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# Natural and Zn exchanged clinoptilolite: *in situ* high temperature XRD study of structural behavior and cation positions

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The thermal stability of the clinoptilolite's structure is reported to vary in a relatively wide range 600–800 °C depending on the sizes of the cations, their sites and occupancies. The aim of this study is to reveal and compare the thermal stability of a natural monomineral clinoptilolite (**CP**) that contains the most common cations: Na, Ca, K and Mg and its Zn-exchanged analogue (**CZN**) having high Zn content of 2.23 at%.

Two different modes of heating were applied: (1) conventional with time-dependent heating/cooling cycles in an electric oven and (2) *in situ* with the sample mounted on a high temperature attachment and continuously heated. In mode (1) the samples were heated up to 600 °C and maintained at this temperature for 3 and 6 hours. With retention time of 3 hours the CP structure collapses, while the CZN one remains stable and does not show visible structural changes. The prolonged retention time of (6 hours at 600 °C) results in the collapse of both structures.

In mode (2), the samples CP and CZN were heated from room temperature to 800 °C with steps of 100 °C and retention time of 20 min. on every step. It was found that the structure of CZN is stable up to 700 °C, while that one of CP collapses around at 600 °C.

Initially we assumed that the high Zn-content in CZN structure is the one that caused its higher short time thermal stability. However, the structural refinement conducted on X-ray powder diffraction patterns of heated samples (2) reveals a continuous displacement of the cations along *a*- and *c*-axis.

**Key words:** clinoptilolite, ion exchange, thermal stability, *in situ* HT X-ray diffraction.

## INTRODUCTION

The zeolite minerals are known for having specific structural features based on the individual topology of their framework and the differences in the amount and type of cations located in the "cavities" of their structures. All these characteristics play a significant role in their thermal stability [1–3]. Thermal behavior is an important part of the overall knowledge of natural zeolites, and each study of these processes could provide a better recognition of their distinctive properties that can be used in various industrial applications. More specifically, the thermal stability may help understanding certain kinetic aspects related to: ion exchange, selective catalysis, molecular sieve properties etc.

The heulandite's group of zeolites is the most abundant on Earth and contains minerals with HEU topology [4]. Clinoptilolite is a member of HEU group with Si/Al ratio greater than four [5]. A widely used empirical method for distinguishing clinoptilolite from heulandite is the different thermal stability [6, 7]. Heulandite undergoes a structural collapse at 350 °C, while clinoptilolite remains stable above this temperature (undergoes structural collapse in the range 550~750 °C).

The clinoptilolite structure has cations and water molecules located inside its framework. The number of cations, their types, site occupancies and charge distribution over the framework are considered as being factors for its higher thermal stability. It is well known that the presence of $K^+$ and $Cs^+$ increases the thermal stability of clinoptilolite [8–12]. Although dehydration and some of the structural changes of heulandite group of minerals upon heating are studied [10, 11, 13, 14,] not all of the associated with heating internal processes are clarified.

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In the current paper we study the thermal behavior of natural, poly-cationic clinoptilolite that was purified from additional phases (CP) and its $Zn^{2+}$ exchanged analogue (CZN).

The thermal stability of both structures was monitored by diffraction patterns taken at various stages of heating. A detailed analysis of the diffraction patterns including Pawley whole pattern decomposition and Rietvled refinement were applied to access changes in lattice parameters, cation positions and site occupancies. In addition, a thermally stable K-exchanged clinoptilolite form was prepared (CK) and heated the same way as the other two in order to control the reliability of the applied heating procedures [1, 8].

Two different heating procedures were applied in this study:

1. Conventional (stationary) heating, in which the sample is placed in an electric furnace, heated and held at a certain temperature for a fixed period of time and then cooled down. This mode was used for evaluation of time-dependent short (3 hours) and long (6 hours) stability of the samples at the critical for CZN clinoptilolite temperature of 600 °C.
2. *In situ* heating process, in which the material is placed in a special "homemade" high temperature (HT) sample holder and mounted on the goniometer. This approach allows an instant monitoring of sample's compositional and structural changes during the entire process of continuous heating between the steps. This way, each diffraction pattern taken at a certain temperature will represent the actual status of the material at this moment of heating process.

## EXPERIMENTAL

### *Materials*

The studied material is a purified clinoptilolite tuff from Beli Plast deposit, Eastern Rhodopes, Bulgaria.

### *Ion exchange*

The clinoptilolite sample was subject to preliminary removal of concomitant minerals such as: quartz, plagioclase, feldspar, mica and was labeled as CP. This material was used for $Zn^{2+}$ and $K^+$ exchange as described below.

Zn-exchange: 1 g of CP, 10 ml 1M $ZnCl_2$ solution and 50 ml distilled water were placed in a Teflon autoclave. The procedure of zinc exchange was performed at 100 °C for a period of 30 days. The autoclave was shook up every day while the solution of 1M $ZnCl_2$ was renewed every second day. The exchanged material (30th day) was triple washed with distilled water, filtered and dried at room temperature. Zinc-exchanged clinoptilolite was labeled as CZN.

K-exchange: 1 g of CP, 10 ml 1M KCl and 50 ml distilled water were placed in a Teflon autoclave. The exchange was carried out at 60 °C for 5 days. The autoclave was shook up every day while the solution of 1M KC1 was renewed every 40 hours. The exchanged material was washed and dried. This potassium-exchanged clinoptilolite was labeled as CK.

### *Chemical analysis*

The chemical composition of the samples was determined by ISP-OES, Varian Vista MPX CCD simultaneous analyses. The structural formulas of the CP, CZN and CK samples were calculated based on 72 framework oxygen atoms. Water molecules were determined using TG data (mass losses).

### *Differential Thermal analysis (DTA)/ Thermogravimetric (TG) analyses*

The thermal effects and mass losses were monitored by DTA/TG analyses in the 30–750 °C temperature range and were obtained from samples CP and CZN (weight 12 ± 0.2 mg) under a constant heating rate of 10 °C $min^{-1}$ and an air flow of 50 ml/min on a Stanton Redcroft thermoanalyzer.

### *Thermal treatment and heating procedures*

Conventional heating: one set of samples CP, CZN and CK were placed in an electric oven, heated and retained at 600 °C for 3 hours. Another set of samples was heated and retained at 600 °C for a prolonged period of e.g. 6 hours.

*In situ* heating – the analyzed samples were placed and mounted on a homemade HT device adapted for powder X-ray diffractometer Dron 3M. They were heated from room temperature (RT) up to 800 °C. The heating scheme was: steps of 100 °C with a constant heating rate of 10 °C/min and 20 minutes retention time.

### *X-ray diffraction*

The X-ray powder diffraction data collection for conventionally heated samples was carried out on a Bruker D2Phaser diffractometer, CuKα radiation, with scan step of 0.02°/s on a range of 5–35° 2θ.

X-ray diffractometer Dron 3M, CoKα radiation, with scan step of 0.02°/s on a range of 5–35° 2θ was used for data acquisition of *in situ* heated samples. A detailed description of high temperature equipment is represented [15].

**Table 1**. Agreement factors and unit cell parameters for samples CP and CZN at different temperatures

| Sample | CP RT | CP 300 °C | CP 500 °C | CZN RT | CZN 300 °C | CZN 500 °C |
|---|---|---|---|---|---|---|
| $R_{exp}$ | 9.64 | 9.74 | 9.79 | 9.44 | 9.28 | 9.44 |
| $R_{wp}$ | 12.7 | 11.8 | 11.85 | 11.37 | 11.22 | 12.05 |
| $R_p$ | 9.68 | 9.22 | 8.96 | 8.69 | 8.73 | 9.46 |
| GOF | 1.32 | 1.21 | 1.19 | 1.23 | 1.21 | 1.28 |
| DW | 1.67 | 2.06 | 1.86 | 1.88 | 2.01 | 1.76 |
| $\alpha$ (Å) | 17.661(2) | 17.635(3) | 17.634(8) | 17.649(2) | 17.637(4) | 17.613(4) |
| $b$ (Å) | 17.931(2) | 17.612(3) | 17.651(5) | 17.960(3) | 17.741(3) | 17.593(4) |
| $c$ (Å) | 7.401(2) | 7.394(4) | 7.384(5) | 7.401(3) | 7.389(4) | 7.382(5) |
| $\beta$(°) | 116.33(4) | 116.67(4) | 116.71(6) | 116.24(5) | 116.29(5) | 116.62(6) |
| V (Å$^3$) | 2100(3) | 2052.6(9) | 2035.4(8) | 2104(3) | 2073(8) | 2045(2) |

### *Rietveld refinement*

The structural properties at RT and high temperatures were investigated by Rietveld [16] analysis on the XRD powder patterns of the *in situ* heated samples using Bruker AXS Topas v. 4.0 [17] suite of programs. A pseudo-Voight profile function was applied. Profile parameters (2θ zero correction, background, cell parameters) were refined first and then the positional parameters (locations and site occupancies) of the cations at three different temperatures: RT (20 °C), 300 °C and 500 °C. Unit cell parameters for all samples (RT to 800 °C) were calculated by Pawley fitting procedure (Table 1).

## RESULTS AND DISCUSSION

The chemical compositions of the samples CP, CZN and CK are shown in Table 2. The obtained formulas indicate that the exchanged samples CZN and CK contain predominantly zinc and potassium cations respectively.

The thermal behavior and mass losses illustrated by DTA/TG data are typical for clinoptilolite and both samples CP and CZN display similar curves (Fig. 1). The thermal curves for both samples are characterized by a broad single endothermic effect between ~100–300 ºC for CP and ~80–250 ºC for CZN. These losses are associated with continuous loss of mass mainly due to dehydration (removal of water molecules located in the channels).

The results of thermogravimetric analysis (RT-750 °C) of CP, CZN and CK show typical values for the mass losses of 14.5, 14.2 and 11.37 wt.%, respectively (Table 2).

XRD powder diffraction patterns obtained from RT, conventional heating (600 °C → 3 hrs) and conventional heating (600 °C → 6 hrs) for CK, CP and CZN samples are shown on Fig. 2 (a–c), respectively. As expected the diffractograms (RT, 600 °C → 3 hrs and 600 °C → 3 hrs) of the CK sample remains unchanged while those of CP and CZN samples exhibit a different behavior and are affected by the conducted thermal treatment. The most important result obtained from the conventional time-dependent mode of heating was the higher thermal stability of Zn-exchanged material after a short-term heating cycle (600 °C → 3 hrs) as shown on Figure 2b. One can see that the diffraction pattern of heated for 3 hours CZN is almost identical with its diffraction pattern at RT (Figure 2a). All

**Table 2**. Chemical composition of the analyzed samples: CP, CZN and CK (results from ICP-OES)

| Oxides Wt % | $SiO_2$ | $Al_2O_3$ | $Fe_2O_3$ | CaO | $Na_2O$ | $K_2O$ | MgO | ZnO | LOI* |
|---|---|---|---|---|---|---|---|---|---|
| CP | 66.10 | 12.08 | 0.28 | 3.45 | 1.16 | 1.92 | 0.72 | >0.01 | 14.20 |
| CZN | 64.75 | 11.74 | 0.31 | 0.80 | 0.21 | 0.70 | 0.29 | 6.59 | 14.56 |
| CK | 66.25 | 11.95 | 0.28 | 0.45 | 0.16 | 9.15 | 0.22 | >0.01 | 11.37 |

Calculated chemical formulas:
CP: $(Na_{1.01}Ca_{1.66}\ K_{1.10}\ Mg_{0.48})\ Al_{6.39}\ Si_{29.52}O_{72}$ 21.20 $H_2O$;
CZN: $(Na_{0.19}Ca_{0.39}K_{0.41}\ Mg_{0.20}Zn_{\ 2.23})Al_{6.31}Si_{29.61}O_{72}$ 22.20 $H_2O$;
CK: $(Na_{0.19}Ca_{0.39}K_{0.41}\ Mg_{0.20}Zn_{\ 2.23})Al_{6.31}Si_{29.61}O_{72}$ 22.20 $H_2O$;
* LOI – Loss on ignition.

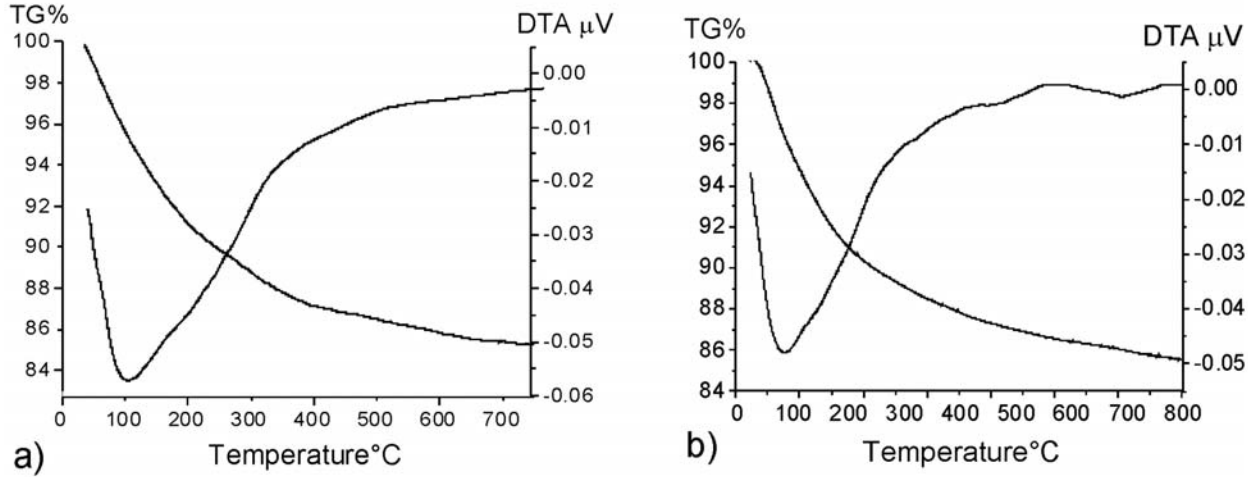

**Fig. 1.** The results obtained by DTA TG analysis for sample CP (a) and CZN (b)

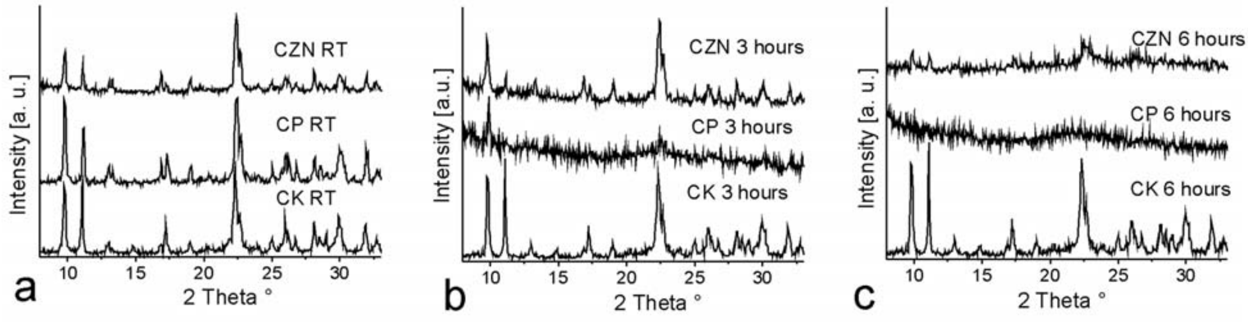

**Fig. 2.** XRD powder patterns of CP, CZN and CK obtained at RT (a), 300 °C (b) and 600 °C (c)

peak intensities and their positions on the pattern indicate that the structure of CZN retains its integrity and long-range ordering. This is a clear indication for unchanged crystal structure in contrast with the behavior of CP structure, which collapsed after identical short-term heating cycle. As shown on Figure 2c the long range order of samples CP and CZN subject to long-term heating cycle (600 °C → 6 hrs) disappears (amorphization).

The results from *in situ* HT x-ray experiments exploring a continuous heating mode do not show any significant structural changes up to 600 °C (Fig. 3). For the next step (700 °C) the structure of CP has collapsed, whereas that one of CZN remains stable. This shows again the enhanced thermal stability of Zn-exchanged material over the purified natural clinoptilolite. I*n situ* HT results show that CZN structure has collapsed at 800 °C.

As expected, there are some variations of the unit cell as a function of temperature. It was found that unit cell parameters *a*, *c* and *β* remain almost unchanged, whereas the heating affects mainly *b* (and thus way the volume, *V*) (Fig. 4). The reduction of *b* and *V* is slightly more noticeable below 300 °C due to ongoing dehydration process, while for next heating steps the contraction mechanism remains unclear. This mechanism could be related to the motion (kinetics and diffusion) of cations inside the channels.

We attempted to understand this short-term stability of the $Zn^{2+}$-exchanged sample by using *in situ* heating XRD powder data followed by Rietveld structural analysis on the diffraction patterns at different temperatures for both samples.

The crystal structure of our clinoptilolite (CP) was found to be very close to that one reported by Koyama et al. [9]. It has the same 4 cation sites for Na, Ca, K and Mg located at almost the same positions in the channels. The calculated XRD powder diffraction pattern is very close to that one obtained

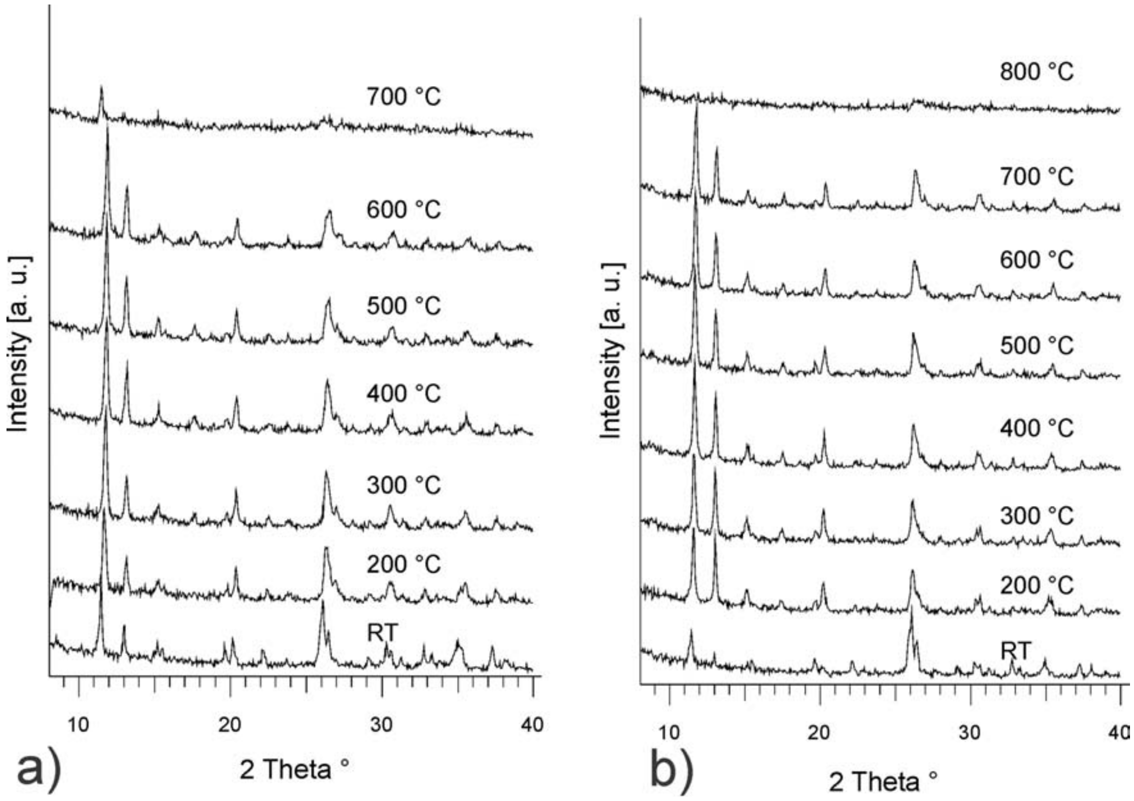

**Fig. 3.** XRD powder patterns of in situ heated samples CP (a) and CZN (b)

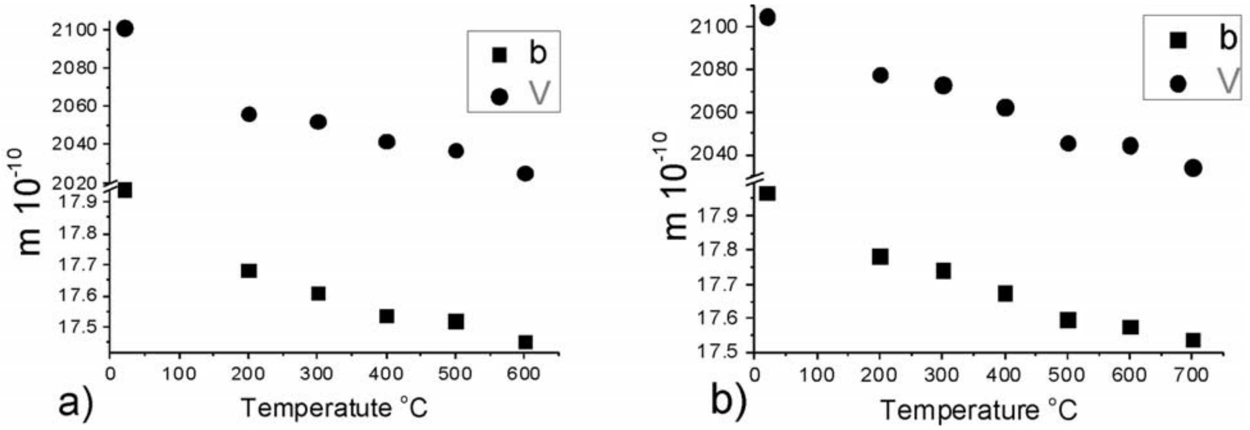

**Fig. 4.** The parameters that vary significantly: unit cell parameters b and V for samples CP (a) and CZN (b) during in situ heating process

for our clinoptilolite. Thus, the structure of Koyama and Takeuchi was used as a starting structural model in this study.

The results from the performed Rietvled refinement reveal that at high temperatures the cations move inside the channels. Some of their positions remain unchanged, while others experience shifts. This is shown on Table 2 and illustrated on Figure 5.

In the refined structure of CP at 300 and 500 °C, both $Na^+$ and $Ca^{2+}$ positions have moved along *a*- and *c*-axes and as a result they have slightly been shifted away from the center of the channel, while K-position remains steady. The most significant change here occurs with $Mg^{2+}$ cation located at the center of the channel. At 300 °C its initial site splits creating new position labeled Mg'. At 500 °C it moves further to another position labeled Mg". This high-temperature transitions of Mg position to Mg' and Mg" changes the symmetry of its initial site from (*2c*) to (*4i*) and finally to (*8j*) (Table 3, Fig. 5).

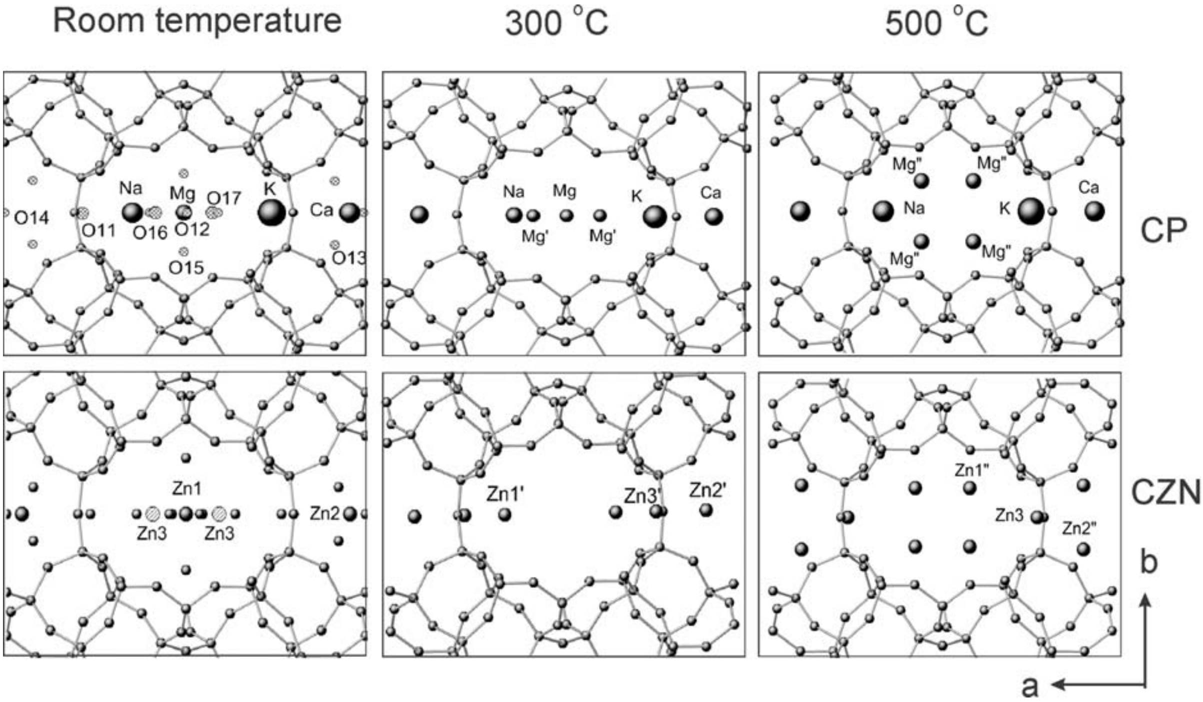

**Fig. 5.** The structures of CP and CZN samples refined in RT, 300 and 500 °C and cation positions obtained by using Rietveld method. The cation labeling is discussed in the text

**Table 3**. Cation positions, atomic coordinates (x, y, z) of the samples CP and CZN, their occupancies and Wyckoff positions (Wp) at RT, 300 and 500 °C. The cation labeling is discussed in the text

| CP | Position | T °C | *x* | *y* | *z* | SOF | Wp |
|---|---|---|---|---|---|---|---|
| | Na | 20 | 0.143(7) | 0 | 0.664(8) | 0.26(3) | *4i* |
| | Na | 300 | 0.145(8) | 0 | 0.664(8) | 0.26(3) | *4i* |
| | Na | 500 | 0.185(9) | 0 | 0.858(9) | 0.26(3) | *4i* |
| | Ca | 20 | 0.038(8) | 0.5 | 0.206(8) | 0.44(2) | *4i* |
| | Ca | 300 | 0.038(8) | 0.5 | 0.131(9) | 0.44(2) | *4i* |
| | Ca | 500 | 0.950(8) | 0.5 | 0.138(8) | 0.44(2) | *4i* |
| | K | 20 | 0.255(9) | 0.5 | 0.088(9) | 0.28(3) | *4i* |
| | K | 300 | 0.255(9) | 0.5 | 0.088(9) | 0.28(3) | *4i* |
| | K | 500 | 0.257(9) | 0.50 | 0.080(9) | 0.28(3) | *4i* |
| | Mg | 20 | 0 | 0 | 0.5 | 0.24 (3) | *2c* |
| | Mg | 300 | 0 | 0 | 0.5 | 0.09 (3) | *2c* |
| | Mg' | 300 | 0.092(8) | 0 | 0.051(8) | 0.08(3) | *4i* |
| | Mg" | 500 | 0.075(9) | 0.077(8) | 0.760(9) | 0.07 (3) | *8j* |
| CZN | Zn1 | 20 | 0 | 0 | 0.5 | 0.52(3) | *2c* |
| | Zn1' | 300 | 0.162(9) | 0 | 0.076(9) | 0.23(4) | *4i* |
| | Zn1" | 500 | 0.080(8) | 0.072(9) | 0.838(8) | 0.07(3) | *8j* |
| | Zn2 | 20 | 0.043(6) | 0.5 | 0.27(9) | 0.17(2) | *4i* |
| | Zn2' | 300 | 0.075(8) | 0.5 | 0.538(9) | 0.20(3) | *4i* |
| | Zn2" | 500 | 0.085(7) | 0.42 | 0.109(9) | 0.11(3) | *8j* |
| | Zn3 | 20 | 0.092(6) | 0 | 0.464(9) | 0.13(2) | *4i* |
| | Zn3' | 300 | 0.721(9) | 0 | 0.127(9) | 0.13(2) | *4i* |
| | Zn3' | 500 | 0.72(8) | 0 | 0.127(9) | 0.19(3) | *4i* |

Similar changes occur in the structure of CZN sample where the high Zn-content is distributed in three $Zn^{2+}$ positions. At RT Zn1 and Zn2 occupy the formerly occupied by $Mg^{2+}$ and $Ca^{2+}$ positions, respectively. The Zn3 position (with low occupancy) is very close to Zn1 and because of this both positions cannot be occupied simultaneously [18].

At 300 °C all three zinc positions: Zn1, Zn2 and Zn3 move along a-axis away from the center of the channels and along c-axis. The initial Zn1 position disappears and transforms to a new position labeled Zn1'. This changes its initial site symmetry from (*2c*) to (*4i*). The shifted position Zn2 and Zn3 are labeled as Zn2' and Zn3' and keep the same symmetry (*4i*).

At 500 °C both Zn1' and Zn2' continue their motion along b-axes. Thus Zn1' moves to a new position labeled Zn1" changing again its site symmetry to (*8i*). The Zn2' moves to a new position Zn2" changing its site symmetry from (*4i*) to (*8j*). The Zn3' position does not change.

We assume that the movements of Zn1 and Zn2 during the heating and the transformation of their initial positions symmetry from (*2c*) to (*4i*) and finally to (*8j*) could be the key factor that increases the HT stability of CZN structure. In the case of CP, Mg-position is the most mobile one, however its very low occupancy is insufficient, to hold the integrity of the structure above 600 °C. In contrast, the Zn-sites in CZN structure are highly occupied and their HT migration (movement) and re-arrangement most likely have an effect on charge balance between the framework and the cations that leads to the observed higher stability of the CZN structure. The smaller size of $Zn^{2+}$ compared with the larger ones of $Na^+$, $K^+$ and $Ca^{2+}$ is in favor for its mobility. On the other hand, the $Zn^{2+}$-positions cannot be fully occupied even at high temperatures due to the limitations imposed by the existing framework's charge. Thus, the initial low symmetry cation positions at RT may uptake only three divalent cations per unit cell and because of this the observed thermal stability of CZN exists only for a limited time and eventually the structure would collapse as it has been observed.

## CONCLUSION

The applied two different modes of heating on purified clinoptilolite and its Zn-analogue ultimately revealed the enhanced thermal stability of Zn-exchanged material. The steadiness of the reference sample CK structure confirmed the correctness of the applied heating procedure. The unit cell of CP and CZN shrinks during heating mainly due to continuous decrease of *b* parameter. The performed Rietveld structural analysis discloses the increased mobility of the cations in the channels. This leads to transformation of their initial crystallographic sites symmetry to new ones. This process is more significant in the Zn-exchanged form and it is assumed that it could be a stabilization factor for its higher thermal stability. Actually, the small Zn cation cannot 'hold' the structure the way this is made by as the bigger potassium one and this high temperature stability is temporary.

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# ПРИРОДЕН И ZN ОБМЕНЕН КЛИНОПТИЛОЛИТ: *IN SITU* ВИСОКОТЕМПЕРАТУРНО ПРАХОВО РЕНТГЕНОСТРУКТУРНО ИЗСЛЕДВАНЕ НА ПОВЕДЕНИЕТО НА СТРУКТУРАТА И КАТИОННИТЕ ПОЗИЦИИ

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(Резюме)

Структурата на клиноптилолита е стабилна при високи температура (600 до 800 °C) в зависимост от типа на катионите в каналите, от техните позиции и от заетостта им. В настоящето изследване е сравнено термичното поведение на природен мономинерален клиноптилолит (CP) и на обменен с цинкови катиони (CZN). В природната CP форма се съдържат Na, Ca, K и Mg катиони, а в CZN 2,23 ат.% цинк. За целта на изследването се използват два метода за нагряване на пробите: (1) конвенционален в пещ и (2) *in situ*, при който пробата е монтирана на високо температурна приставка и постепенно се нагрява. При (1) се достига температура 600 °C, като продължителността е 3 и 6 часа. При образците загрявани 3 часа структурата на проба CP се разрушава, докато тази на CZN остава стабилна. При (2) загряването на образците CP и CZN започва от стайна температура и достига до 800 °C със стъпка 100 °C и задържане от 20 min за всяка стъпка (~ 3 часа). Структурата на проба CZN остава стабилна до 700 °C, докато тази на CP се разрушава при температура около 600 °C. Направено е структурно уточнение по метода на Rietveld на *in situ* нагряваните проби, за да се установи причината за кратката термична стабилност на цинково обменения клиноптилолит.