Materials Science-Poland, Vol. 25, No. 3, 2007

The influence of Al containing component on synthesis of analcime of various crystallographic systems

A. BALANDIS[*], A. TRAIDARAITE

Department of Silicate Technology, Faculty of Chemical Technology,
Kaunas University of Technology, Radvilenu st. 19, 50254 Kaunas, Lithuania

The influence of the form of the Al-containing component, molar ratio of $Na_2O:Al_2O_3:SiO_2$, and the duration of isothermal curing under saturated steam at 180 °C have been examined. The results obtained experimentally show that the form of the Al-containing component ($Al(OH)_3$ or γ-Al_2O_3) significantly affects the formation of crystal system of analcime. Pure analcime of the tetragonal crystallographic system forms under saturated steam at 180 °C after 7 h of isothermal curing, in the presence of considerable excess of NaOH, only when $Al(OH)_3$ is used in the initial mixture. Pure analcime of the cubic crystallographic system forms when γ-Al_2O_3 is used in the initial mixture of hydrothermal synthesis.

Key words: *analcime; zeolite;* $Al(OH)_3$; γ-Al_2O_3; *hydrothermal synthesis*

1. Introduction

Analcime $NaAl(Si_2O_6)\cdot(H_2O)$ belongs to minerals of tectosilicate group with zeolitic structure [1]. Due to the similarity of structure, under natural conditions it often crystallizes in magmatic vein rocks with a low SiO_2 content, as well as in metamorphic and hydrothermal vein rocks in paragenetic associations together with pollucite, wairakite, faujasite, paulingite, viseite and other zeolites [2]. New examinations have shown that natural analcime, depending on the conditions of its formation and impurities, may belong to the cubic, tetragonal, orthorhombic, monoclinic or triclinic crystallographic systems. At room temperature, differences between the crystal lattice parameters a, b, and c normally do not exceed a few hundred or even thousand nanometers, and deviations of the angles α, β, and γ from 90° are also minor and do not exceed 0.2–0.4°. These facts explain certain difficulties in identifying analcime modifications belonging to various crystallographic systems in the products of the synthesis.

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[*] Corresponding author, e-mail: alfredas.balandis@ktu.lt

Analcime, like other minerals of zeolitic structure, boasts a variety of application possibilities in technologies. Recently, analcime has received increased attention from electronics specialists who have started research on synthetic pure fine-dispersive minerals of the zeolitic structure due to their specific interaction with magnetic fields. The centres of positive and negative charges in the crystal lattice of analcime with the orthorhombic crystal system do not coincide, resulting in formation of a polar lattice. Another field of analcime application is stomatology. Cubic analcime can be used for obtaining cubic leucite (through ion exchange under hydrothermal conditions), which is a very important component of dental porcelain [3–6].

Despite the fact that natural zeolites are cheaper than their synthetic counterparts, their use is limited by contamination with impurities. Such important fields as energy economy control of environment pollution, hydrocarbon separation, bifunctional catalysis, production of dental porcelain and other normally use pure synthetic zeolites.

Synthetic analcimes, as a rule, belong to tetragonal, orthorhombic or cubic crystallographic systems. It has been established [2] that during heating of the orthorhombic analcime from room temperature to 150 °C, the *a* parameter of its crystal lattice slightly increases from 1.3720 to 1.3728 nm. However, it unevenly declines with a further increase of temperature from 150 °C to 400 °C and at 800 °C it slumps to 1.3640 nm. Consequently, at 400 °C, the crystal lattice of the orthorhombic analcime greatly differs from the cubic one. If, under change of temperature, such uneven changes in the size of the crystal analcime lattice take place within a crystal, they cause internal tensions in the crystal along with significant decrease in the material strength leading to its cracking, for instance, in dental porcelain veneers. With regard to temperature impact, cubic analcime and cubic leucite are more preferable in ceramic composites because increasing temperature does not change the type of their crystal lattice.

The syngonic type of an analcime forming during the synthesis has a great practical importance. However, the conditions influencing the syngonic type of analcime have not been sufficiently examined. The changes in the crystallographic system of analcime synthesized from amorphous melts under hydrothermal conditions, the impact of high temperatures and high pressures have been analysed [7]. It has been established that analcimes of low category crystallographic systems, i.e. triclinic and monoclinic form at low temperature (80–160 °C) under the pressure of 100 MPa. When the temperature of synthesis rises, the number of symmetry elements grows and analcimes of orthorhombic, tetragonal and cubic crystal systems are formed.

Various authors [8–10] report on very different conditions of synthesis of analcime. Some authors [7] claim that the crystal system of analcime synthesized depends on the temperature and pressure of the hydrothermal synthesis. Under the pressure from 100 MPa to 200 MPa and within the temperature range of 160–400 °C, the analcime of cubic crystal system is the final product of the synthesis. But other authors [11], having examined the synthesis of analcime under 100 MPa, stated that the symmetry of the formed analcime depends on the initial materials and on the temperature of hydrothermal synthesis.

The synthesis of analcime under hydrothermal conditions and at comparatively low pressures, which could also be maintained in industrial equipment, has not been explored much. All the papers state that the synthesis of analcime has to be carried out in the presence of NaOH excess but there are different opinions on the minimal ratio of $Na_2O:Al_2O_3$ in initial mixtures.

So far too little attention has been paid to the Al containing component being one of the most important initial components of analcime synthesis. Taking into consideration the fact that the synthesis of analcime occurs in aqueous suspensions, in our opinion, the Al containing component is very important in the processes of analcime formation with regard to the amphoteric properties of aluminium compounds (Al_2O_3 or $Al(OH)_3$) and the formation of an isoelectric point in the suspensions of synthesis.

Analcime belongs to zeolites whose crystal structures do not change during the dehydration when they are heated up to 900–1000 °C. However, parameters of the crystalline lattice of analcimes of different crystal system change nonuniformly upon changing temperature. The parameters of the crystal lattice of analcime of cubic crystal system change most evenly when the temperature is increasing. This stipulates the importance of the analcime of cubic crystal system in the processes of sorption, catalysis and production of technical ceramics. However, the factors determining the crystal system type of analcime which is formed during hydrothermal synthesis have been investigated very poorly.

The aim of this paper was to analyze the influence of chemical properties of Al containing component and preparation conditions of γ-Al_2O_3 on the crystal system of analcime, forming under hydrothermal conditions.

2. Experimental

Amorphous $SiO_2{\cdot}nH_2O$ was milled in a porcelain grinder for 1 h and sieved through a sieve with a mesh width of 80 μm (specific surface area S_a = 1301 m^2/kg by Blaine, ignition losses – 23.84%). The following Al containing components were used: $Al(OH)_3$ pure – gibbsite (S_a = 104.9 m^2/kg by Blaine) and two types of γ-Al_2O_3 γ-Al_2O_3 (I) (S_a = 273,9 m^2/kg by Blaine) was obtained by heating $Al(OH)_3$ at 550 ºC for 3 h while γ-Al_2O_3 (II) (S_a = 179,6 m^2/kg by Blaine) was obtained by heating $Al(OH)_3$ at 475 ºC for 4 h. NaOH solution (c = 11%) was obtained by dissolving NaOH in distilled water.

Analcime was synthesized from the mixtures $Na_2O:Al_2O_3:SiO_2$ in stainless steel and/or fluoroplastic vessels in an autoclave *Lampart* using the compositions of initial mixtures given in Table 1.

NaOH was added as an aqueous solution. An addition of NaOH corresponded to 11% of Na_2O in the dry materials, so that the water/solid ratio of the suspension was equal to 5.0.

Table 1. Compositions of initial mixtures used for synthesis of analcime

No.	Molar content in mixture			Percentage content in mixture		
	Na_2O	Al_2O_3	SiO_2	Na_2O	Al_2O_3	SiO_2
1	2	1	3	30.54	25.12	44.34
2	2	1	4	26.61	21.89	51.50
3	2	1	5	23.57	19.39	57.04
4	2	1	6	21.16	17.41	61.43
5	4	1	3	46.79	19.25	33.96
6	4	1	4	42.03	17.29	40.68
7	4	1	5	38.15	15.69	46.15
8	4	1	6	34.93	14.37	50.70

Hydrothermal synthesis of analcime in unstirred suspensions has been carried out under the saturated steam pressure at a temperature of 180 °C; the duration of isothermal curing was 5 or 7 h. The products were filtrated, rinsed with ethyl alcohol to prevent carbonization of the material, dried at 30±5 °C and sieved through a sieve with a mesh width of 80 μm. The X-ray powder diffraction data were collected with DRON–6 X-ray diffractometer with the Bragg–Brentano geometry using Ni-filtered Cu K_α radiation and graphite monochromator, operating with the voltage of 30 kV and emission current of 20 mA. The step-scan covered the angular range 2–60° (2θ) in steps of $2\theta = 0.02^\circ$. Differential scanning calorimetry (DSC) was employed for measuring the thermal stability and phase transformation of the synthesized products at the heating rate of 15 °C/min, the temperature ranged from 30 °C up to 1000 °C under ambient atmosphere. The test was carried out on a Netzsch instrument STA 409 PC Luxx. The ceramic sample handlers and crucibles of Pt-Rh were used. The specific surface area was determined by Blaine's method with air permeability apparatus (Model 7201, Toni Technik Baustoffprufsysteme GmbH).

3. Results and discussion

A series of analcime syntheses with the molar Na_2O:Al_2O_3:SiO_2 ratios of 2:1:3, 2:1:4, 2:1:5, 2:1:6 were performed with the aim to investigate the possibility of analcime synthesis under a minimal excess of NaOH (2 mole Na_2O). The use of Al_2O_3 in the synthesis as an Al containing component is related to certain peculiarities of chemical processes. Al_2O_3 reacts with sodium hydroxide and sodium aluminate $NaAl(OH)_4$, well dissolving in water, forms. However, when the molar ratio of Na_2O:Al_2O_3 is around 1.7, $Al(OH)_3$ crystals precipitate from sodium aluminate solutions. To prevent the precipitation, the solution should be heated at 150–200 °C for 4–6 h [13]:

$$Al(OH)_3 + NaOH + H_2O \rightarrow NaAl(OH)_4 + H_2O$$

The decomposition of sodium aluminate accelerates when the solution contains large amounts of $Al(OH)_3$. When NaOH solution contains soluble SiO_2, the reaction between Na_2SiO_3 and $NaAl(OH)_4$ results in formation of sodium aluminium silicates, including analcime. However, the lower the concentration of sodium aluminium silicate, the more energetic is formation of sodium aluminium silicate. Thus, to avoid decomposition of sodium aluminate and formation of less soluble crystals of $Al(OH)_3$, the molar ratio of Na_2O:Al_2O_3 in initial mixtures should be higher than 2.0. Another important factor in is the dissolving rate of Al_2O_3 that depends on both the modification of Al_2O_3 and the size of its crystals.

The Al containing component for the synthesis was prepared by heating pure $Al(OH)_3$ at 550; 525; 500; 475 and 450 °C for 1–6 h in order to avoid formation of high-temperature, less soluble, and chemically less active α-Al_2O_3, and, on the other hand, to reduce the energy used to prepare the Al containing component. Basing on the results of X-ray diffraction analysis, it has been established that an active γ-Al_2O_3 forms when $Al(OH)_3$ is heated at 550 °C for 1 h. Therefore, the formation processes of γ-Al_2O_3 were analyzed at lower temperatures (525, 500, 475 and 450 °C). The characteristic curves of X-ray diffraction analysis of the obtained products are shown in Fig. 1.

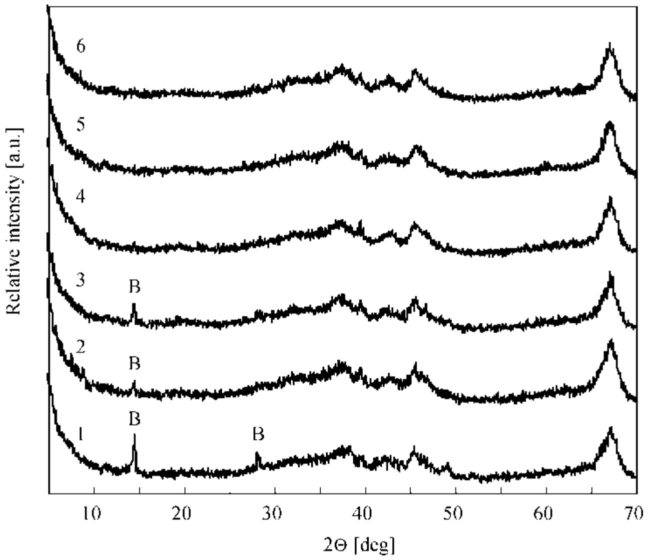

Fig. 1. X-ray diffraction patterns of the Al containing component – γ-Al_2O_3 obtained from pure $Al(OH)_3$ at various conditions: 1 – 450 °C, 5 h; 2 – 450 °C, 8 h; 3 – 475 °C, 3 h; 4 – 475 °C, 4 h; 5 – 550 °C, 1 h; 6 – 550 °C, 3 h; B – boehmite

The X-ray diffraction analysis of the obtained products has shown that even after 8 h of isothermal curing at 450 °C, not only γ-Al_2O_3, but also hydrated Al_2O_3 – boehmite – forms during decomposition of $Al(OH)_3$. At a higher decomposition temperature of $Al(OH)_3$ – 475 ºC, γ-Al_2O_3 can be obtained after 4 h of isothermal curing. But the specific surface of the obtained crystals is 179.6 m^2/kg, whereas that of γ-Al_2O_3 obtained at 550 ºC amounts to 273.9 m^2/kg. These data confirm formation of bigger γ-Al_2O_3 crystals at 475 ºC, which, in turn, might have a negative influence on the dissolution processes of the Al containing component during the synthesis of analcime.

Having evaluated the modification activity, purity and dispersity of forming Al_2O_3, γ-Al_2O_3 (I) and γ-Al_2O_3 (II) were used for the synthesis of analcime. Another series of analcime syntheses was performed by using pure $Al(OH)_3$ as the Al containing component.

In the first stage of this research, analcime was synthesized from initial mixtures with the following component ratios after recalculation into molar oxide ratios: $Na_2O:Al_2O_3:SiO_2$ = 2:1:3; 2:1:4; 2:1:5; 2:1:6. Hydrothermal synthesis was performed at 180 ºC with isothermal curing of 5 h. After filtering and rinsing the products of synthesis, the amount of NaOH in the filtrate was established, and the reaction degree of NaOH was determined. The mineral composition of the solid phase was analyzed using X-ray diffraction and differential scanning calorimetry. The filtrate analysis data are given in Table 2.

Table 2. NaOH reaction degree [%] at 180 ºC after 5 h of isothermal curing

Al containing component	Molar ratio $Na_2O:Al_2O_3:SiO_2$			
	2:1:3 (44.34% SiO_2)	2:1:4 (51.50% SiO_2)	2:1:5 (57.04% SiO_2)	2:1:6 (61.43% SiO_2)
$Al(OH)_3$	94.04	94.87	93.36	90.07
γ-Al_2O_3 (I)	95.33	94.38	93.69	91.36
γ-Al_2O_3 (II)	92.19	96.62	95.99	90.77

At the $Na_2O:Al_2O_3$ molar ratio equal to 2.0, nearly all sodium hydrate contained in the initial mixture reacts (94–97%) under the conditions of synthesis. The degree of sodium hydrate reaction is noticeably lower at the presence of an excess of SiO_2 (molar ratio of $SiO_2:Al_2O_3$ equal to 6:1). The highest NaOH reaction degree was obtained for the initial mixture $Na_2O:Al_2O_3:SiO_2$ = 2:1:4. Since the obtained products had grey colour, the synthesis was repeated by synthesizing analcime not only in stainless steel, but also in small white fluoroplastic vessels. The products obtained in fluoroplastic vessels had clear white colour, and, in addition, for all Al containing components, the NaOH reaction degree was higher: in stainless steel vessels it was 91.85–93.21%, while in fluoroplastic vessels it amounted to 94.38–96.62%. This makes us suppose that during the synthesis of analcime, the sodium solution interacts even with stainless steel, slowing down the processes of analcime synthesis.

The X-ray diffraction analysis of dried reaction products (Fig. 2) has shown that during 5 h of isothermal curing at 180 ºC, pure analcime did not form in the initial mixtures with the molar ratios of 2:1:(3–6), neither using $Al(OH)_3$ nor γ-Al_2O_3, obtained under various conditions as the Al containing component.

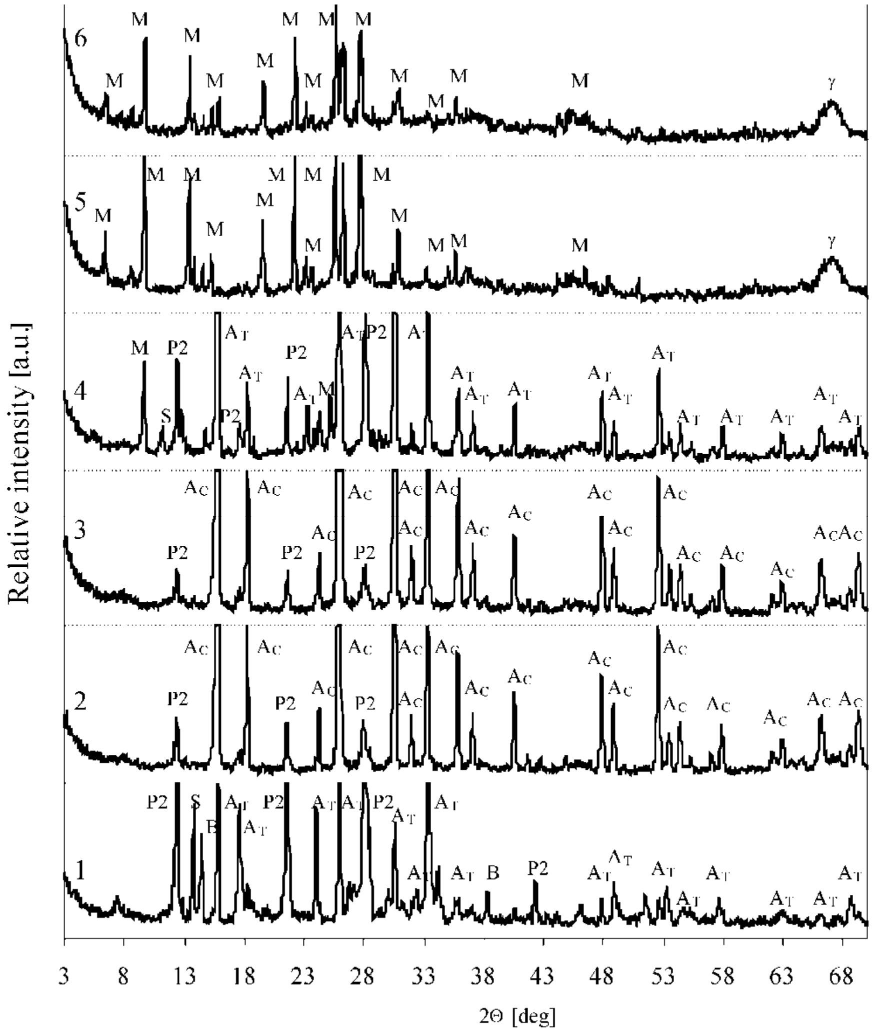

Fig. 2. X-ray diffraction patterns of the products formed after 5 h of hydrothermal synthesis at 180 °C. The molar ratios of the initial mixtures Na_2O:Al_2O_3:SiO_2 are: 2:1:4 (curves 1–3) and 2:1:6 (curves 4–6). Al containing components: 1, 4 – $Al(OH)_3$; 2, 5 – γ-Al_2O_3 (I); 3, 6 – γ-Al_2O_3 (II); A_C – cubic analcime, A_T – tetragonal analcime, B – boehmite, P2 – zeolite P2, S – sodium aluminium silicate, M – mordenite

Apart from analcime $Na(AlSi_2O_6)\cdot(H_2O)$, also sodium aluminium silicate $Na_6(AlSiO_4)_6$ and zeolite P2 – $Na_4(Al_4Si_{12}O_{32})(H_2O)_{14}$ have been identified in the products of reaction. The mixtures prepared with $Al(OH)_3$ as an Al containing component produced analcime of the tetragonal crystallographic system (diffraction reflections established with 100% reliability: 5.6124; 4.8587; 3.4307; 2.9253 nm, etc). At the same time, the synthesis of initial mixtures prepared with γ-Al_2O_3 as an Al containing component produced analcime of the cubic crystallographic system (diffraction reflections established with 100% reliability: 5.6072; 3.4294; 2.9235; 2.2230 nm etc.).

DSC curves of products of the synthesis showed (Fig. 3) that pure analcime did not form during this synthesis. Curve 1 shows that not only the "broadened" endothermic effect at 342 °C of the main product is present but also the endothermic effect of zeolite P2 and the effect of unreacted $Al(OH)_3$ at 139 °C and 570 °C, respectively, are observed. The exothermic effect at 954 °C is not related to weight loss at this temperature, i.e. the sample does not contain water, and therefore it shows the change of structural zeolite frame. When γ-Al_2O_3 (I) was used for the synthesis (curve 2), it was observed that less byproducts were formed and the obtained product was more stable. Changes of the structure of analcime are not observed even between 900 °C and 1000 °C, when all forms of water have been removed.

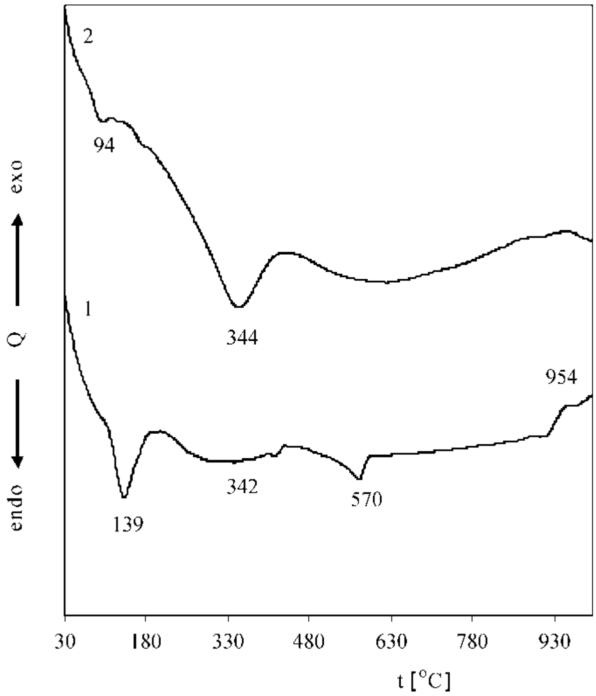

Fig. 3. DSC curves of the products formed after 5 h of hydrothermal synthesis at 180 °C. The molar ratio of the initial mixture Na_2O:Al_2O_3:SiO_2 – 2:1:4. The Al containing components: 1 – $Al(OH)_3$; 2 – γ-Al_2O_3 (I)

Upon prolongation of the synthesis time at 180 °C to 7 h, the trends of NaOH reaction practically did not change both in stainless steel and in fluoroplastic vessels. The composition the products also remained the same but, apart from analcime of the cubic and tetragonal crystallographic system, less hydrated sodium aluminium silicates, such as mordenite, formed.

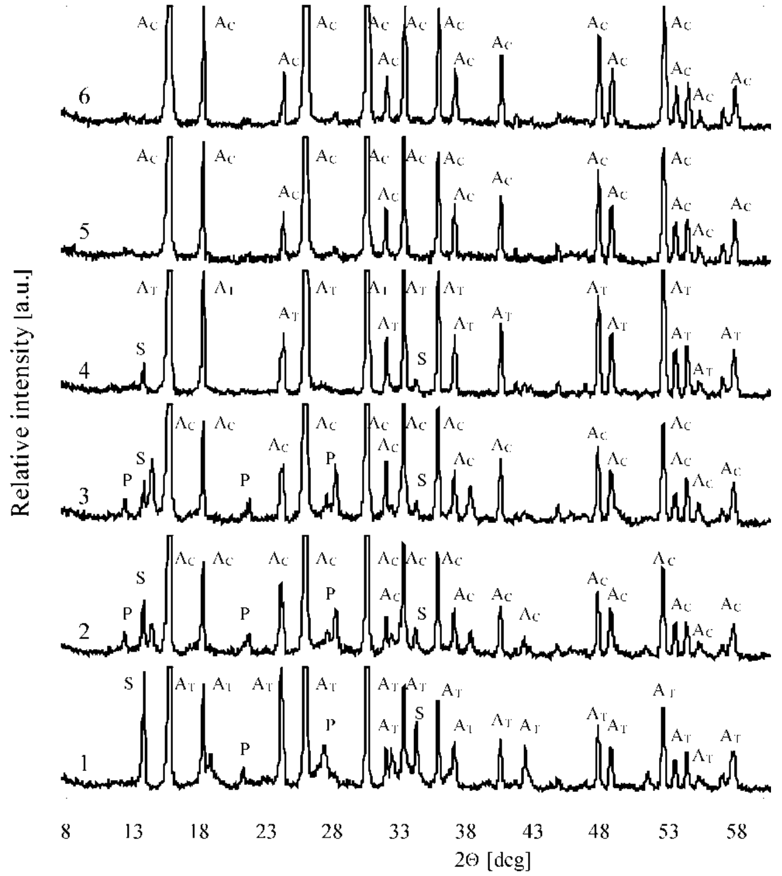

Fig. 4. X-ray diffraction patterns of the products formed after 7 h of hydrothermal synthesis at 180 °C. The molar ratios of the initial mixtures $Na_2O:Al_2O_3:SiO_2$: 4:1:4 (curves 1–3) and 4:1:6 (curves 4–6). The Al containing components were: 1, 4 – $Al(OH)_3$; 2, 5 – γ-Al_2O_3 (I); 3, 6 – γ-Al_2O_3 (II); A_C – cubic analcime, A_T – tetragonal analcime, P – zeolite P, S – sodium aluminium silicate

Taking into consideration the results of these syntheses and the influence of sodium hydroxide on the solubility and stability of sodium aluminates, in the next stages analcime was synthesized from the mixtures $Na_2O:Al_2O_3:SiO_2$ of molar ratios 4:1:(3–6). Hydrothermal synthesis was performed at 180 °C, the period of isothermal curing was 5 h and 7 h. According to expectations, the products of synthesis after reaction contained a higher amount of unreacted NaOH, thus ensuring a sufficient excess of sodium hydroxide within the entire period of the synthesis of analcime. Based on the results of X-ray diffraction analysis and DSC methods, it has been established that pure analcime also did not form at 180 °C after 5 h of isothermal curing. Sodium aluminium silicates and zeolite P have been identified in the products of reaction. However, on extending the duration of isothermal curing to 7 h (Fig. 4), the mixture $Na_2O:Al_2O_3:SiO_2$ with the molar ratio 4:1:6, produced pure analcime: the tetragonal crystallographic system analcime when using $Al(OH)_3$ as an Al containing component (curve 4), and the cubic crystal system analcime when using γ-Al_2O_3 as an Al containing component (curves 5, 6).

DSC curves (Fig. 5) of the products of synthesis of analcime confirm that an increase of the amount of NaOH in the initial mixtures influences the formation of analcime and making it easier even when $Al(OH)_3$ is used as an initial Al source, (curve 1). In addition, the amount of zeolite P decreased in the products obtained if compared with analcime, when the mixture of Na_2O and Al_2O_3 with the molar ratio of 2:1 was used for the synthesis. If the amount of SiO_2 was increased in the initial mixtures, no byproducts, i.e. other zeolites, were observed during the DSC experiments (curves 3, 4). Although the DSC behaviour of analcime crystals belonging to tetragonal and cubic crystallographic systems during the DSC experiment is similar, still some differences could be observed and probably it could be related to higher stability of cubic crystal system analcime crystals during dehydration process. The endothermic effect for both analcimes was observed in the temperature range of 350–360 °C in the DSC experiment and this effect is due to dehydration process but the area under the DSC curve in the same temperature range is 20% smaller in the case of cubic analcime.

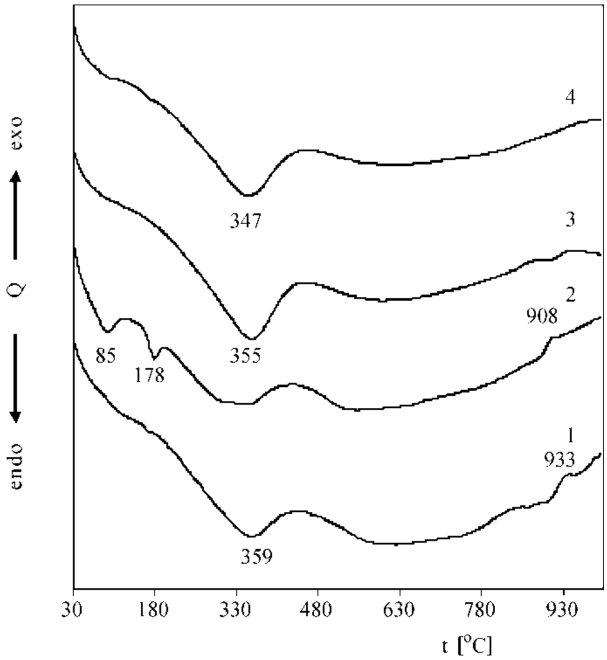

Fig. 5. DSC curves of the products formed after 7 h of hydrothermal synthesis at 180 °C. The molar ratios of the initial mixtures are: Na_2O:Al_2O_3:SiO_2 – 4:1:4 (curves 1, 2) and 4:1:6 (curves 3, 4); Al containing components: 1, 3 – $Al(OH)_3$; 2, 4 – γ-Al_2O_3 (I)

When the excess of NaOH was greater, a larger amount of SiO_2 also reacted during the formation of analcimes. For other molar ratios of initial components sodium aluminium silicates and zeolite P have been identified in the products of reaction. In addition, it has been noticed that the reaction degree of sodium hydroxide was slightly higher (by ca. 1.0–1.5%) when using pure $Al(OH)_3$ as an Al containing component and performing synthesis in fluoroplastic vessels.

4. Conclusions

- Chemical nature of Al containing components is very important for the course of synthesis of analcime and its crystal structure. Tetragonal analcime formed only when using $Al(OH)_3$ in the initial mixtures, while cubic analcime – when using γ-Al_2O_3.
- Pure tetragonal and cubic analcimes formed at 180 °C after 7 h of isothermal curing only in the presence of considerable excess of NaOH in the initial mixtures when the molar ratio of the components $Na_2O:Al_2O_3:SiO_2$ was 4:1:6.
- The conditions of γ-Al_2O_3 formation from pure $Al(OH)_3$ affect the course of analcime synthesis. If pure $Al(OH)_3$ is heated at 475 °C, larger γ-Al_2O_3 crystals of smaller specific surface have formed compared to the product heated at 550 °C; therefore, the synthesis of analcime at 180 °C is impeded and the NaOH reaction degree decreases.
- The synthesis of analcime is a little more efficient when using $Al(OH)_3$ as an Al containing component.

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Received 7 September 2006
Revised 8 January 2007