Thermal transformation of Na-LTA zeolite into low-carnegieite: The influence of residual sodium and aluminium species

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ABSTRACT

The influence of residual sodium and aluminium species on the mechanism of commercial and laboratory-synthesized Na-LTA zeolite thermally induced transformation (ZTIT) was investigated. A phase transformation route between zeolite and low-temperature carnegieite (lt-carn) during heating, is evolving in two different pathways. In one aspect, Na-LTA zeolite transforms directly into lt-carn, while in the other, transformation unfolds through amorphous state.

The samples with significant amount of sodium and aluminium residues: $(1.05–1.06)$ Na$_2$O:$(1.02–1.07)$ Al$_2$O$_3$:2SiO$_2$ did not show intermediate amorphous state during heat treatment. It was implicitly shown that investigated ZTIT process is enhanced by residual species. The residues are extracted from all investigated samples during refluxing treatment at 100 °C. The intermediary amorphous states were created from all refluxed Na-LTA samples. Common characteristics of such prepared amorphous NaAlSiO$_4$ states are narrow temperature stability range (cca. 50 °C) and low-density.

1. Introduction

Synthetic zeolites and their cation-exchanged forms have attracted considerable interest as precursors [1–3] for preparation of advanced ceramics [4–10], silicate/oxide composites [11–13], "perfect glasses" [14–16] and even novel materials [17–20]. Zeolite thermally induced transformation (ZTIT) route into structurally new phase is usually multiple step process which is dependent on several factors such as: type of exchangeable cation, zeolite structure type, Si/Al ratio, precursor stoichiometry [2], etc. In general, conversion processes are driven by the tendency of temperature-unstable low-density zeolite framework structure to collapse into more stable and structurally compact polymorphs. During ZTIT processes, diverse materials like intermediate amorphous products and crystalline polymorphs can be observed.

Appearance of amorphous material during zeolite heating is an interesting phenomenon which occurs primarily as a consequence of breaking Al–O–Si bridges and collapsing of low-density crystal structure. Intermediate amorphous substance with glassy characteristics and inherited zeolite composition has been discussed by Dimitrijevic et al. [21–23], although this phenomenon

has been observed in the early works cited above. According to cited authors, the zeolite amorphization stage is classified as a second step of conversion mechanism in ZTIT processes, after zeolite dehydration. This stage is characterized by complete collapse of low-density precursor zeolite structure into the relicts of (Al,Si)O$_4$ tetrahedral secondary building units (SBU) [24–26]. By prolonged temperature-time treatment of an amorphous substance, discussed tetrahedral relicts spontaneously assemble to other regular SBUs as building blocks of a new crystalline polymorph. Discussed destruction/reconstruction processes have been proven and clearly demonstrated in the case of Ba-LTA → amorphous Ba(AlSiO$_4$)$_2$ → hexacelsian ZTIT [23].

Recently published papers on collapse of synthetic and natural zeolites into amorphous materials during heating or compression [14–16], showed that structural evolution of amorphized zeolites (the term amorphization is used here in the meaning of transformation of a crystalline phase into an amorphous substance without melting or vitrification) can be followed by in situ X-ray diffraction, small angle X-ray scattering, Raman spectroscopy and inelastic neutron scattering experiments, as well. It was shown that discussed amorphous zeolite substances are characterized by phenomenon of polyamorphism (the coexistence of different amorphous phases with the same composition but diverse densities). Thus, polyamorphous phases, called LDA (low-density amorphous phase or "perfect glass") and HDA (high-density amorphous phase), are well defined in the case of synthetic Na-FAU and natural natrolite, leucite and some other zeolites. In our recently published

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Table 1
Chemical compositions of reaction mixtures and as-synthesized Na-LTA zeolites.

Sample Na-LTA	Reaction conditions					Chemical composition of synthesized samples		
	Batch compositions				Time (min)	Na_2O	Al_2O_3	SiO_2
	Na_2O	Al_2O_3	SiO_2	H_2O				
Na-LTA$_1$	3.75	1.33	2.00	133	150	1.05	1.07	2.00
Na-LTA$_2$	3.75	1.33	2.00	133	270	1.05	1.06	2.00
Na-LTA$_3$	4.10	1.11	2.00	133	150	1.06	1.05	2.00
Na-LTA$_4$	4.10	1.11	2.00	122	270	1.06	1.04	2.00
Na-LTA$_5$	4.10	1.05	2.00	95	270	1.05	1.02	2.00

series of papers [27–29] we presented the results on ZTIT of synthetic Na-LTA, Na-FAU and Na-GIS zeolite structure types into low and high-temperature carnegieites (lt-carn and ht-carn) and pure Na-nephelines. Moreover, their conversion mechanisms are distinctive. Whereas Na-FAU and Na-GIS zeolites undergo amorphization processes, this phenomenon is not observed in the case of Na-LTA zeolite. According to the best of our knowledge, Na-LTA zeolite structure can be collapsed into amorphous $NaAlSiO_4$ substance by discussed ZTIT heating route (after cca. 80 h of heating) [26,30], mechanochemical treatment [31] or high pressure action [32], by microwave heating [33] or simply by melting Na-LTA zeolite above 1550 °C.

In one aspect, Na-LTA zeolite transforms directly into lt-carn between 700 and 850 °C [27], while in the other, transformation unfolds through amorphous state: Na-LTA → amorphous $NaAlSiO_4$ → lt-carn, between 790 and 850 °C [26,30].

Differences in conversion route during heating can be related to different amounts of Na and Al species which remain in zeolite cages during synthesis. The presence of these unidentified impurities can significantly change Na-LTA course of thermal transformations. There are no data in the literature on the influence of small differences in stoichiometric composition of Na-LTA zeolites on their conversion route during heating. Thus, the aim of this paper is to investigate the nature of above discussed conversion, i.e. investigate the influence of residual species on Na-LTA transformation to low-carnegieite and to find fast and simple preparation route for synthesis of stable amorphous $NaAlSiO_4$ substance.

2. Experimental

The thermally induced transformation of commercial and a series of Na-LTA zeolite samples synthesized in our laboratory were investigated. Zeolites purchased from Albemarle (Na-LTA$_{AB}$), Fluka (Na-LTA$_{FL}$) and Union Carbide (Na-LTA$_{UC}$), were used for comparisons. Na-LTA zeolite samples were synthesized under hydrothermal conditions. The oxide molar compositions of gels were the following: $xNa_2O:yAl_2O_3:2SiO_2:zH_2O$, where x ranged from 3.75 to 4.10, y ranged from 1.05 to 1.33, while z ranged from 95 to 133 (Table 1). Sodium hydroxide (Aldrich), amorphous hydrated aluminium hydroxide (Aldrich) and sodium silicate solution (10% Na_2O, 24% SiO_2, $\rho = 1.350$ g cm^{-1}, Galenika) were used. The initial aluminosilicate gels were prepared by drop-wise addition of sodium silicate solution into sodium aluminate solution, under continuous stirring and heating at 90 °C. Reaction gels, formed in time interval of 30 min, were left to crystallize for 2–4 h at 90 °C (Table 1). After filtration, solid phases were carefully washed in two steps: at room temperature and at 100 °C. In the first step, samples were re-dispersed in de-ionized water (H_2O:solid = 30:1) and placed in the chamber of ultrasonic bath at 25 °C, for 15 min. This washing procedure was repeated several times, until the pH value, of filtrate, was 11. In the refluxing procedure, previously washed samples were additionally treated (1 g Na-LTA:100 ml H_2O) at 100 °C for 1 h in flask equipped with reflux condenser. This procedure was repeated three times. After washing, suspensions were filtered and

solid samples were dried overnight, at 105 °C, and saturated with water above NH_4Cl solution for 24 h.

The thermal treatment of the samples was performed in a chamber furnace equipped with temperature controller (± 2 °C). Heating rate in all experiments was 10 °C min^{-1}. After annealing at elevated temperature, for 1 h, the samples were cooled down in a furnace chamber spontaneously to room temperature. Samples were annealed by increasing temperature from 600 up to 950 °C, in 10 °C intervals.

Chemical compositions of Na-LTA zeolite samples were determined after dissolution in aqueous solution of HF and $HClO_4$. Sodium content was determined by atomic absorption spectrometry, using PerkinElmer 390 spectrophotometer, while aluminium content was established by titration with EDTA. Silicon content in the zeolite samples was determined by conventional gravimetric analysis, while silicon concentration in filtrate solutions were determined by Mo blue spectrometric method using Evolution 600 UV–vis spectrophotometer. Differences in chemical compositions of samples, before and after refluxing treatment, were measured by energy dispersive X-ray spectroscopy (EDS) using Jeol JSM-6460 LV electron microscope. The EDS analysis of each examined lt-carn sample was conducted in the same length range, 30 μm, and results are presented in Table 2. The results were collected for two characteristic samples. It was shown that Na/Al ratio, of lt-carn decreased after refluxing treatment.

Prior to X-ray powder diffraction (XRPD) measurements, samples had been heated at different temperature/time conditions. Powder patterns were recorded after cooling to room temperature on Philips, PW-1710 automated diffractometer, using Cu tube operated at 40 kV and 30 mA. The instrument was equipped with diffracted beam curved graphite monochromator and Xe-filled proportional counter. Diffraction data were collected in 2θ range, 4–70°, counting for 0.5 s at 0.02° steps. Fixed 1° divergence and 0.1 mm receiving slits were used. Silicon powder was used as a standard for calibration of diffractometer.

Thermal analysis was performed using a SDT Q-600 simultaneous DSC-TGA instrument (TA Instruments New Castle, Delaware, US). The samples (mass approximately 10 mg) were heated in a standard alumina sample pan. All experiments were carried out under nitrogen with a flow rate of 0.1 dm^3 min^{-1} using a heating rate of 10 °C min^{-1}.

3. Results and discussion

The transformation rates of Na-LTA zeolites are different and most probably depend on the course of zeolite preparation and pre-treatment. Thus, in order to investigate conditions for formation of intermediary amorphous $NaAlSiO_4$ we decided to prepare series of Na-LTA samples, by varying synthesis conditions, and compare their thermal behaviour with previously published results [26,27,30]. The initial molar ratios of components were designed to cover the gel compositions which are known to yield Na-LTA zeolite. Molar ratio SiO_2/Al_2O_3 in reaction mixture was (1.50–1.90), while Na_2O/Al_2O_3 ratio in reaction mixture was very

Table 2
Chemical analysis of filtrates and zeolite samples after refluxing treatment; EDS analysis of the corresponding lt-carn phases obtained from zeolites before and after refluxing treatment.

Sample	Chemical compositions after refluxing treatment						EDS analysis of lt-carn samples			
	Filtrates			Zeolite samples			Before refluxing treatment		After refluxing treatment	
	Na_2O (mg g^{-1})	Al_2O_3 (mg g^{-1})	SiO_2 (mg g^{-1})	Na_2O	Al_2O_3	SiO_2	Na/Al	Al/Si	Na/Al	Al/Si
Na-LTA$_1$				1.01	0.98	2.0				
Na-LTA$_2$	24	34	35	1.02	1.01	2.0	1.36	1.06	1.04	0.97
Na-LTA$_3$				1.02	0.99	2.0				
Na-LTA$_4$				1.01	1.00	2.0				
Na-LTA$_5$	27	28	34	1.01	0.99	2.0	1.24	0.98	1.01	0.99

high (2.82–3.90). Table 1 shows batch compositions, gel crystallization times and compositions of synthesized Na-LTA samples. In all cases, the only crystallization product was pure Na-LTA zeolite, free of admixtures of other phases such as Na-SOD, Na-GIS or Na-FAU zeolites.

As can be seen, chemical analysis of synthesized samples showed deviation from ideal Na-LTA zeolite stoichiometry: $Na_2O:Al_2O_3:2SiO_2$. The prepared zeolite samples contained different amounts of species, which remained in zeolite cages and channels after synthesis. Although the washing procedure of prepared samples was repeated several times, the excess of Na_2O and Al_2O_3 in synthesized samples remained. All synthesized Na-LTA samples, showed Na_2O excess, ranging from 0.05 to 0.06. The excess of Al_2O_3 in synthesized samples was dependent on the initial gel composition and crystallization time and was in the range 0.02–0.07. By prolonged gel formation and crystallization times the excess of Al species was reduced (samples Na-LTA$_1$ and Na-LTA$_2$ as well as samples Na-LTA$_3$ and Na-LTA$_4$). By these investigations once again it is confirmed that synthesized Na-LTA zeolites are characterized by lattice occlusion of unidentified species from Al_2O_3–Na_2O–SiO_2–H_2O phase system as proposed earlier by many authors [25,26,34–44]. Thus, it is believed that every synthesized Na-LTA sample is "impure" in crystallographic sense and contains occluded varying amounts of above mentioned species. Discussed species are homogenously dispersed and most probably located inside α and β cages. However, the possibility of their location along some crystallographic preferred direction such as a twin boundary could not be excluded, too.

Thus, in order to investigate the possible influence of species occluded in zeolite cages on transformation mechanism of Na-LTA into lt-carn, all examined samples, were additionally washed by refluxing. The chemical analysis of zeolite samples after refluxing treatment are presented in Table 2. The residues were effectively removed after the samples were washed in refluxing conditions. The total amounts of Na_2O, Al_2O_3 and SiO_2 removed from the initial Na-LTA samples calculated as mg per 1 g of hydrated zeolite are given in Table 2. The total amounts of Na_2O, Al_2O_3 and SiO_2, removed from synthesized zeolite samples, under refluxing conditions, were significant: 24–35 mg g^{-1}. The chemical compositions of the refluxed series of samples were very close or equal to Na-LTA zeolite stoichiometry: $(1.01–1.02)Na_2O:(0.98–1.01)Al_2O_3:2SiO_2$ (or unit cell of Na-LTA $Na_{12}Al_{12}Si_{12}O_{48}$). As a result, the chemical composition of Na-LTA zeolites after refluxing treatment approached the ideal stoichiometry ($Na_2O:Al_2O_3:2SiO_2$).

3.1. Thermal transformation of initial Na-LTA zeolites

The XRPD patterns of commercial Na-LTA samples and phases formed upon heating are given in Fig. 1(a–c). As it was expected, the commercial zeolites were transformed into lt-carn phases [27–29]. In all investigated systems during heating between 600 and 850 °C only crystalline phases: Na-LTA zeolite (below 600 °C), mixture of zeolite Na-LTA and lt-carn (between 600 and 750 °C) or pure lt-carn (above 800 °C), were detected. Here is very important to point out, that amorphous phase was not observed in any of the investigated commercial Na-LTA samples, even after varying temperature/time conditions in either wide or narrow range. It is obvious that the thermal transformation of commercial Na-LTA$_{AB}$ zeolite, Fig. 1(a), was much faster process than conversion of Na-LTA$_{FL}$ and Na-LTA$_{UC}$ species, Fig. 1(b and c), respectively.

The observed XRPD characteristics are in good agreement with DSC results shown in Fig. 2(a). Thermal curve of Na-LTA$_{AB}$, displays very sharp exothermic peak, with its maximum at T_m = 822 °C. Corresponding Na-LTA$_{FL}$ curve shows broader exothermic peak at T_m = 898 °C, whereas the diagram of Na-LTA$_{UC}$ sample shows very broad peak, centered at T_m = 915 °C. These results indicate differences in the rates of transformation processes.

Thermal characteristics of laboratory-synthesized samples are dependent on their chemical composition. This is proved by DSC results shown in Fig. 2(b). The peak maximum corresponding to lt-carn crystallization was shifted towards lower temperatures with increasing Al_2O_3 content in zeolite sample (Al_2O_3 = 1.04; 1.05; 1.06; 1.07 and corresponding T_m = 900 °C; 896 °C; 892 °C and 880 °C, respectively).

The ZTIT of the as-synthesized Na-LTA samples were investigated by XRPD method, as well. The samples were treated in the temperature range from 600 to 950 °C under the same conditions as commercial samples. In all investigated systems only crystalline phases such as zeolite, mixture of zeolite and lt-carn, or pure lt-carn, were detected. All discussed Na-LTA zeolites were transformed into lt-carn phase (JCPDS file card No. 11-0221) up to 850 °C. Typical diffraction patterns of phases formed after thermal treatment at 800 °C for 1 h are shown in Fig. 3. The influence of chemical composition on the transformation rate is evident. According to the rate of transformation, all prepared Na-LTA samples can be categorized into three groups. The highest rate of transformation was observed in the case of samples Na-LTA$_1$ and Na-LTA$_3$. After thermal treatment at 800 °C, only the phases of pure lt-carn were detected, Fig. 3(C). The chemical compositions of the samples Na-LTA$_1$ and Na-LTA$_3$ were: 1.05:1.07:2.0 and 1.06:1.05:2.0, respectively. In both cases the excess of Na_2O (0.05 and 0.06, respectively), and Al_2O_3 (0.07 and 0.05, respectively) were significant. Also, in both cases the crystallization times (Table 1) in the comparison with other synthesized Na-LTA zeolite samples were much shorter. The thermal conversion of Na-LTA zeolite into lt-carn was enhanced with high amount of residual species.
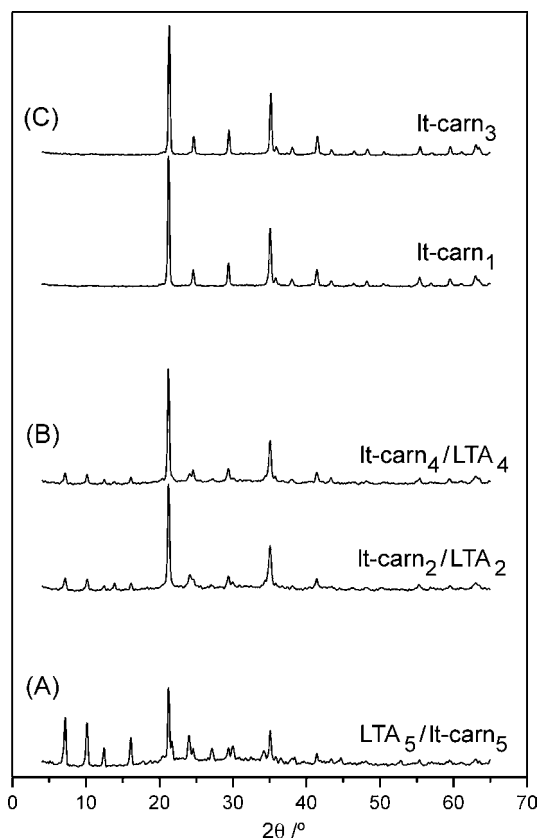
The slowest rate of transformation was observed in the case of sample Na-LTA$_5$. The Al_2O_3 excess, present in this sample was 0.02 which is close to ideal SiO_2/Al_2O_3 = 2 stoichiometry. This sample annealed at 800 °C for 1 h showed significant amount of zeolite phase. Discussed sample represents mixture with approximately equal quantities of Na-LTA and lt-carn phases, Fig. 3(A). Other as-synthesized Na-LTA$_2$ and Na-LTA$_4$ samples had lower Fig. 3(B) thermal stability. These samples showed significant amount of lt-
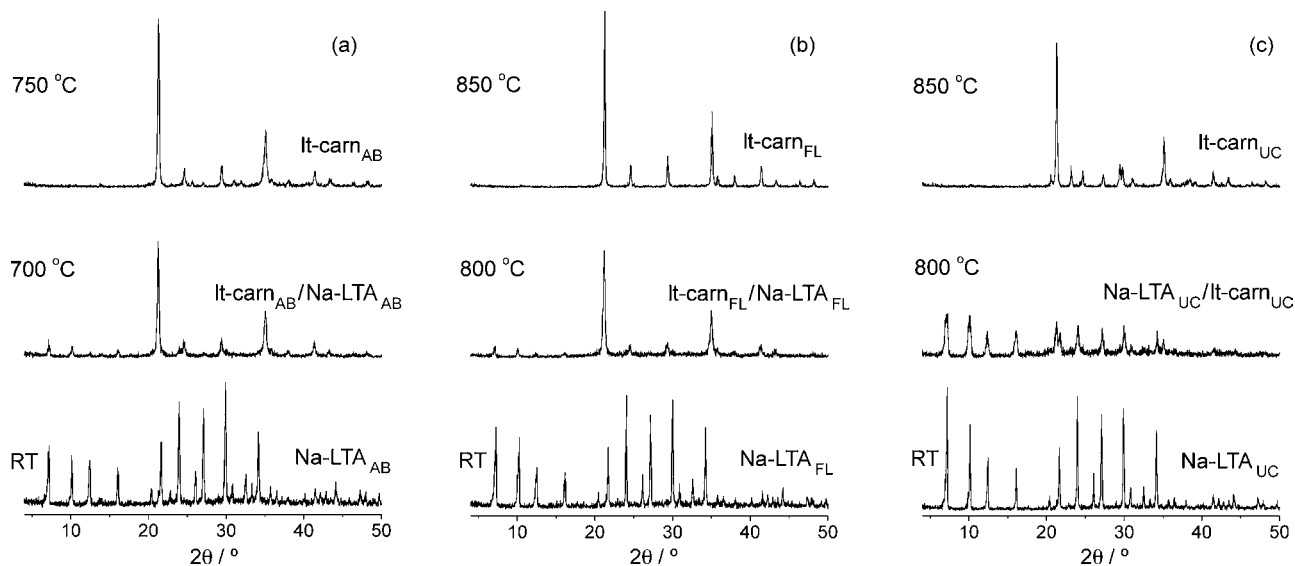
Fig. 1. XRPD patterns of commercial Na-LTA zeolites, induced by heating between RT and 850 °C. (a) Na-LTA$_{AB}$, (b) Na-LTA$_{FL}$ and (c) Na-LTA$_{UC}$.
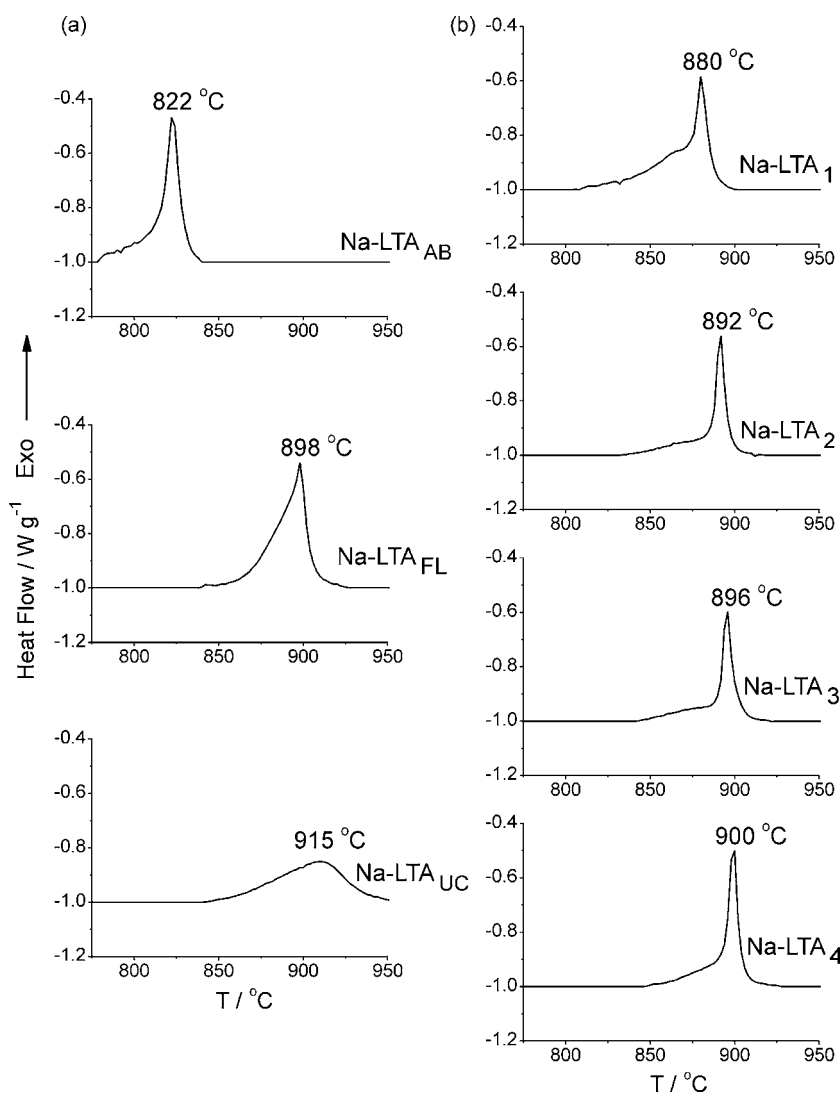
Fig. 2. DSC curves of investigated Na-LTA zeolites: (a) commercial species and (b) some of laboratory-synthesized species having different Al$_2$O$_3$:SiO$_2$ ratios.

Fig. 3. XRPD patterns of phases obtained in the ZTIT process of as-synthesized Na-LTA zeolites after heating at 800 °C for 1 h; (A) mixture with approximately equal quantities of Na-LTA/lt-carn phases; (B) mixtures with high/low quantity ratios of lt-carn and Na-LTA phases, respectively and (C) samples with pure lt-carn.

ertheless has to be broken and converted into lt-carn polymorph. At the moment of breaking Si–O–Al bridges, Na-LTA polymorph loses long range structure ordering (crystallinity) and becomes amorphous for X-rays. It is important to point out that amorphous phase was not observed in any of the investigated systems through whole temperature treatment. Typical XRPD patterns taken at each 10 °C in the temperature interval between 730 and 830 °C in the case of Na-LTA$_2$ zeolite are presented in Fig. 4(a). It is obvious from this figure that in the region where transition occurred, coexistence of both Na-LTA$_2$ and corresponding lt-carn$_2$ phases can be observed. By raising the temperature, the amount of zeolite phase was decreasing, while the amount of lt-carn phase was increasing, until pure phase was formed at 830 °C. It is clear from Fig. 4(a) that expected amorphization process was not detected. This is an additional experimental proof that discussed conversion process is extremely rapid.

As it was previously mentioned, the secondary building units S6Rs are common building units for both Na-LTA zeolite and carnegieite. The zeolite's S6Rs are preserved during transformation and lt-carn is formed through S6R inherited transformation, but the connectivity between tetrahedral units is changed and some bonds break while some reform. The AlO$_4$ and SiO$_4$ tetrahedra in zeolite structure are linked by sharing oxygen atoms. It is known that Al–O bond is weaker than Si–O bond and one can expect the influence of Al excess in zeolite cages on the rate of transformation. The presence of chemical residues homogeneously occluded inside zeolite voids could give rise to a rapid bonds breaking and new bonds formation. In the series of investigated zeolites the rate of Na-LTA → lt-carn transformation increases with increasing amount of Al. Thus, we believe that discussed occluded residues influence conversion mechanism as a "perfect" nucleating agent, making impossible to detect amorphous phase as an unavoidable intermediary product.

3.2. Thermal transformation of Na-LTA zeolites after refluxing treatment

Thereafter, in order to investigate the possible influence of species occluded in zeolite cages on the above discussed transformation mechanism of Na-LTA into lt-carn all investigated samples were additionally washed by refluxing. The additionally washed samples (refluxed samples) were thermally treated under the same conditions as other previously discussed Na-LTA samples. The typical XRPD patterns of refluxed Na-LTA$_2$ zeolite sample conversion, between 830 and 880 °C, is focused in Fig. 4(b), whereas one commercial and two laboratory-synthesized zeolites and phases formed upon heating are compared in Fig. 5, respectively. The simultaneous temperature coexistence of cubic lt-carn and Na-LTA phases was not detected. Intermediate amorphous phase is formed during thermally induced transformations of reflux-treated sam-
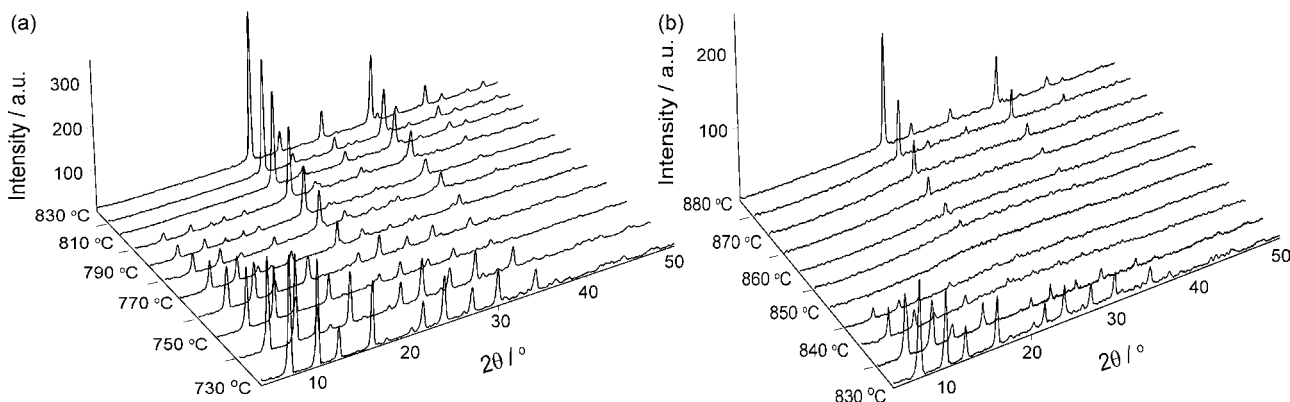
carn phase and low amount of zeolite phase. The presented results indicate that the amount of residual species in zeolite samples change the rate of Na-LTA transformation into lt-carn. Discussed conversion looks like solid–solid structural transformation. However, due to structural reasons the transition of Na-LTA zeolite into lt-carn phase must be reconstructive transformation as a consequence of their known crystal structures [45,46]. Namely, at critical temperature ($T_c = 700$–800 °C) dehydrated Na-LTA compound is NaAlSiO$_4$ polymorph having diverse TO$_4$ (T = Si,Al) framework compared to lt-carn. The common characteristic of their frameworks is the presence of S6R TO$_4$ secondary building units (SBU) [24] which are mutually connected in a distinct structural manner. Thus, D4R SBU in dehydrated Na-LTA zeolite (cubic NaAlSiO$_4$ polymorph) nev-

Fig. 4. XRPD patterns of phases obtained in the ZTIT process of Na-LTA$_2$ zeolite sample, after heating at various temperatures for 1 h (a) before refluxing treatment, 1.06Al$_2$O$_3$:2SiO$_2$; (b) after refluxing treatment, 1.01Al$_2$O$_3$:2SiO$_2$.
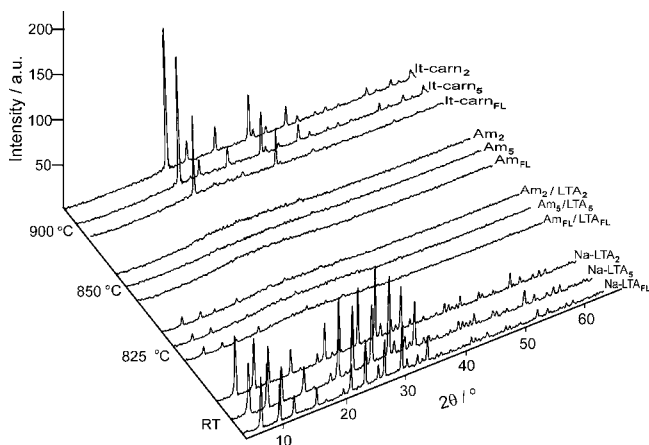
Fig. 5. XRPD patterns of phases obtained in the processes of thermal transformations of three characteristic zeolite samples (Na-LTA$_{FL}$, Na-LTA$_2$ and Na-LTA$_5$) subjected to refluxing treatment.

ples which contained very low amount of residual species, Table 2. Discussed zeolite structural collapse was followed by formation of an amorphous matter. Such prepared amorphous NaAlSiO$_4$ substance remained stable in narrow temperature interval, between 850 and 900 °C, Fig. 4(b) and Fig. 5, respectively. With prolonged heating, at 900 °C, the pure lt-carn phase started to crystallize gradually from discussed amorphous NaAlSiO$_4$ substance [47,48]. The crystallization process was completed at aforementioned temperature in 60 min. Thus, having in mind obtained results and considerations discussed conversion mechanism is advanced and is presented by scheme (1).

$$\text{Na-LTA} \xrightarrow[\text{heating at 850 °C, 1 h}]{\text{reflux treatment at 100 °C}} \text{amorphous NaAlSiO}_4 \xrightarrow{\text{heating at 900 °C, 1 h}} \text{lt-carn} \qquad (1)$$

Here is important to emphasize that described procedure for preparation of amorphous NaAlSiO$_4$ substance is more efficient and rapid approach than long time-consuming route proposed in earlier papers [26,30].

Our study undoubtedly demonstrates that initial zeolite samples (as-synthesized commercial and laboratory-synthesized) do not show intermediary amorphous state during short-term ZTIT treatment. This is evidenced on all investigated samples by varying time/temperature conditions in very narrow intervals. Thus, at short-term heating zeolite phase conversion process is extremely fast action which makes observation of intermediary amorphous state impossible in real time. Subsequently, the initial samples were exposed to mild refluxing treatment and then heating experiments were repeated in order to find optimal conditions for faster preparation of stable amorphous NaAlSiO$_4$ substance and its crystallization into lt-carn.

4. Conclusions

The main goal of this work was to check and upgrade a knowledge about controversial conversion mechanism of Na-LTA zeolite into cubic lt-carn traditionally presented by two diverse processes described in introduction.

The information summarized upon refluxing treatment and heating showed remarkable changes in ZTIT route. Upon refluxing action a stable amorphous NaAlSiO$_4$ substance can be prepared for cca. 1 h by thermal treatment. From these results we concluded that Na and Al excess present as non-stoichiometric residual species in un-refluxed Na-LTA zeolites reacts during heating as a strong catalyst changing significantly zeolite stability and the course of thermal transformation contrary to refluxed samples. In addition, it is shown how by simple refluxing and heating procedure the initial Na-LTA zeolite can be amorphized in a short time which is significant contribution to rapid

preparation of amorphous NaAlSiO$_4$, i.e. polyamorphism of this substance.

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