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Thermochimica Acta 317 (1998) 25–37

thermochimica acta

Thermally induced phase transformations in cation-exchanged zeolites 4A, 13X and synthetic mordenite and their amorphous derivatives obtained by mechanochemical treatment

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Received 10 May 1997; received in revised form 20 January 1998; accepted 6 April 1998

Abstract

Thermal transformations of Li^+, K^+, Cs^+ and NH_4^+-exchanged zeolite A, NH_4^+-exchanged zeolite X, NH_4^+-exchanged synthetic mordenite and the X-ray amorphous materials obtained by ball milling of crystalline phases (the exchanged zeolites A, X and synthetic mordenite) were investigated by different methods such as differential-scanning calorimetry (DSC), differential thermal gravimetry (DTG), X-ray powder diffractometry, FTIR spectroscopy and scanning-electron microscopy (SEM). Thermal stability of the investigated solids depends on the type of zeolite, type of exchanged cation and SiO_2/Al_2O_3 molar ratio in the starting crystalline and amorphous samples. Most crystalline zeolites transform to other crystalline phase(s) without formation of amorphous intermediates, but in some cases of Li^+, K^+-exchanged zeolite A, a transformation to amorphous intermediate proceeds into secondary crystalline phase(s). Both crystalline and amorphized NH_4^+-exchanged zeolites A and X transform to a mixture of mullite and amorphous silica, whereas the NH_4^+-exchanged synthetic mordenite transforms to amorphous phase only. A special attention is paid to the transformation of crystalline and amorphized samples.

Keywords: Amorphization; Cation exchange; Phase transformations; Zeolites

1. Introduction

One very attractive and promising area of zeolite research is that of obtaining new materials by thermal treatment of different types of zeolites modified by ion exchange. The thermal transformation of zeolite precursors is a novel route for the synthesis of aluminosilicate-based ceramic materials [1] which has found numerous uses in the ceramic industry [2]. By varying the SiO_2/Al_2O_3 ratio in the zeolite framework and the type, charge and number of extra-lattice cations in the zeolite cavities, appropriate compositions for the required product are obtained. For example, sodium form of zeolite A (4A) transforms to a mixture of carnegieite and nepheline at 900°C and the mixture recrystallizes to nepheline at >1000°C [3].

The sodium form of zeolite X (13X) transforms to an amorphous phase at 850°C which recrystallizes to nepheline at >1000°C [3] The crystal structures of zeolites Y and synthetic mordenite collapse at >800°C and >900°C, respectively, giving amorphous aluminosilicate phases [3]. Cesium-exchanged zeolite A transforms at 900°C to carnegieite and recrystallizes to a mixture of nepheline and pollucite at >1000°C [3].

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PII S0040-6031(98)00353-0

Cesium-exchanged zeolites X and Y transform to amorphous material at 800–900°C and 1000°C, respectively, and recrystallize to pollucite at >1100°C and 1200°C, respectively [3].

It is interesting to note that some of zeolite precursors transform into non-zeolite crystalline aluminosilicates directly without the formation of amorphous intermediates, and that in other cases the formation of amorphous aluminosilicate intermediates proceeds via the transformation into secondary crystalline phase(s). In order to find the pathways of the transformation process and to understand the role of amorphous intermediates, we previously investigated [4] the high-temperature solid-state transformation of potassium-exchanged zeolite A and its amorphous derivative obtained by mechanochemical amorphization [5]. The heating of the potassium-exchanged zeolite A at 962°C for 30 min resulted in the formation of an amorphous phase that have recrystallized to a mixture of kalsilite and kaliophilite on prolonged heating at the same temperature, or in pure kaliophilite during the heating at 1064°C [4]. On the other hand, mechanochemically amorphized sample of the potassium-exchanged zeolite A was transformed to a mixture of kalsilite (60 wt%) and kaliophilite (30 wt%) in <30 min at 962°C [4]. A prolonged heating at the same temperature caused complete transformation of amorphous into crystalline phases and additionally transformation of kaliophilite into kalsilite, so that the product obtained by the heating at 962°C for 3 h contained only kalsilite with traces of leucite. Based on these results it was assumed that activation energy of the breaking of 'external' Si–O–Si and Si–O–Al bonds of zeolite is lower than the activation energy of the appropriate rotation and translation of primary and secondary building units of zeolite framework, and hence that the transformation does not occur by the reorganization (rotation, translation) of primary and secondary building units of zeolite framework into other crystalline phases, but that nucleation and crystal growth of kalsilite and kaliophilite take place by reaction of primary building units (SiO_4, AlO_4 tetrahedra) at the amorphous phase.

Since this assumption was made on the basis of a single example the objective of this work is to investigate the processes of transformation of different types of zeolites (A, X, synthetic mordenite) loaded with various cations (Na^+, K^+, Li^+, Cs^+, NH_4^+) and their amorphous derivatives obtained by mechanochemical amorphization (high-energy ball milling) in order to confirm or reject the above mentioned assumption on the transformation process.

2. Experimental

Zeolites Linde 4A, Linde 13X and synthetic mordenite, all produced by Union Carbide were used as starting materials. Analytical grade LiCl, KCl, CsCl and NH_4Cl were used to prepare 0.5 M solutions.

Partial exchange of the original Na^+ ions of the zeolites used as starting materials with Li^+, K^+, Cs^+ and NH_4^+ ions (in zeolite 4A) and NH_4^+ ions (in zeolite 13X and synthetic mordenite, respectively) from 0.5 M LiCl, KCl, CsCl and NH_4Cl solutions was carried out by the method described earlier [5]. The exchanged zeolites were kept in a desiccator with saturated NaCl solution for 24 h before analysis.

The chemical composition of the exchanged zeolites was determined by dissolution of the solids in concentrated HNO_3 and/or by the digestion with HF. The concentration of silicon, aluminum and alkali ions in the solutions obtained by the dissolution of the solids were measured using a Shimadzu AA-660 atomic absorption/flame emission spectrophotometer [5].

Samples of hydrous zeolites 4A, 13X and synthetic mordenite, as well as samples obtained by partial exchange of Na^+ ions from the hydrous zeolites with Li^+, K^+, Cs^+ and NH_4^+ ions from appropriate solutions were milled in a planetary ball mill (Fritsch Pulverisette 7) at room temperature. For this purpose, a certain amount of each was put in an agate vessel containing 10 tungsten carbide balls (ϕ=10 mm), and rotated at 3000 rpm until the crystalline powder was completely transformed into X-ray amorphous material. The time was 2 h for zeolites A and X and 3 h for synthetic mordenite [5–7]. The process of amorphization was followed by powder X-ray diffractometry (Philips PW 1820 vertical goniometer with CuK_α graphite radiation) [5–7]. Depending on the duration of milling, the outer temperature of the agate vessel can be increased to 40–60°C. The samples amorphized by ball milling were kept in a desiccator with saturated NaCl solution for 24 h before analysis.

Each crystalline sample, both in the original Na-form and cation-exchanged one, as well as of their amorphous derivatives obtained by ball milling were heated at appropriate temperatures for various times, 0.5 and 3 h, respectively, in a chamber furnace with controlled temperature (ELPH-2, Elektrosanitarij).

All samples (original, exchanged, amorphized) were characterized by powder X-ray diffractometry, before and after thermal treatment. The X-ray diffractograms of the powdered samples were measured using a Philips PW 1820 diffractometer with vertical goniometer and CuK_α graphite radiation. The integral intensities of non-overlapping sharp and broad amorphous peaks were used for calculating the weight fractions of the different amorphous and crystalline phases.

The different weight fractions of the phases in the two-phase systems (carnegieite–nepheline, γ-eucryptite–carnegieite, β-eucryptite–nepheline, pollucite–nepheline and mullite-amorphous) were using the Hermans–Weidinger method [8] but because of overlapping the strongest X-ray diffraction peaks of kalsilite and kaliophilite, quantitative evaluation was performed using their literature intensity values [9] and on the basis of little overlap of the reflections. The weight fractions of the different phases in the multi-phase systems were calculated by external and mixing method respectively [10].

3. Results and discussion

The oxide compositions of the original and exchanged zeolites used in experiments are given in Table 1.

X-ray diffractograms of the original and exchanged zeolites (Fig. 1) showed that the exchange of Na^+ ions in zeolites 4A, 13X and synthetic mordenite by monovalent alkali cations and NH_4^+ ions, respectively, except in the case of lithium-exchanged zeolite A, produced little change in the zeolite framework, in contrast to the deformation or even destruction to the lattice caused by perturbations in mutual arrangement of framework SiO_4 and AlO_4 tetrahedra in the close vicinity of bivalent cations, e.g. Co^{2+} and Mn^{2+} in zeolite X [11]. The lowering of the cell constant, a, in the case of zeolite A in which part of the Na^+ was exchanged by Li^+ [12] (see also Table 1 in Ref. [5]),

Table 1
Chemical compositions of the original and exchanged zeolites used as precursors in the thermal and mechanochemical treatment. The chemical composition is expressed as numbers of moles of the constituent oxides (Na_2O, R_2O, SiO_2, H_2O) per mol of Al_2O_3 in accordance with the oxide compositions of the zeolites: (x_1Na_2O, $x2R_2O$ [a]).$Al_2O_3.ySiO_2.2H_2O$ [a]

Type of zeolite	x_1	x_2	y	z
NaA	1	—	2	4.5
(Li,Na)A	0.36	0.64	2	3.82
(K,Na)A	0.22	0.78	2	3.48
(Cs,Na)A	0.66	0.34	2	2.98
(NH_4,Na)A	0.21	0.79	2	4.15
NaX	1	—	2.46	6.13
(NH_4,Na)X	0.32	0.68	2.44	5.5
NaSM [b]	1	—	8.7	6
(NH_4,Na)SM [b]	0.05	0.95	8.7	7.24

[a] R_2O= Li_2O, K_2O, Cs_2O and $(NH_4)_2O$.

[b] SM= synthetic mordenite.

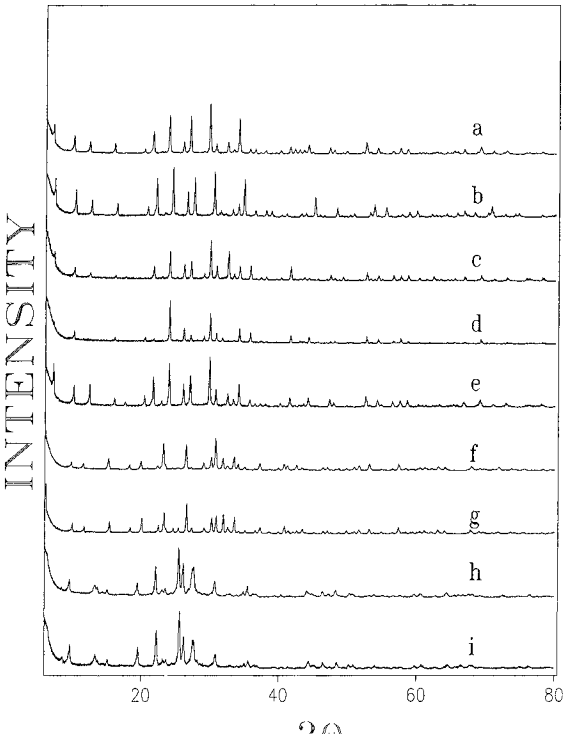


Fig. 1. X-ray diffractograms of the: original (Na-form) of zeolite 4A (a) and zeolite A in which part of sodium ions were exchanged by K^+ (b), Li^+ (c), Cs^+ (d), NH_4^+ (e) cations, original (Na-form) of zeolite 13X (f), NH_4^+ -exchanged zeolite X (g), original (Na-form) of synthetic mordenite (h) and NH_4^+ -exchanged s. mordenite (i).

Table 2
Temperatures, $T_p(n)$, of the exothermic peaks in the DSC analyses of crystalline and amorphized samples of zeolite A. A portion of the original sodium ions has been exchanged by Li^+, K^+, Cs^+ and NH_4^+ ions as well as zeolites X and synthetic mordenite (SM) (in which a part of the original sodium ions has been exchanged by NH_4^+ ions)

Zeolite	Crystalline samples			Amorphized samples	
	$T_p(1)$/°C	$T_p(2)$/°C	$T_p(3)$°C	$T_p(1)$/°C	$T_p(2)$/°C
(Na,Li)A	760	822	1150	768	1150
NaA(4A)	899	1003	—	901	1118
(Na,K)A	962	1064	—	962 [a]	1064 [a]
(Na,Cs)A	1057	—	—	997	—
$(Na,NH_4)A$	997	—	—	997	—
$(Na,NH_4)A$	1000	—	—	1000	—
$(Na,NH_4)SM$	968	—	—	968	

[a] The peak temperatures $T_p(1)$ and $T_p(2)$ for the amorphized sample of zeolite (Na,K)A are taken from the DSC analyses of crystalline samples because the amorphous samples have no exothermic peak.

can be explained by the distortion of the zeolite framework caused by the strong electrostatic interaction between the zeolite framework and the small strongly polarizing Li^+ [13]. Similar effects was observed in lithium-exchanged zeolite X [14].

The temperatures at which the samples were heated corresponded to the temperatures, $T_p(n)$, of the exothermic peaks in the DSC curves of the treated samples [15,16]. The peak temperatures, $T_p(n)$ (n=1,2,3) corresponding to each of the crystalline, original and exchanged zeolites and amorphous samples, obtained by mechanochemical amorphization, are shown in Table 2. From this, one can see that the temperature $T_p(1)$ of the crystalline samples of zeolite A, its thermal stability, increases with increasing ionic radii of the ions in the channel-void system. One possible explanation for this effect is that the polarization of the alkali ions, and thus the distortion of the zeolite framework by electrostatic interactions, decreases with the increase in ionic radius. Hence, the thermal stability of the zeolite increases, and the temperature $T_p(1)$ increases with the increase of the ionic radius of the exchanged ions. Another explanation is related to the occupancy of the voids and channels in the zeolite structure by the cations. Tables 1 and 3 of Ref. [5] show that the volume, V_{oc}, occupied by the cations (Na^++R^+) in the unit cell of zeolite A increases in the following sequence:

$$V_{oc}(Li^+, Na^+) < V_{oc}(Na^+) < V_{oc}(Na^+, K^+) \\ < V_{oc}(Na^+, Cs^+)$$

Heating the samples produces more bending and stretching of the Si–O–Si bonds in the void and channel structure and more breaking at some critical point in the stretching/bending. On the other hand, bending and stretching allows the Si, Al and O atoms of the framework to get closer to the cations. Lowering the distance between the cations and the framework atoms increases the repulsive electrostatic and van der Waals forces that partially compensates for the tendency of the Si–O–Si and Si–O–Al bonds to break in bending and stretching. A similar relationship was found earlier between the mechanical stability of zeolites and the occupancy of the voids and channels of the zeolite structure with template molecules [7] or alkaline cations [5]. It is not easy, at the moment to discriminate between these two explanations but it is easier to assume that the increase in thermal stability of the zeolites with increasing ionic radius is caused both by a decrease in the distortion of the zeolite framework and by an increase in the compensation effect with the increase of the ionic radius of the exchanged ions.

Table 3 shows the results of thermal treatment of the original crystalline Na-form of zeolite 4A (CP) and the amorphous material obtained by ball and, as expected [3], the thermal treatment of zeolite 4A results in the formation of different mixtures of carnegieite and nepheline depending both, on the time and temperature of heating. For instance, carnegieite is the dominant phase (93.9%) obtained during the heating of zeolite 4A at 899°C for 30 min. Heating for the same time at 1000°C, however, results in the formation of a mixture containing 50% of carnegieite and nepheline. Prolonged heating at 1000°C results in a gradual transformation of carnegieite to nepheline, the transformation being completed in <3 h.

It is evident that the thermodynamic stability of the different phases at temperatures ≥900°C increases in the following sequence:

$$\text{zeolite 4A} < \text{carnegieite} < \text{nepheline}$$

and that the transformation pathway: zeolite 4A⇒carnegieite⇒nepheline is in accordance with the Ostwald's rule of stages [17]. It is interesting that

Table 3
Products obtained by heating crystalline Na-form of zeolite A(CP) and amorphous phase formed by ball milling of CP(AP) at specified temperatures and time

Temperature of heating/ °C	Time of heating/ h)	CP	AP
899 for CP, 901 for AP	0.5	93.9% low-carnegieite [11–220]+6.1% nepheline	92.4%carnegieite+7.6%nepheline
1000	0.5	50% carnegiete[11–220]+50%nepheline+traces of high nepheline	
1000	3	100%nepheline[35-424]+traces of high nepheline	100%nepheline[19-1176]+traces of high nepheline
1000	3.5		100%nepheline+traces high of nepheline
1000	4		100%nepheline+traces of high nepheline
1118	0.5		41.1%low carnegiete+58.9%nepheline+ traces of high nepheline

almost identical results were obtained in the thermal treatment of amorphized zeolite A (see Table 3). This clearly indicates that the pathway of the transformation is not controlled by the structure, but only by the chemical composition of the precursor, i.e. $NaAlSiO_4$ and, hence, the transformation does not occur by reorganization, by rotation, nor by translation of the primary and secondary building units of the zeolite A framework, but involves nucleation and crystal growth of carnegieite by a reaction of the primary building units, i.e. SiO_4, and AlO_4 tetrahedra. This, on the other hand, implies that the original crystal structure of zeolite A is destroyed and formation of an amorphous aluminosilicate precedes the formation of carnegieite and perhaps nepheline.

This mechanism is implicit in the finding of Stock and Waclawska [18] that zeolite 4A can be transformed to an X-ray amorphous phase at 800°C, and cristobalite crystallizes from the amorphous aluminosilicate matrix at 860°C [18]. The same authors have found that, at somewhat higher temperatures, cristobalite reacts with the amorphous matrix and crystallizes as nepheline [18]. Crystallization of carnegieite has not been observed in this study.

Taking into consideration these findings, it was postulated that the thermal transformation of zeolite 4A takes place in the following sequence:

$$\begin{aligned}\text{zeolite 4A} &\Rightarrow *\text{amorphousaluminosilicate}\\ &\Rightarrow (\text{cristobalite}) \Rightarrow \text{carnegieite}\\ &\Rightarrow \text{nepheline}\end{aligned}$$

where the amorphous aluminosilicate can both be the amorphous phase obtained by heating zeolite 4A [18] or produced by ball milling of zeolite 4A [6]. From the data in Ref. [18] and Table 3, respectively, it was concluded that above some 'critical' temperature, >860°C, the order of the transformation process did not depend on the transformation temperature, but the individual processes zeolite 4A⇒amorphous, amorphous⇒(cristobalite)⇒carnegieite, carnegieite⇒nepheline, as well as the overall transformation process (zeolite 4A⇒nepheline) increased with increasing temperature.

While thermal transformation of zeolite 4A to amorphous aluminosilicate can be readily explained in terms of the breaking of 'external' Si–O–Si and Si–O–Al bonds [6], and the collapse of the open zeolites framework [18,19], detailed kinetic and particulate analyses of the transformation process(es) are necessary to understand the mechanism of the transformation of amorphous aluminosilicate(s) to cristobalite, carnegieite and nepheline.

Analysis of the X-ray diffractograms of nephelines crystallized under different conditions, i.e. precursor, temperature and time showed that the X-ray diffractogram of nepheline obtained by heating zeolite 4A at 1000°C for 30 min was very similar to that quoted in JCPDS File, Card Nos. 35–424 for nepheline formed by heating zeolite 4A at 1000°C for 6 days [20]) and that the X-ray diffractogram of nepheline obtained by heating an amorphous sample, i.e. milled zeolite A, was closer to the pattern quoted in JCPDS File, Card Nos. 19–1176 for nepheline formed by heating zeolite 4A at 1100°C for 4 days [21]. In particular, the relative intensities of the reflections due to 200, 201, 210 and

Table 4
Products obtained by heating of crystalline Li-exchanged zeolite A(CP) and amorphous phase formed by ball milling of CP(AP) at specified temperatures and time

Temperature of heating/ °C	Time of heating/ h	CP	AP
760 for CP, 786 for AP	0.5	52.5% γ-eucryptite $LiAlSiO_4$+47.5% amorphous phase	39.5% $LiAlSiO_4$ carnegieite [11-220]+ 34.5% $LiAlSiO_4$ γ-eucryptite [17-533]
760 for CP	3	51.9% $LiAlSiO_4$ type carnegiete [11-220]+48.1% $LiAlSiO_4$ carnegiete [11-220]	
822	0.5	49.9% $LiAlSiO_4$ γ-eucryptite+50.1% $LiAlSiO_4$ carnegieite[11-220]	
122	3	51.8% $LiAlSiO_4$ type carnegieite [11-220]+ 48.2% $LiAlSiO_4$ γ-eucriptite+traces β-eucryptite+nepheline	
1150	0.5	87.4% $LiAlSiO_4$ β-eucryptite [17-533]+ 12.4% $LiAlSiO_4$ nepheline	83% $LiAlSiO_4$ β-eucryptite [17-533]+17% $LiAlSiO_4$ nepheline [35-424]
1150	3	86.4% $LiAlSiO_4$ β-eucryptite [17-533]+ 12.4% $LiAlSiO_4$ nepheline	83% $LiAlSiO_4$ β-eucryptite [17-533]+17% $LiAlSiO_4$ nepheline [19-1179]

520 with respect to the intensity of the strongest peak, due to the 202 plane of nepheline [22], depended on the conditions under which it had been formed. These findings will be taken into consideration in further studies on the transformation kinetics and mechanisms.

Table 4 shows that, on heating at 760°C, zeolite A containing 64% Na^+ ions exchanged by Li^+ ions a mixture containing 52.5% γ-eucryptite and 47.5% amorphous aluminosilicate resulted. Taking into consideration the previous results on thermal transformation of zeolite 4A (see Table 3), it is possible to assume that the first step is the transformation of zeolite (Li,Na)A into amorphous (Li,Na)-aluminosilicate. The temperature of this transformation is somewhat lower (<760°C) than the temperature of transformation of zeolite A to the amorphous Na-aluminosilicate (800°C [8]) and this can be explained by the lower thermal stability of the zeolite (Li,Na)A relative to that of zeolite 4A. This is followed at 760°C by the recrystallization of γ-eucryptite from the amorphous (Li,Na)-aluminosilicate. An earlier study of the thermal transformation of zeolite Li-A(BW) to eucryptite [23] has shown that the transformation of anhydrous Li-A(BW) zeolite into γ-eucryptite takes place at 650°C directly without the formation of any intermediate amorphous and/or crystalline phases.

Based on the assumption that the framework structure of anhydrous Li-A(BW) is that of the ABW-type, Norby [23] concluded that anhydrous Li-A(BW) zeolite may easily by transformed into γ-eucryptite with a cristobalite-type structure, by moving half of the aluminium atoms from one tetrahedral hole to another while keeping the oxygen distribution almost intact.

Since the framework structure of zeolite (Li,Na)A is not of the ABW-type, but of LTA-type, it is resonable to assume that the formation of γ-eucryptite occurs by crystallization from the amorphous (Li,Na)-aluminosilicate matrix rather than by the direct rearrangement of the LTA-framework. The formation of γ-eucryptite from amorphous (Li,Na)-aluminosilicate obtained by ball milling of zeolite (Li,Na)A (see Table 4) on heating at 768°C corroborates this assumption.

A comparison of the products of heating of zeolite (Li,Na)A at 760 and 822°C, for both 0.5 and 3 h, shows that they all contain ca. 50% γ-eucryptite and the rest either amorphous (Li,Na)-aluminosilicate as in the sample heated at 860°C for 0.5 h or carnegieite in the sample heated at 860°C for 3 h (see Table 4). This indicates that crystallization of γ-eucryptite is rapid relative to all the other processes and the crystallization is accomplished in <0.5 h, even at 760°C, but that the amount of γ-eucryptite is determined by the proportion of Li^+ ions in the precursor zeolite.

Based on the oxide composition of the anhydrous zeolite (Li,Na)A, see Table 1, ca. 60% of $LiAlSiO_4$ of the γ-eucryptite-type would be expected to be present in the products obtained on heating. The reason for the amount of γ-eucryptite being ca. 10% less than expected could be explained by a ‘locking’ of part of the Li^+ ions at some specific sites in the amorphous matrix which makes them inaccessible for reaction with the silicate and aluminate species in the amorphous precursor. At present, this has not been confirmed and will require further investigation. As expected on the basis of the results presented in Table 3 prolonged heating at 760°C enables (Li,Na)$AlSiO_4$ to crystallize as a carnegieite-type structure from the rest of the amorphous (Li,Na)-aluminosilicate. An increase in the transformation temperature from 760 to 822°C increases the transformation rates. The ‘equilibrium’ composition at ca. 50% γ-eucryptite and carnegieite at 822°C is established in <0.5 h, and does not markedly influence the composition of the products of heating. It is interesting that, on heating at 768°C for 0.5 h, the amorphous sample obtained by ball milling of zeolite (Li,Na)A results in the formation of a crystalline mixture containing 39.5% carnegieite, 34.5% γ-eucryptite and 26% β-eucryptite. Since the transformation of γ-eucryptite into carnegieite, and vice versa, was not observed at temperatures <822°C, as can be seen from the results of the thermal treatment of zeolite (Li,Na)A at 760 and 822°C listed in Table 4, and the transformation of γ-eucryptite into β-eucryptite cannot take place <900°C [23], it is reasonable to assume that the crystallization of all three phases occurs independently within the amorphous matrix, and that the relative proportions of the crystalline phases in the product of heating depend on their relative rates of crystallization. The percentages of carnegieite (39.5%) and eucryptite (γ-eucryptite+β-eucryptite= 60.5%) correspond to the percentages of $NaAlSiO_4$ (ca. 40%) and $LiAlSiO_4$ (ca. 60%) in the precursor. It can be concluded that the chemical composition of carnegieite is $NaAlSiO_4$ and that the chemical composition of both γ- and β-eucryptite is $LiAlSiO_4$. This indicates that all the Li^+ ions in the amorphous phase obtained by ball milling of zeolite (Li,Na)A are available for the crystallization of eucryptite(s). This is different from the amorphous phase obtained by thermal treatment of zeolite (Li,Na)A.

The heating at 1150°C for 0.5 and 3 h, respectively, of both zeolite (Li,Na)A and the amorphous aluminosilicate obtained by ball milling of the zeolite (Li,Na)A results in the formation of crystalline mixtures containing 83–87.5% β-eucryptite and 12.5–17% nepheline (see Table 4). An almost identical composition was obtained by heating the crystalline and amorphous precursor indicating that the first stage of the transformation of zeolite (Li,Na)A at 1150°C is the same as that at lower temperatures, i.e. 760 and 822°C, and involves the formation of the amorphous (Li,Na)-aluminosilicate. This also indicates that the high content of β-eucryptite (83–87%), which is almost the same in the samples obtained by heating of the precursors for 0.5 and 3 h, respectively, is not a consequence of the transformation of carnegieite and/or nepheline into β-eucryptite, but rather of a higher rate of crystallization of eucryptite relative to the rate of crystallization of carnegieite and/or nepheline in the simultaneous crystallization of eucryptite, carnegieite and nepheline from the amorphous precursors. While it is certain that nepheline is formed by a series of changes

$$\text{amorphous aluminosilicate} \Rightarrow \text{carnegieite} \Rightarrow \text{nepheline}$$

(see the analysis of transformation pathways for zeolite 4A in Table 3).

The pathway for the formation of β-eucryptite cannot be directly determined without detail kinetic analyses of the individual stages..

Calculations based on the chemical composition of the precursors, the phase composition in the products of heating (see Table 4) and an assumption that nepheline is recrystallized in Na-form ($NaAlSiO_4$) indicate that the β-eucryptite obtained by heating of both the crystalline and amorphous precursors at 1150°C appears to contain not only Li, but is a mixture of Li and Na having the chemical composition $Li_xNa_yAlSiO_4$ with x=0.725–0.76 and y=0.24–0.275.

The results of the thermal transformations of crystalline (CP) and amorphous (AP) zeolite (Na,K)A (see Table 5), have been briefly discussed in the and in more detail in our previous work [5] dealing with this subject. For this reason, the results in Table 5 will not be discussed in detail here.

Table 6 shows that on heating both zeolite (Na, Cs)A and the amorphous form obtained by ball milling of the zeolite (Na, Cs)A, at the DSC peak temperature (≈1000°C) for 0.5 and 3 h. crystalline mixtures containing different proportions of nepheline and pollucite are formed. The similarity of the phase

Table 5
Products obtained on heating of crystalline K-exchanged zeolite A(CP) and amorphous phase formed by ball milling of CP(AP) at specified temperatures and time

Temperature of heating/ °C	Time of heating/ h	CP	AP
962	0.5	100% amorphous phase	60.3% kalsilite+29.7% kaliophiltie
962	3	82% kalsilite+18% kaliophilite	100% kalsilite+traces of leucite $KAlSi_2O_6$
1064	0.5	73% kalsilite+27% kaliophilite	100% kalsilite

Table 6
Products obtained on heating crystalline Cs-exchanged zeolite A(CP) and amorphous phase formed by ball milling of CP(AP) at specified temperatures and time

Temperature of heating/ °C	Time of heating/ h	CP	AP
1057 for CP and 997 for AP	0.5	55.6% $CsAlSiO_2O_6$ pollucite [25-194]+44.4% (Cs,Na)$AlSiO_4$ nepheline	66.1% Cs $AlSiO_2O_6$ pollucite+[25-194]+ 33.9% (Cs,Na)$AlSiO_4$ nepheline
1000	3	72.9% $CsAlSiO_2O_6$ pollucite+ [25-194]+27.1% (Cs,Na)$AlSiO_4$ nepheline+traces of high nepheline	82.0% $CsAlSi_2$ pollucite [25-194]+17.5% (Cs,Na)$AlSiO_4$ nepheline+traces of high-nepheline

composition indicates that the first step in the thermal transformation of the crystalline zeolite (Na,Cs)A is that of preventing the formation of the amorphous (Na,Cs)-aluminosilicate; and the formation of new non-zeolitic aluminosilicates (nepheline, pollucite) takes place by their crystallization from the amorphous aluminosilicates. An earlier study of the thermal transformation of cesium-exchanged zeolite A [3] showed that the zeolite (Na,Cs)A transforms to carnegieite at ca. 900°C and that the carnegieite transforms to pollucite and nepheline at >1000°C. Taking into consideration that the formation of carnegieite and nepheline within the aluminosilicate matrix is preferred in the presence of Na^+ ions [3,18] (see also Table 3), and that the formation of pollucite is preferred in the presence of Cs^+ ions [18], it is reasonable to assume that the heating of an amorphous (Na,Cs)-aluminosilicate induces a simultaneous crystallization of $NaAlSiO_4$ to produce carnegieite structures, or even a mixed carnegieite–nepheline structure, and $CsAlSiO_4$ to produce pollucite structures. Since nepheline is thermodynamically more stable than carnegieite, the rate of crystallization of nepheline, in accordance with Ostwald's rule of stages [17], is faster but, on the other hand, the order of thermodynamic stability also implies a spontaneous transformation of less stable carnegieite to the more stable nepheline. Hence, one can assume that, at any time during the heating, a quasi-equilibrium state determined by the chemical composition of the precursor (ca. 52 wt% $NaAlSiO_4$ and ca. 48% $CsAlSiO_4$) and characterized by the phase composition of ca. 52 wt% $NaAlSiO_4$ of nepheline-type and ca. 48% of $CsAlSiO_4$ pollucite-type will be achieved.

A somewhat higher percentage of pollucite and, consequently, a lower percentage of nepheline than was predicted on the basis of the chemical composition of the (Na,Cs)-aluminosilicate precursors, was observed in the samples obtained by heating both, crystalline and amorphous precursors at 1000°C for 0.5 h, indicated the following:

1. The quasi-equilibrium state was achieved in <0.5 h of heating.
2. A spontaneous recrystallization of nepheline to pollucite occurs in the mixture of nepheline and pollucite. An increase in nepheline during the prolonged heating supports such a conclusion. Because nepheline appears at 1000°C as a stable phase in the absence of any other (see Table 3), it can be assumed that particles of the thermodynamically more stable pollucite acts as 'seed crystals' and nepheline serves as a 'reservoir' of silicate and aluminate species needed for the recrystallization.
3. Since the thermally induced amorphization of zeolite (Na,Cs)A is time-consuming, the quasi-equili-

Table 7
Products obtained by heating of crystalline NH_4-exchanged zeolite A(CP) and amorphous phase formed by ball milling of CP(AP) at specified temperatures and time

Temperature of heating/°C	Time of heating/h	CP	AP
997	0.5	60.5% $Al_6Si_2O_{13}$ mullite mullite[15-776]+ 39.5% amorphous SiO_2	62.5% $Al_6Si_2O_{13}$ mullite [15-776]+ 37.5% amorphous SiO_2
1000	1	62.2% $Al_6Si_2O_{13}$ mullite[15-776]+37.8% amorphous SiO_2	
1000	3	64.1% $Al_6Si_2O_{13}$ mullite[15-776]+35.9% amorphous SiO_2	63.3% $Al_6Si_2O_{13}$ mullite [15-776]+ 36.7% amorphous SiO_2
1000	4	64.3% $Al_6Si_2O_{13}$ mullite[15-776]+ 35.7% amorphous SiO_2	

brium state will be established earlier in the amorphous rather than in the crystalline precursors and the ratio of pollucite to nepheline will be higher in the amorphous as compared to the crystalline precursors on heating for the same time (see Table 6).

Tables 7 and 8 show that heating both, ammonium-exchanged zeolites A and X, and the corresponding amorphous derivatives obtained by ball milling at ca. 1000°C, results in the formation of a mixture of mullite and an amorphous phase (S). The weight fractions of mullite ($Al_6Si_2O_{13}$) was ca. 60–64 wt% in the case of ammonium exchanged zeolite A and ca. 47–59 wt% in the case of ammonium-exchanged zeolite X and was very close to the stoichiometric fractions calculated on the basis of the chemical compositions of the precursors (see Table 1), i.e. 60.4 and 53 wt% respectively. The amorphous phase(s) which appeared in the heating products arose from the unreacted Na_2O and SiO_2. Hence, the amorphous products were most probably composed of the mixtures of sodium silicate and amorphous silica in the proportions 1 : 2–6 for the (Na,NH_4)A precursor and 1 : 2.2 for the (Na,NH_4)X precursors. Almost the same results were obtained on heating both, the crystalline (CP) and amorphous (AP) precursors (see Tables 7 and 8) indicating that as in the case of zeolite 4A exchanged with different alkali cations (Li^+,K^+,Cs^+), the ammonium-exchanged zeolites A and X transform to amorphous aluminosilicates before crystallizing to mullite. The mechanism of crystallization of mullite from amorphous aluminosilicate precursors is probably the same as the mechanism of crystallization of mullite from the aluminosilicate gels obtained by different sol–gel procedures [24–26].

The high rates of transformation of both, ammonium-exchanged zeolites A and X to amorphous aluminosilicates and the crystallization of mullite from the amorphous aluminosilicates, were the reason for the products of heating to contain only amorphous phases based on silicates ($Na_2O.SiO_2$, SiO_2) and not aluminosilicate derived from amorphous materials formed from the collapse of the zeolite framework.

Heating ammonium-exchanged synthetic mordenite at the DSC-peak temperature of 968°C resulted in its transformation to an X-ray amorphous alumi-

Table 8
Products obtained by heating of crystalline NH_4-exchanged zeolite X (CP) and amorphous phase formed by ball milling of CP(AP) at specified temperatures and time

Temperature of heating/ °C	Time of heating/ h	CP	AP
1007	0.5	47.5% $Al_6Si_2O_{13}$ mullite[15-776]+ 52.5% amorphous SiO_2	57.1% $Al_6Si_2O_{13}$ mullite[15-776]+ 42.9% amorphous SiO_2
1000	3	59.1% $Al_6Si_2O_{13}$ mullite[15-776]+ 40.9% amorphous SiO_2	59.3% $Al_6Si_2O_{13}$ mullite[15-776]+ 40.7% amorphous SiO_2

Table 9
Products obtained by heating of crystalline NH_4-exchanged synthetic mordenite (CP) and amorphous phase formed by ball milling of CP(AP) at specified temperatures and time

Temperature of heating/ °C	Time of heating/ h	CP	AP
968	0.5	100% amorphous phase	100% amorphous phase
968	3	73.0% amorphous phase+27.0% fine cryst. mordenite	≈100% amorphous phase+(cryst. reflections from WO_3)

nosilicate in <0.5 h. This is in accordance with earlier published results on thermal transformations of Na-, Cs- and Sr- exchanged synthetic mordenite [3]. The appearance of broad, weak reflections of mordenite, superimposed on the amorphous maximum in the X-ray diffractogram of the sample obtained on prolonged heating (for 3 h) indicates the existence of very fine mordenite particles about 10 nm in size. This is close to the line resolution between crystalline and amorphous phases. It is found that about 27 wt% of mordenite is dispersed through the amorphous matrix of the sample obtained by the heating ammonium-exchanged mordenite at 968°C for 3 h (see Table 9). Taking into consideration the thermal stability of 5–1 secondary building units (SBU) of the mordenite structure [3], this effect can be explained by recrystallization of the mordenite from the amorphous matrix through a deposition of the undestroyed 5–1 SBU on to the very small crystalline particles, i.e. nuclei having a size below that of the X-ray detection limit, within the amorphous matrix formed in the first step of the transformation process.

At present, this hypothesis has not been confirmed through investigation. The absence of fine mordenite particles in the thermally treated amorphous material obtained by ball milling of the ammonium-exchanged synthetic mordenite possibly indicates that the destruction of the mordenite structure is greatest during ball milling rather than during heating, that is to say there are no nuclei, or even 5–1 SBU needed for the crystallization of mordenite from the amorphous matrix obtained by ball milling of mordenite.

On the other hand, the weak though sharp peaks at 2θ=31.5, 35 and 48.3° in the X-ray diffractograms of the amorphous precursor obtained by ball milling of ammonium-exchanged mordenite belong to tungsten carbide from the balls used in milling. Oxidation of the tungsten carbide during prolonged heating of the ball milled sample at 1000°C causes peaks of tungsten oxide to appear in the product.

4. Conclusion

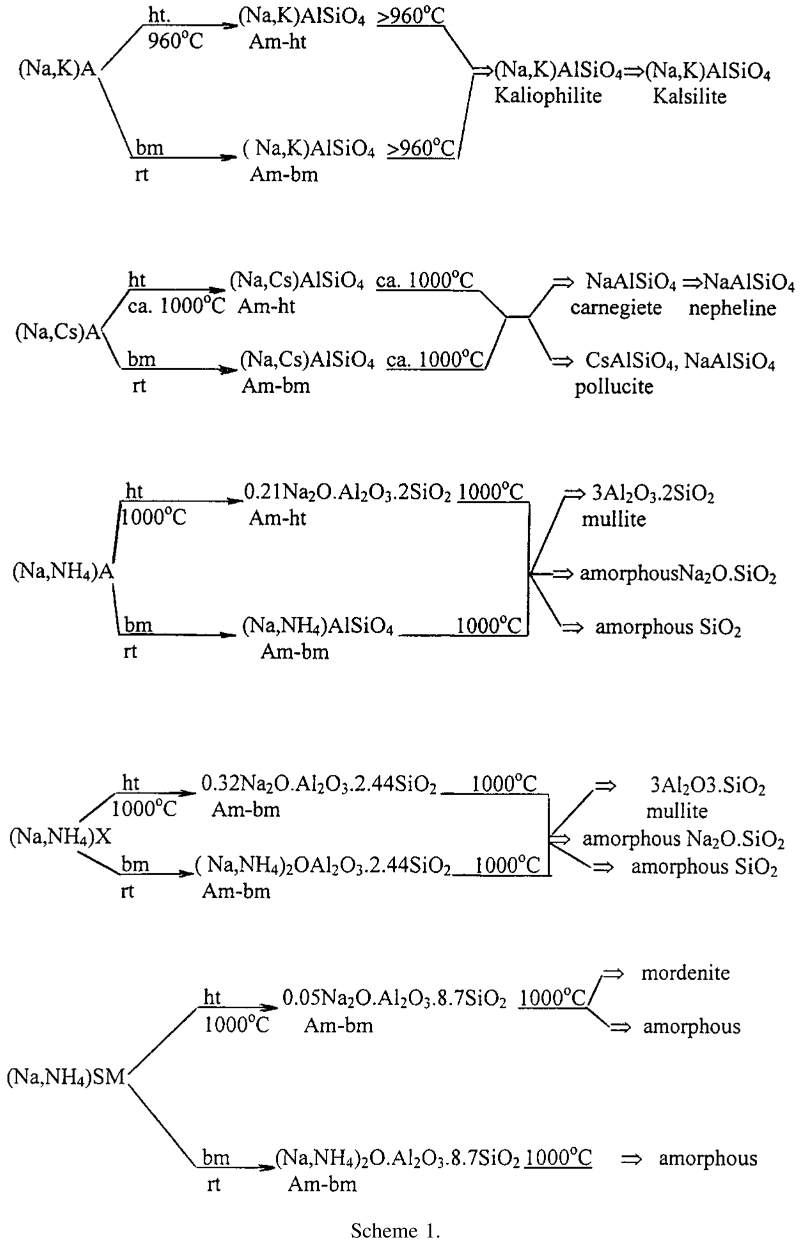
Analysis of the phase composition in the products obtained on heating of Li^+, K^+, Cs^+ and NH_4^+-exchanged zeolite A, ammonium-exchanged zeolites X and synthetic mordenite and the amorphous aluminosilicates obtained by ball milling of the crystalline precursors at the DSC-peak temperatures for 0.5 to 4 h has shown that the thermally induced transformations of the crystalline and amorphous precursors can be represented by the following transformation schemes; Scheme 1, Scheme 2

The abbreviations: ht., bm., rt., Am-ht. and Am-bm stand for heating, ball milling at room temperature, amorphous aluminosilicate obtained by heating of crystalline zeolite precursors (Am-bm) and amorphous aluminosilicate obtained by ball milling of the crystalline zeolite precursors 4A (Na-form of zeolite A), (Li,Na)A (Li-exchanged zeolite A), (Na,K)A, (K-exchanged zeolite A), (Na,Cs)A (Cs-exchanged zeolite A), $(Na,NH_4)A$ (NH_4-exchanged zeolite A, $(Na,NH_4)X$ (NH_4-exchanged zeolite X) and $(Na,NH_4)SM$ (NH_4-exchanged synthetic mordenite) (Am-bm).

The first steps in the thermal transformation of crystalline ion-exchanged zeolites are the formation of amorphous aluminosilicate phases by destroying the zeolite structure.

The thermal stability of the zeolite framework and, thus, the temperature of its transformation to the amorphous phase increase with the increase in ionic radius of the alkali cations present in the channel-voids.

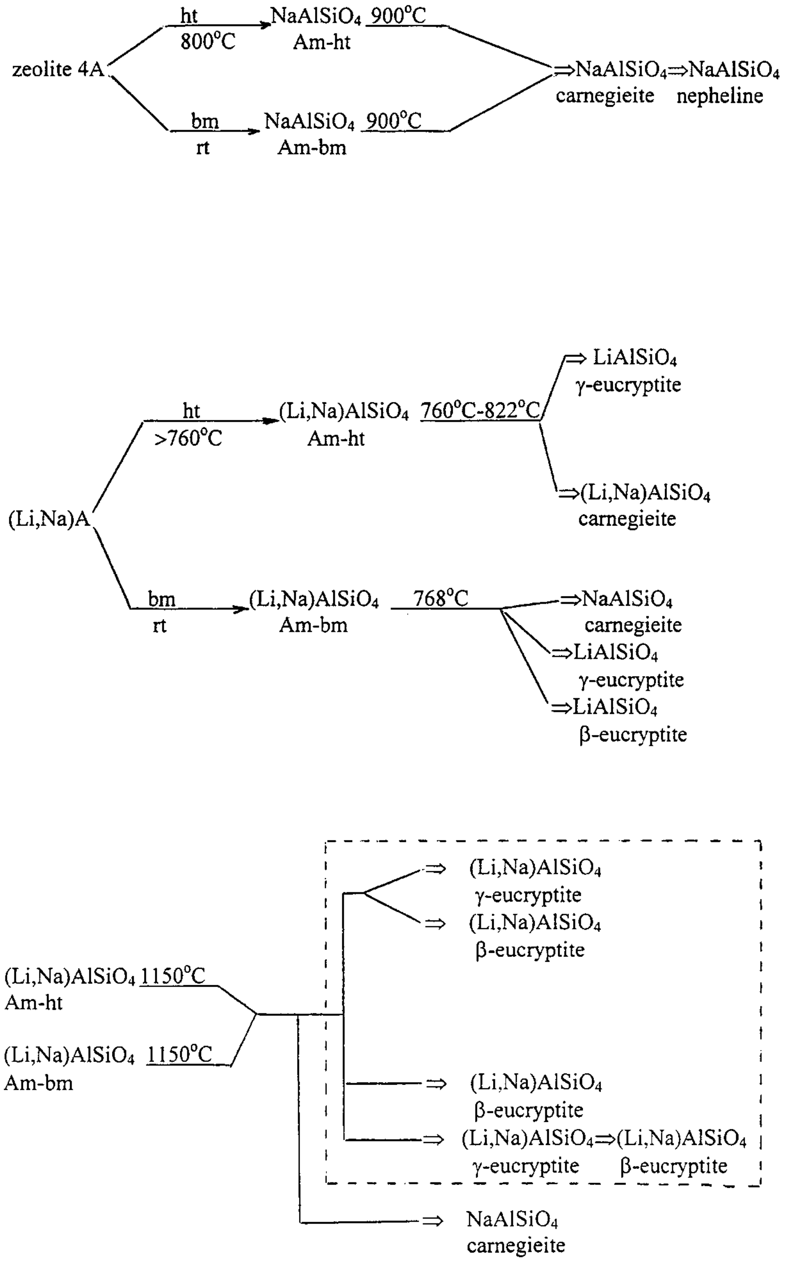
Further transformation pathways for the amorphous precursors formed both by heating and ball milling



Scheme 1.

depend on the type of cation(s) present in the precursors: The presence of Na^+ ions favours the crystallization of carnegieite and nepheline with a tendency to transformation further from the thermodynamically unstable carnegieite to the more stable nepheline at higher temperatures and prolonged heating.

The presence of Li^+ ions favours the crystallization of γ-eucryptite at 760–822°C and β-eucryptite at higher temperatures, namely 1150°C. The γ-eucryptite which may also form with β-eucryptite at 1150°C will tend to be transformed to β-eucryptite on prolonged heating. The formation of carnegieite at the lower temperature of 760–822°C and the formation of nepheline at the higher temperature of 1150°C is caused by the presence of Na^+ ions in the (Na,Li)-aluminosilicate precursors.



Scheme 2.

The presence of K^+ ions favours the crystallization of $(Na,K)AlSiO_4$ in the kaliophilite-type structure and its subsequent transformation to $(Na,K)AlSiO_4$ with a kalsilite-type structure. The presence of Cs^+ ions encourages the crystallization of pollucite. The nepheline formed due to the presence of Na^+ ions in the (Na,Cs)-aluminosilicate precursors tends to be transformed to $(Na,Cs)AlSiO_4$ with a pollucite structure during prolonged heating.

The amorphous precursors formed by both thermal treatment and ball milling of the ammonium-exchanged zeolites A and X transform at ca.

1000°C to a mixture of mullite and an amorphous phase composed of Na_2OSiO_2 and SiO_2.

The percentage of mullite in the products formed on heating is determined by the Al_2O_3 while Na_2OSiO_2 and SiO_2 are determined by the Na_2O and SiO_2 contents of the precursor, respectively.

Finally, heating ammonium-exchanged synthetic mordenite results in the formation of an amorphous aluminosilicate initially, followed by recrystallization of mordenite during prolonged heating. The amorphous precursor obtained by ball milling of the ammonium-exchanged synthetic mordenite remains amorphous during heating at 1000°C. The mechanisms of the transformation will be studied in further work.

Acknowledgements

We thank the Ministry of Science and Technology of the Republic of Croatia for its financial support.We also thank Dr. Poul Norby, Chemistry Department of the Brookhaven National Laboratory, Upton, NY 11973, USA for useful suggestions.

References

[1] M.A. Subramanian, D.R. Corbin, R.D. Farlee, Mat. Res. Bull. 21 (1986) 1525.
[2] W.D. Kingery, H.K. Bowen, D.R. Uhlmann, Introduction to Ceramics, 2nd edn., Wiley, New York, 1976.
[3] H. Mimura, T. Kano, Sci. Rep. RITU 29A (1980) 102.
[4] C. Kosanović, B. Subotić, I. Šmit, A. Čižmek, M. Stubičar, A. Tonejc, J. Mat. Sci. 32 (1997) 73.
[5] C. Kosanović, A. Čižmek, B. Subotić, I. Šmit, M. Stubičar, A. Tonejc, Zeolites 15 (1995) 51.
[6] C. Kosanović, J. Bronić, B. Subotić, I. Šmit, M. Stubičar, A. Tonejc, T. Yamamoto, Zeolites 13 (1993) 261.
[7] C. Kosanović, J. Bronić, A. Čižmek, B. Subotić, I. Šmit, M. Stubičar, A. Tonejc, Zeolites 15 (1995) 247.
[8] P.H. Hermans, A. Weidinger, Makromol. Chem. 44/46, (1961) 24.
[9] Powder diffraction file JCPDS, ICDD, Swartmore, PA USA, 1972, Card Nos. 11–313 and 11–579.
[10] L.S. Zevin, L.L. Zavyalova, Kolichestvenniy Rentgenographicheskiy Prazoviy Analiz, Nedra, Moscow, 37 (1974).
[11] Z. Sarbak, Cryst. Res. Technol. 28 (1993) 979.
[12] D.W. Breck, W.G. Eversok, R.M. Milton, T.B. Reed, T.L. Thomas, J. Am. Chem. Soc. 78 (1956) 5963.
[13] P.K. Dutta, B. Del Barco, J. Phys. Chem. 108 (1986) 1861.
[14] C.A. Fyfe, G.T. Kokotailo, J.D. Graham, C. Browning, G.C. Gobbi, M. Hyland, G.J. Kennedy, C.T. De Shutter, J. Am. Chem. Soc. 108 (1986) 522.
[15] C. Kosanović, Mechanochemistry of zeolites, Ph.D. thesis, Institut Ruðer Bošković, University of Zagreb, Zagreb, 1994.
[16] C. Kosanović, B. Subotić, A. Čižmek, Thermochim. Acta 276 (1996) 91.
[17] W. Ostwald, Z. Physik. Chem. 22 (1897) 289.
[18] L. Stock, I. Waclawska, High Temp. Materials and Processes 13 (1994) 181.
[19] Y. Oumi, H. Yamano, M. Kubo, R. Vetrivel, A. Miyamoto, Catal. Today 23 (1995) 417.
[20] Powder diffraction file, JCPDS, ICDD, Swarthmore, PA USA 1990, Card No. 35–424.
[21] Powder diffraction file, JCPDS, ICDD, Swarthmore, PA, USA, 1990, Card No. 19–1176.
[22] J.V. Smith, O.F. Tuttle, Am. J. Sci. 255 (1957) 282.
[23] P. Norby, Zeolites 10 (1990) 193.
[24] A. Yasumori, M. Iwasaki, H. Kawazoe, M. Yamane, Y. Nakamura, Diff. Defect Data 283 (1987) 53.
[25] T.J. Mroz Jr.J.W. Laughner, J. Am. Ceram. Soc. 72 (1989) 508.
[26] Y. Hirata, K. Sakeda, Y. Matsuhita, K. Shimada, Y. Ishihara, J. Am. Ceram. Soc. 72 (1989) 995.