods

**Raw materials.** Preparation of synthetic zeolite materials was carried out using sodium analcime from Chachubeti with Si/Al~2 and phillipsite from the Akhaltsikhe field with Si/Al~2 described and characterized previously [13].

**Processing of raw in target material.** Zeolite-containing rocks were crushed in the planetary micro mill Pulverisette 7 (Fritsch Laboratory Instruments, Idar-Oberstein, Germany) to a size less than 0.063 mm (250 BSS mesh). Analcime powder was treated at room temperature by HCl water solution (12%) under stirring, washed by water before the complete disappearance of  $\text{Cl}^-$  ions, and dried in thermostat oven at 100-105°C; water suspension (the solid to liquid ratio of 1 : 3) of homogeneous amorphous (XRD tested) material was prepared in Teflon flask; suspension was treated at room temperature by NaOH water solution (20%) under stirring. Phillipsite powder was suspended in Teflon flask placed in shaking water bath OLS 26 Aqua Pro (Grant Instruments, Cambridge, UK) controlling temperature at 90-95°C; suspension was processed with a 12% hydrochloric acid solution at the rate of 5 mL per gram of the solid raw material; activated suspension was diluted with water and treated by adding of a 25% sodium hydroxide solution, followed by the formation of a homogeneous gel. The molar ratios  $\text{SiO}_2/\text{Al}_2\text{O}_3$ ,  $\text{Na}_2\text{O}/\text{Al}_2\text{O}_3$ , and  $\text{H}_2\text{O}/\text{Na}_2\text{O}$ , optimal for obtaining zeolite A from analcime and zeolite X from phillipsite, are given in the Table 1, as well as duration of the gel aging at room temperature and crystallization in temperature-controlled water bath adjusted to prepare micrometric single crystals. Beginning of crystallization was detected by sampling and X-ray diffraction analyses. Separation of produced crystalline material was carried out by filtration of mother solution, solid

**Table 1. Optimal chemical composition of the gel, duration of its aging and crystallization**

Raw material	Chachubeti analcime	Akhaltsikhe phillipsite
Target product structure	LTA	FAU
Molar ratio $\text{SiO}_2/\text{Al}_2\text{O}_3$	2.2	3.8
Molar ratio $\text{Na}_2\text{O}/\text{Al}_2\text{O}_3$	9.8	12
Molar ratio $\text{H}_2\text{O}/\text{Na}_2\text{O}$	40	55
Gel aging duration, hr	72	96
Beginning of zeolitization, hr after start	30	16
Total crystallization time, hr	up to 120	up to 55

material was cleaned by distilled water until pH 8.0-8.5, and dried at 90-100°C.

**Characterization.** Chemical composition of samples was determined by elemental and energy dispersive X-ray (EDS) analysis. The crystalline phase was identified by powder X-ray diffraction (XRD) patterns obtained from a Dron-4 X-ray diffractometer (Russia) employing the Cu-K $\alpha$  line ( $\lambda=0.154056$  nm), scanning in the  $2\Theta$  range of 5° to 50° with a speed of 1°/min. Fourier transform infrared spectra (FTIR) were collected by a 10.4.2 FTIR spectrometer (Perkin-Elmer, UK) over the range of 400-4000 cm $^{-1}$  with a resolution of 2 cm $^{-1}$  using the KBr pellet technique for sample preparation. The morphology was observed by scanning electron microscope JSM6510LV (Jeol, Japan) equipped with X-Max 20 analyzer (Oxford Instruments, UK) for EDS. Nitrogen adsorption-desorption isotherms were measured at 77 K using an ASAP 2020 Plus analyzer (Micromeritics, Norcross, GA, USA), after evacuation of the samples at 350°C during 2 hours; water adsorption capacity was measured under static conditions.

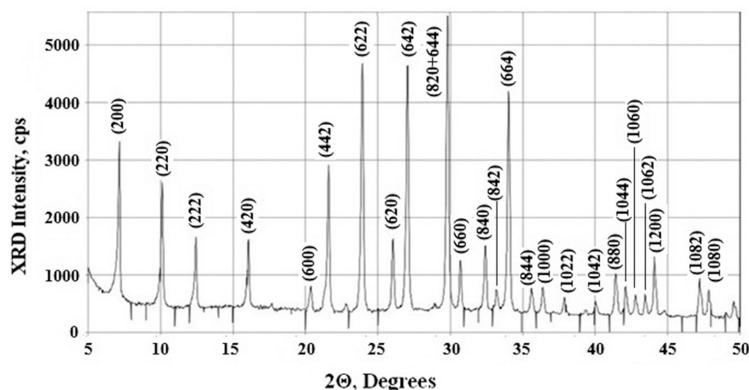
## Results and Discussion

**Chemical composition and XRD.** The chemical composition of material, obtained from analcime, is described by the empirical formula Na<sub>11.25(25)</sub>(K, $\frac{1}{2}$ Ca, $\frac{1}{2}$ Mg)<sub>0.7(1)</sub>(Al<sub>11.95(25)</sub>Si<sub>12.3(3)</sub>O<sub>48</sub>) · 18H<sub>2</sub>O, and is in a good accordance with crystal chemical formula of the LTA structure. There is

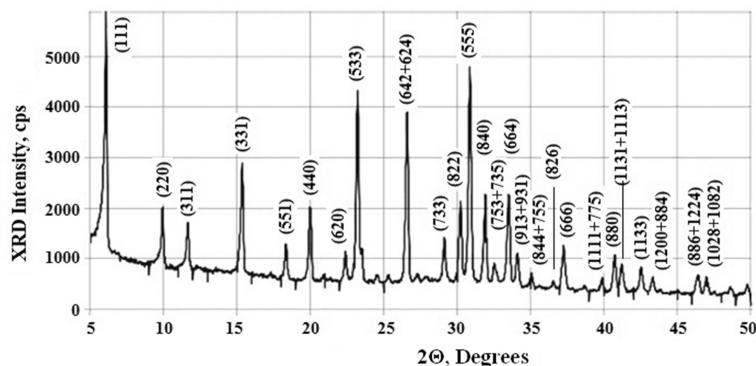
only a small “lack” of the Al atoms (Si/Al=1.03±0.025), samples of zeolite A obtained from kaolin usually have Si/Al values from 1.15 [14,15] to 1.3 [16]. According to the data of the elemental and EDS analysis, counted on 384 oxygen atoms and 192 T-atoms in the unit cell, the empirical formula of the phillipsite recrystallization product can be represented as |Na<sub>66(3)</sub> [Me]<sub>12(1)</sub> (H<sub>2</sub>O)<sub>248(10)</sub>| (Al<sub>78(3)</sub>Si<sub>114(4)</sub>O<sub>384</sub>) (Me = K,  $\frac{1}{2}$ Ca,  $\frac{1}{2}$ Mg,  $\frac{1}{2}$ Cu and  $\frac{1}{2}$ Zn, the latter is unevenly distributed). Compared to the crystal chemical formula of FAU with (Al<sub>58</sub>Si<sub>134</sub>O<sub>384</sub>) and (H<sub>2</sub>O)<sub>240</sub>, the resulting compound has elevated aluminum content with about the same number of crystallization water molecules.

Unambiguous assignment of peaks in the XRD patterns of compounds obtained from analcime (Fig. 1) and from phillipsite (Fig. 2), confirms the receipt of the target products, zeolites NaA and NaX, respectively.

**FTIR characterization.** The mid infra red peak patterns in FTIR spectra (Fig. 3) testify formation of zeolite structure in both cases. The band of the internal deformation vibration modes of T-O-T bridges and the band of the internal vibration of T-O symmetric stretching have little influence from the Si/Al ratio: absorption peaks are at 465 and 663 cm $^{-1}$  for zeolite NaA, and at 461 and 668 cm $^{-1}$  for zeolite NaX, respectively. The band associated with the asymmetric external vibration of double

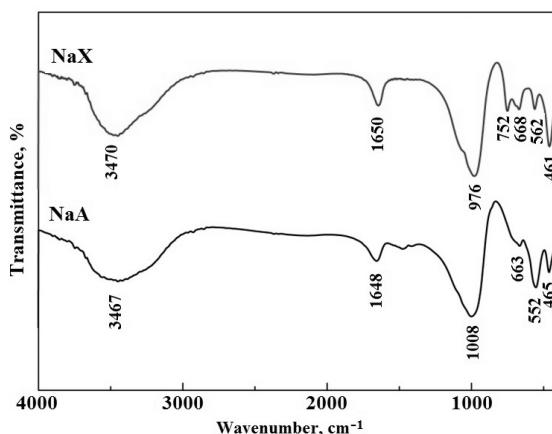


**Fig. 1.** Assignment of powder XRD pattern of the analcime recrystallization product to the LTA structure and corresponding Miller indices (hkl).



**Fig. 2.** Assignment of powder XRD pattern of the phillipsite recrystallization product to the FAU structure and corresponding Miller indices (hkl).

4-rings is more sensitive to the Si/Al ratio: 552 cm<sup>-1</sup> for zeolite NaA, and 562 cm<sup>-1</sup> for zeolite NaX. The band of valence T–O–T vibrations gives resolved peak at 752 cm<sup>-1</sup> only for zeolite NaX. The internal vibration of T–O asymmetric stretching gives peak at 1008 cm<sup>-1</sup> for the NaA sample, for zeolite NaX it is shifted to the lower wavenumbers (976 cm<sup>-1</sup>) due to higher silicon content [17]. In both spectra, bands are observed at ~1650 and ~3470 cm<sup>-1</sup> corresponding to the presence of H<sub>2</sub>O and hydroxyls, respectively. The observed FTIR bands are in good agreement with those reported for both zeolites [18], further proving the successful synthesis of zeolite NaA from analcime and NaX from phillipsite.



**Fig. 3.** FTIR spectra of obtained zeolites NaA and NaX.

**Optimal conditions and parameters of transformation.** Obtaining of zeolite NaX from

a gel with molar ratio SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> = 3.8 corresponds to preparation of a single phase NaX zeolite from sodium silicate and sodium aluminate with the SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> molar ratio of 1.5–4.0 [19]. The use of pure chemicals leads to development of the NaA at SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> = 1.0 in addition to the NaX, and generation of a single phase NaA at SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> = 0.5. However, the use of natural precursors leads to other results, the synthesis of zeolite X from coal fly ash was carried out at SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> = 5, and zeolite A at SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> = 1.67 [18], so that the preparation of zeolite NaA by recrystallization of analcime at SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> = 2.2 and large molar ratio Na<sub>2</sub>O/Al<sub>2</sub>O<sub>3</sub> is understandable. The optimal conditions for the recrystallization of the phillipsite in zeolite Na-X are 2.9Na<sub>2</sub>O/SiO<sub>2</sub> and ~50H<sub>2</sub>O/Na<sub>2</sub>O. The same zeolite was synthesized from the coal fly ash at lower sodium content, 2.2Na<sub>2</sub>O/SiO<sub>2</sub>, compensated by comparatively low dilution, ~40H<sub>2</sub>O/Na<sub>2</sub>O [18], synthesis of zeolite X from diatomite was carried out in conditions of slightly higher sodium content (3.0Na<sub>2</sub>O/SiO<sub>2</sub>) and lower dilution factor, 40H<sub>2</sub>O/Na<sub>2</sub>O [20]. As can be seen, the crystal structure of phillipsite PHI [9] has a rather low framework density (15.8T/1000Å<sup>3</sup>), and high alkalinity is not needed for its transformation.

Aging also plays an important role in the nucleation of amorphous gel. In the study, out of

considerations of energy saving, the room temperature was chosen for aging the gel and the optimum crystallization temperature was selected below the boiling point of water, eliminating the need for an autoclave and conducting the process of hydrothermal crystallization in a water bath. Of course, this led to a significant increase in the duration of aging, from about six to ten hours to several days, but this saves more than 100 Joules per gram of the reaction mixture.

**Sorption properties.** The  $N_2$  adsorption-desorption plot at 77 K for the prepared zeolite NaX (Fig. 4) up to relative pressure  $p/p_0 \sim 0.92$  corresponds to typical Langmuir isotherm attributed to the filling of micropores. The specific surface area calculated by the Brunauer-Emmett-Teller (BET) method is 589  $m^2/g$ , the total pore volume is 0.578  $cm^3/g$ , the volume of micropores with a diameter of less than 8 Å is 0.301  $cm^3/g$ .

Type H<sub>1</sub> narrow hysteresis loop, corresponding to the filling of well defined cylindrical channels [21], is observed at high relative pressures (from 0.925 to 0.999). Average channel diameter calculated by the Barrett-Joyner-Halenda (BJH) method is 55 nm, and a specific volume of channels is 0.277  $cm^3/g$ , constituting ~48% of the total adsorption capacity of the zeolite.

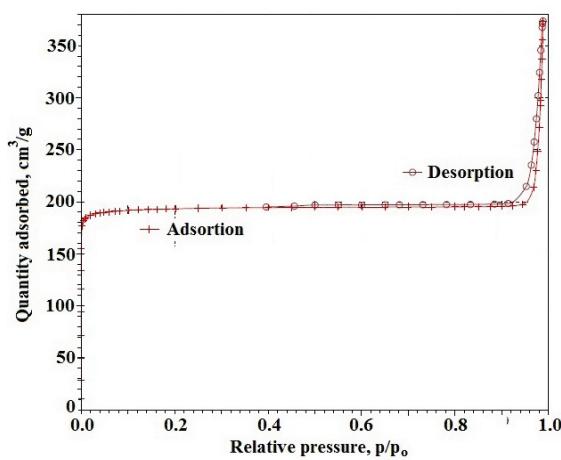


Fig. 4.  $N_2$  adsorption-desorption isotherms on NaX.

The LTA structure has small pores (0.41 nm) comparable with the kinetic diameter of  $N_2$  (0.364 nm), therefore, the BET surface area of the synthesized NaA sample was not measured; water adsorption capacity of micropores ( $p/p_0=0.40$ ) is up to 0.24  $cm^3/g$  and is consistent with most of the reports on phase-pure zeolite NaA.

**Morphology.** In general, more than 92% of NaA crystallites have uniform size of 3–5  $\mu m$  and cubic or rhombus morphology (Fig. 5, left), and more than 95% of NaX crystallites have octahedral habit and uniform size of 2 – 7  $\mu m$  (Fig. 5, right). In the process of crystallization, a small amount (<2-3 wt.%) of spherical or ellipsoidal nano (0.1 – 0.25

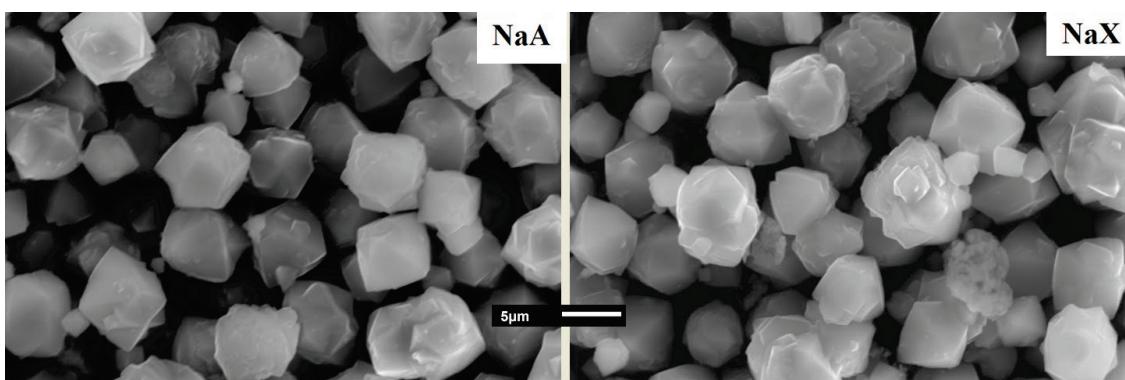


Fig. 5. SEM images (x2,700) of zeolite NaA (left) and zeolite NaX (right).

( $\mu\text{m}$ ) crystallites is also formed, long crystallization results in micrometric crystals combined into honeycomb-like structure through nanocrystal bridges.

### Conclusion

Thus, it is established, that by hydrothermal recrystallization of natural analcime it is possible to receive phase-pure zeolite NaA with Si/Al~1, and recrystallization of natural phillipsite results in phase-pure zeolite NaX with Si/Al~1.5, characterized by high specific surface area (589  $\text{m}^2/\text{g}$ ) and volume of pores (0.578  $\text{cm}^3/\text{g}$ )

including uniform zeolitic micropores and cylindrical channels with an average diameter of 55 nm. Both zeolites are prepared in the form of micrometric crystallites and are competitive in their properties with commercial zeolites NaA and NaX.

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## ფიზიკური ქიმია

# ბუნებრივი ანალციმისა და ფილიპსიტის ჰიდროთერმული გარდაქმნა

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თბილისის სახელმწიფო უნივერსიტეტი, პეტრე მელიქიშვილის ფიზიკური და ორგანული ქიმიის  
ინსტიტუტი, თბილისი, საქართველო

\*\* ივანე ჯავახიშვილის სახ. თბილისის სახელმწიფო უნივერსიტეტი, პეტრე მელიქიშვილის  
ფიზიკური და ორგანული ქიმიის ინსტიტუტი, თბილისი, საქართველო

წარმოდგენილ ნაშრომში შესწავლილია საქართველოში ფართოდ გავრცელებული ბუნებრივი  
ცეოლითების – ანალციმისა და ფილიპსიტის ჰიდროთერმული გარდაქმნა ადგილობრივი  
ნედლეულის საფუძველზე ღირებული პროდუქტების მიღების მიზნით. აღმოჩენილია, რომ  
ფაზურად სუფთა NaA ტიპის ცეოლითი, სილიკატური მოდულით Si/Al~1, ერთგვაროვანი  
მიკრომეტრული (3-5 მკმ) კუმური და რომბული კრისტალიტების სახით, მიიღება  
მარილმჟავას წყალხსნარში წინასწარ დამუშავებული ბუნებრივი ანალციმისაგან მისი  
სუსკენდირებით, ნატრიუმის ჰიდროქსიდთან შერევით, ჰომოგენიზაციის შედეგად  
მიღებული ალუმინ-სილიკატური გელის (4,5Na<sub>2</sub>O: 0,45Al<sub>2</sub>O<sub>3</sub>: 1SiO<sub>2</sub>: 178H<sub>2</sub>O) ოთახის  
ტემპერატურაზე ხანგრძლივი დაბერებით და შემდგომი ჰიდროთერმული კრისტალიზაციის  
გზით. ფაზურად სუფთა NaX ტიპის ცეოლითი, სილიკატური მოდულით Si/Al~1,5,  
ერთგვაროვანი მიკრომეტრული (2-7 მკმ) ოქტაედრული კრისტალიტების სახით, მიიღება  
ბუნებრივი ფილიპსიტის წყლიანი სუსკენზისაგან, მისი მუავური დამუშავებით, ტუტესთან  
შერევის შედეგად მიღებული და დაბერებული გელის (2,9Na<sub>2</sub>O: 0,26Al<sub>2</sub>O<sub>3</sub>: 1SiO<sub>2</sub>: 150H<sub>2</sub>O)  
ჰიდროთერმული კრისტალიზაციის გზით. ორივე ტიპის ცეოლითის კრისტალური  
სტრუქტურა დადასტურებულია რენტგენოგრამებით და ინფრაწითელი სპექტრებით.  
მიღებული NaX ტიპის ცეოლითი ხასიათდება მაღალი ხვედრითი ზედაპირის ფართობით  
(589 მ<sup>2</sup>/გ, გამოანგარიშებულია ბრუნაუერ-ემეტ-ტელერის მეთოდით აზოტის ადსორბცია-  
დესორბციის დაბალტემპერატურული იზოთერმების გამოყენებით) და ფორების  
მოცულობით (0,578 სმ<sup>3</sup>/გ); ერთგვაროვან, მოწესრიგებულ ცეოლითურ ფორებთან ერთად NaX  
ტიპის ცეოლითში არის ცილინდრული არხების (საშუალო დიამეტრი 55 ნმ, გამოთვლილია  
ბარეტ-ჯოინერ-ჰალენდას მეთოდით) განვითარებული სისტემა. ამ მხრივ, მისი გამოყენება  
მეტად პერსპექტიულია კატალიზურ პროცესებში.

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