

## Two-stage protonation of a small-pore microporous zirconosilicate $\text{Na}_2\text{ZrSi}_2\text{O}_7 \cdot \text{H}_2\text{O}$

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The crystal chemical changes occurring upon protonation of the small-pore zirconosilicate  $\text{Na}_2\text{ZrSi}_2\text{O}_7 \cdot \text{H}_2\text{O}$  have been studied. It has been noticed that variations of the reaction's medium initial pH influence the degree of sodium leaching of this material. It is found that this dependence is closely related to the structural positions of the Na atoms. The crystal structures of partially and completely protonated samples were refined and compared with the one of the as-synthesized material. In general, the protonation process preserves the framework topology but, however, it noticeably causes mutual shifting of the adjacent layers, which affects the unit cell parameters. Initially, the unit cell volume increases from  $673.56 \text{ \AA}^3$  (as-synthesized phase) to  $684.9 \text{ \AA}^3$  (partially protonated sample) and next shrinks to  $660.8(1) \text{ \AA}^3$  (completely protonated material). The monoclinic arrangement becomes pseudo-orthorhombic with values of  $\beta = 89.519(9)^\circ$  and  $89.872(3)^\circ$  for the partially and fully protonated samples, respectively. The evaluation of the framework deformation evidences that protonation causes higher degree of framework deformations than the dehydration process.

**Key words:** zirconosilicate, protonation, crystal structure, framework deformation.

### INTRODUCTION

A new microporous phase was hydrothermally synthesized in the system  $\text{Na}_2\text{O}-\text{ZrO}_2-\text{SiO}_2-\text{H}_2\text{O}$  [1]. Subsequently, the structure of this powdered material was successfully solved based on the Rietveld refinement routine carried out with the GSAS program [2] and EXPGUI [3] and using the suitably modified atomic coordinates of the topologically identical  $\text{Na}_3\text{ScSi}_2\text{O}_7$  as a starting structural model [4]. It has been found that  $\text{Na}_2\text{ZrSi}_2\text{O}_7 \cdot \text{H}_2\text{O}$  is a small-pore compound with framework built up of  $\text{ZrO}_6$  octahedra and  $\text{SiO}_4$  tetrahedra in a manner that results in the formation of layers (alpha-ZrP type [5]) parallel to (001), where silicate groups lie both above and below the plane of the zirconium atoms. The adjacent layers are related by rotation and are connected to each other *via* oxygen atoms creating  $[\text{Si}_2\text{O}_7]$  pyrogroups. The structure is thus a three-dimensional framework and possesses system of two interconnected channels running parallel to (001). The sodium ions and water molecules reside within

the channels. Sodium occupies two crystallographic positions – general and special ones. While the occupied in half “general” Na resides together with the water molecules almost in the central parts of the channels, the “special” Na lies in cavities set up between the alpha-ZrP type of layers building up the polyhedral ( $\text{ZrSi}_2\text{O}_4$ ) framework [4]. Lately, it was found that upon heating the monoclinic structure of the title compound converts into orthorhombic one, however preserving the initial topology. The process is accompanied by water release and a slowly rehydration is possible for this material only up to  $300 \text{ }^\circ\text{C}$ . Above this temperature the orthorhombic structure is preserved up to  $800 \text{ }^\circ\text{C}$  and next an irreversible transition into a phase with denser triclinic structure occurs thus, precluding the ion-exchange properties of this compound [6]. Further on, the ion-exchange properties of  $\text{Na}_2\text{ZrSi}_2\text{O}_7 \cdot \text{H}_2\text{O}$  have been investigated (unpublished data). Upon exchange on Sr, substantial changes of the peaks intensity ratios in the powder XRD patterns of the final products have been detected being more pronounced at lower initial pH of the reaction media. Chemical analyses and simulated XRD pattern of “fully exchanged” on Sr material have been indicative that such drastic peak ratio differences could not be obtained only on the account of Sr uptake. Thus, it has become clear

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that the observed changes are due to Na leaching. Taken alone this fact confirms the microporosity of the title compound. However, our attention was attracted by the possibility to investigate the mechanism and degree of protonation of  $\text{Na}_2\text{ZrSi}_2\text{O}_7\cdot\text{H}_2\text{O}$  upon various experimental conditions (initial pH) as well as the structural changes occurring upon these processes.

## EXPERIMENTAL

### *Sample preparation*

The starting compound  $\text{Na}_2\text{ZrSi}_2\text{O}_7\cdot\text{H}_2\text{O}$  was hydrothermally synthesized following a procedure described by Kostov-Kytin and Kalvachev [1]. Best results were achieved from gels with the following starting composition (moles):  $37.5\text{Na}_2\text{O} - 2.5\text{ZrO}_2 - 8\text{SiO}_2 - 675\text{H}_2\text{O}$  and 480 hours synthesis duration at  $200^\circ\text{C}$ .

### *Protonation procedure*

Several samples of the as-synthesized material of one gram each were stirred in distilled water for 7 hours at  $60^\circ\text{C}$  and solid-to-liquid ratio of 1:200. The initial pH was adjusted by adding  $\text{HNO}_3$ . Subsequently, only two of the samples were chosen for further investigations designated as HM-1 and HM-2, 1 and 2 meaning 0.1 and 0.2N acid solution used in each experiment, respectively.

### *Analytical Procedures*

Initial characterization of the  $\text{HNO}_3$  treated samples were performed by powder X-ray diffraction (XRD) analysis using a Bruker D2Phaser diffractometer with  $\text{CuK}\alpha$  radiation in the  $2\theta$  range from  $5$  to  $90^\circ$  and in a step-scan regime (step  $0.015^\circ$  and time 6 s). Sodium content in the run products after the treatment was determined by AAS (Perkin Elmer 3030) under conditions prescribed by the manufacturer. TG and DTA studies were performed on a Stanton Redcroft thermal analyzer (STA 780) at a heating rate  $10\text{ deg/min}$  in static air.

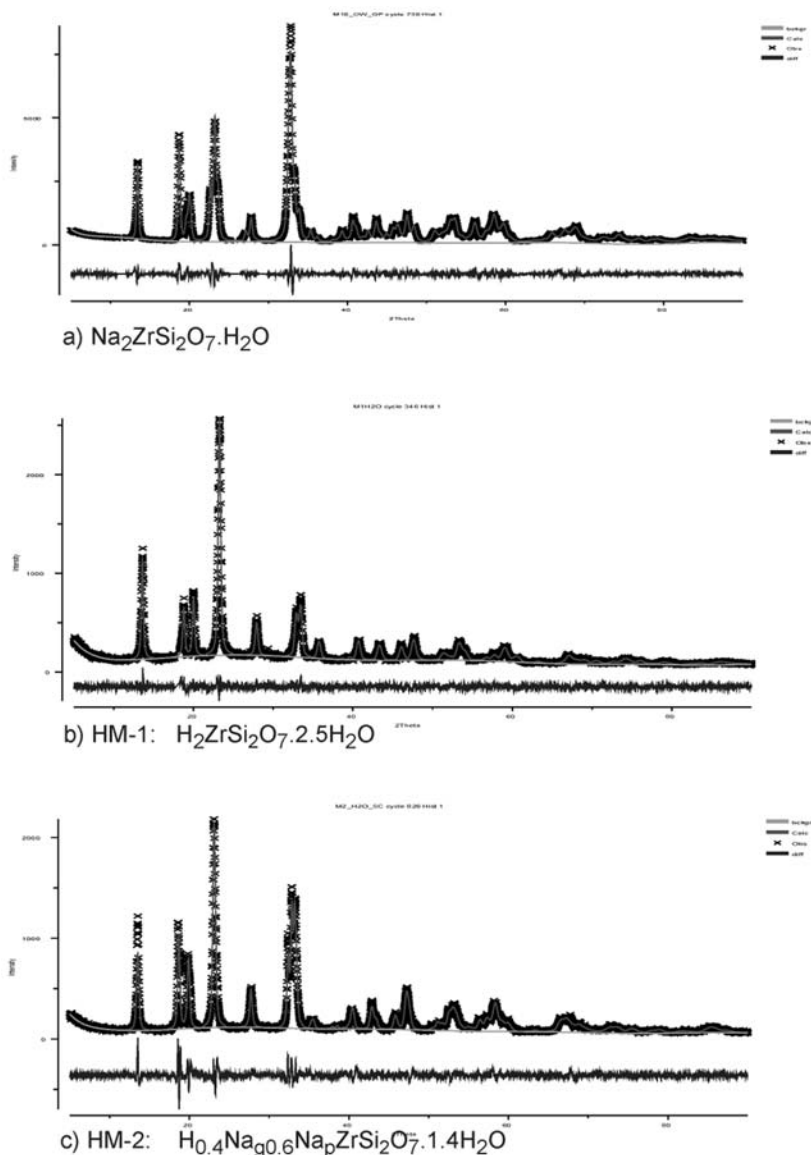
### *Structure Refinement*

The atomic coordinates of  $\text{Na}_2\text{ZrSi}_2\text{O}_7\cdot\text{H}_2\text{O}$  were used as a starting structural model for Rietveld refinement of HM-1 and HM-2 carried out with the GSAS program [2] and EXPGUI [3]. Initial chemical compositions for the acid-treated phases were adjusted in accordance with the number of water molecules and sodium content obtained from the TG-DTA data and the chemical analyses, respec-

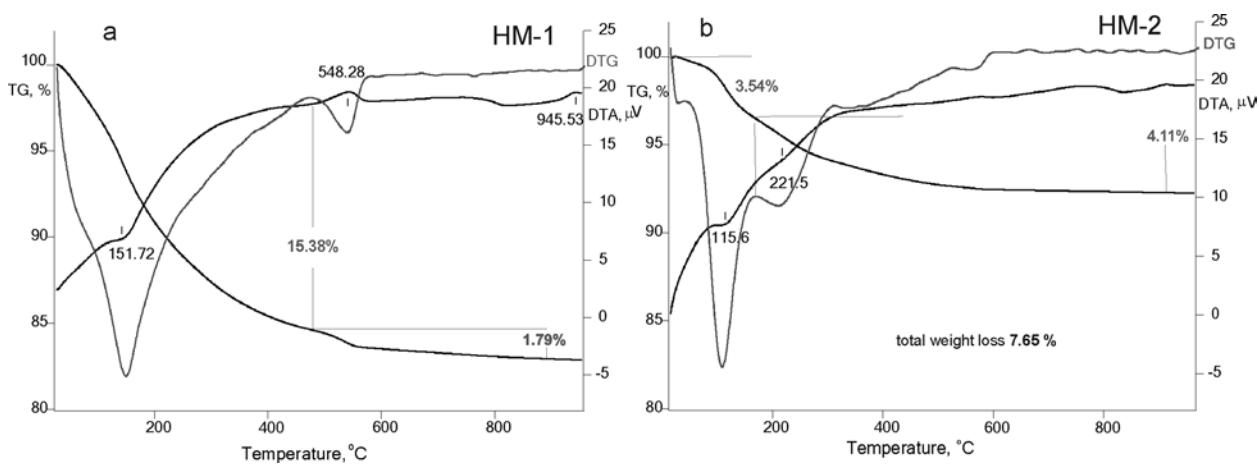
tively - a procedure, which will be described in details in the following section. Both structures were initially refined with soft constraints imposed on the Zr-O and Si-O bond distances and in the final refinement cycles they were released. In the case of HM-2 this did not cause substantial structural distortions before convergence achievement. However, unrealistic bond distances and angles were received for HM-1, whereas no substantial improvement of the statistical Rietveld parameters was achieved. Thus, only the results for the constrained structural refinement of HM-1 are presented, here. The bond restraints  $\chi^2$  contribution for each one of the 10 restraints inserted is 6.71. In addition, a small  $2\theta$  range from  $17.615$  to  $18.245^\circ$  has been excluded from the refinement of HM-1 due to the presence of a negligible amount of impurity phase. In both refinements: (i) all atoms in the structures were refined isotropically, (ii) expecting similar  $U_{\text{iso}}$  values for the O atoms these ones were refined in a group, (iii) neutral atomic scattering factors, as stored in GSAS, were used for all atoms, and (iv) no corrections were made for absorption.

## RESULTS

Figure 1 presents the powder XRD patterns of the as-synthesized  $\text{Na}_2\text{ZrSi}_2\text{O}_7\cdot\text{H}_2\text{O}$  and the two acid-treated samples together with the final difference plot of the XRD Rietveld refinement. Results from DTA-TG analyses of the investigated materials are shown in Figure 2. The 1.79% weight loss after  $500^\circ\text{C}$  (Fig. 2a) is assumed to be due to decomposition of some nitrogen-containing products. Whereas water liberates HM-1 within a single stage, two distinct stages of water release are detected for HM-2, most probably being due to the interrelation peculiarities of the sodium cations and  $\text{H}_2\text{O}$  molecules. Based on the chemical analyses and assuming that weight losses in the temperature range of  $100$ – $500^\circ\text{C}$  are being totally due to water release the following empirical formulas have been calculated:  $\text{H}_2\text{ZrSi}_2\text{O}_7\cdot 2.6\text{H}_2\text{O}$  for HM-1 and  $\text{H}_{0.5}\text{Na}_{1.5}\text{ZrSi}_2\text{O}_7\cdot 1.4\text{H}_2\text{O}$  for HM-2, respectively. Further on, taking into consideration the crystallographic position peculiarities of sodium atoms in the initial phase and assuming that Na from the general position ( $\text{Na}_g$ ) is more susceptible to the protonation process than the structurally more "hidden" Na from the special position ( $\text{Na}_p$ ) occupying the cavities attached to the structural layers we have suggested the following formula for HM-2:  $\text{H}_{0.5}\text{Na}_{g0.5}\text{Na}_p\text{ZrSi}_2\text{O}_7\cdot 1.4\text{H}_2\text{O}$ . Initially, no other crystallographic position has been suggested for the excessive water in this structure. As for the totally protonated HM-1 we have assumed three crystallographically distinct positions for the  $\text{H}_2\text{O}$



**Fig. 1.** Powder XRD patterns of: a) as-synthesized  $\text{Na}_2\text{ZrSi}_2\text{O}_7 \cdot \text{H}_2\text{O}$ ; b) HM-1; c) HM-2; The difference (bottom line) of the observed (crosses) vs. calculated (continuous line) profiles for each sample after the final XRD Rietveld refinement are plotted below each pattern



**Fig. 2.** TG-DTA curves of: a) HM-1 and b) HM-2

molecules: first of them coinciding with that one of the water in the structure of the as-synthesized compound, and the other two have been placed in the positions of  $\text{Na}_p$  and  $\text{Na}_g$ , respectively. Namely these considerations have been used to prepare the structural models of both acid-treated phases for the Rietveld procedure. In the final stages of the structure refinements structural positions and occupancies of the two sodium atoms in the partially protonated HM-2 and the same for the water molecules in both phases have been refined. In contrast to the completely protonated phase an unrealistic excess of water has been established for HM-2. Then we inserted additional  $\text{H}_2\text{O}$  molecule ( $\text{Ow}_g$ ) there and constrained its coordinates and occupancy with those ones of  $\text{Na}_g$  taken from the structure of the as-synthesized compound. The subsequent refine-

ment of atomic coordinates and occupancies of the extra-framework species completed with a structural model, which crystal chemistry stays very close to our notion about the occurring changes and the mechanism of protonation. The resulting compositions are in perfect agreement with the obtained chemical analyses. The final crystallographic and Rietveld parameters for the studied compounds are listed in Table 1. The crystal structures of the initial and the protonated samples are presented in Fig. 3.

## DISCUSSION

As seen from Figure 3 the investigated material preserves its framework topology despite the intensity of the applied treatment. As it was pointed out

**Table 1.** Crystallographic data and results of the Rietveld refinement of  $\text{Na}_2\text{ZrSi}_2\text{O}_7 \cdot \text{H}_2\text{O}$

	Reference [4]	HM-2 this study	HM-1 this study
Space group	$C2/c$	$C2/c$	$C2/c$
Cell parameters:			
$a$ (Å)	5.4715(4)	5.4552(6)	5.4227(7)
$b$ (Å)	9.4111(6)	9.6215(13)	9.4160(27)
$c$ (Å)	13.0969(8)	13.0505(19)	12.9418(21)
$\alpha$	90.0000	90.0000	90.0000
angles (°) $\beta$	92.851(7)	89.519(9)	89.872(3)
$\gamma$	90.0000	90.0000	90.0000
$V$ (Å <sup>3</sup> )	673.56(7)	684.9(2)	660.8(3)
Empirical formula	$\text{Na}_2\text{ZrSi}_2\text{O}_7 \cdot (\text{H}_2\text{O})$	$\text{H}_{0.4}\text{Na}_{g0.6}\text{ZrSi}_2\text{O}_7 \cdot 1.4(\text{H}_2\text{O})$	$\text{H}_2\text{ZrSi}_2\text{O}_7 \cdot 2.5(\text{H}_2\text{O})$
Fw	1285.46	1276.98	1198.49
Z	4	4	4
$P_{\text{calc}}$ (g cm <sup>-3</sup> )	3.17	3.096	3.012
Wavelength (Å)	1.5419	1.5419	1.5419
$2\theta$ range (deg)	5–90	5–90	5–90
Step-scan increment			
(2 $\theta$ ), deg	0.01	0.015	0.015
Step-scan time, s	5	6	6
No of data points	4089	5665	5632
No of contributing reflections	514	594	583
No of structural parameters	29	43	33
No of profile parameters	7	5	5
Profile function	Pseudo-Voigt	Pseudo-Voigt	Pseudo-Voigt
$R_{\text{wp}}$	0.0914	0.1249	0.0911
$R_p$	0.0713	0.0962	0.0707
$R_F^2$	0.0207	0.1053	0.2132
$\chi^2$	4.33	2.6	1.468
Occupancies of extra-framework species:			
$\text{Na}_g$		0.29	–
$\text{Na}_p$		1	–
$\text{Ow}$		0.52	0.49
$\text{Ow}_g$		0.21	0.49
$\text{Ow}_p$		–	0.55



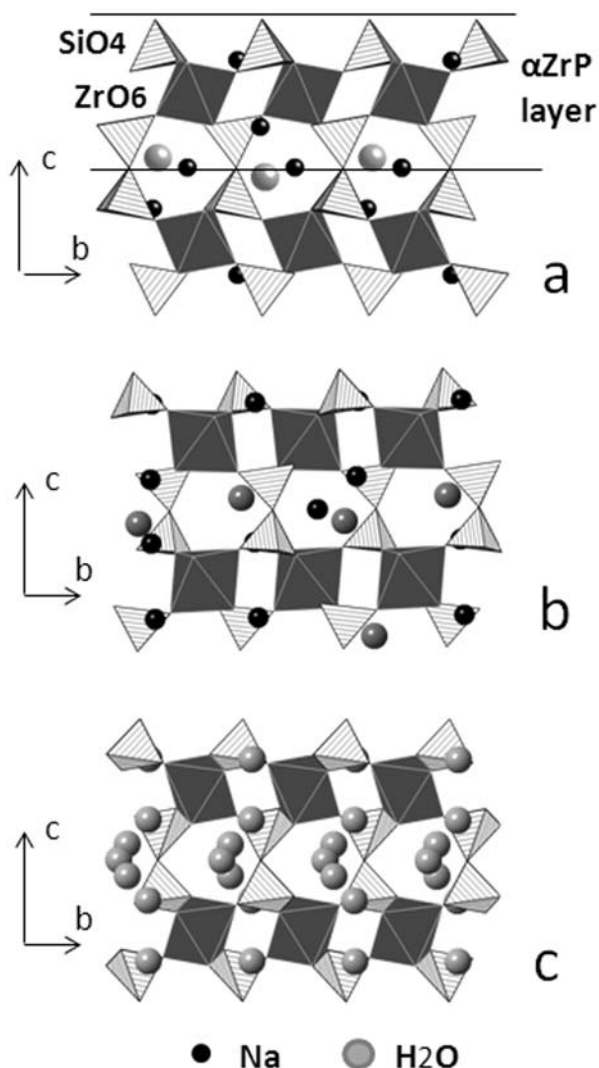


Fig. 3. Crystal structure of initial (a) and protonated samples HM-2 (b) and HM-1 (c)

earlier [4] such kind of framework is very flexible with respect to the exhibited geometrical features of the  $[\text{Si}_2\text{O}_7]$  pyrogroup. Its configuration can be described by two angles:  $\text{T-O-T}'$  ( $\tau$ ) angle corresponding to the tilting of the  $\text{TO}_4$  tetrahedra over the common oxygen atom and  $\text{O}_p\text{-T}_p\text{-O}_p'$  ( $\rho$ ) angle indicating the twisting of the triangular faces set by the terminal oxygen atoms (Fig. 4). Such approach was applied before to describe the degree of structural deformations occurring upon thermal treatment of the studied material [6]. Thus, we can now compare the values of the tilting and twisting angles for the as-synthesized compound with those ones obtained after its heating and/or protonation. As mentioned in the “Introduction” section water releasing upon heat treatment of the as-synthesized phase causes framework relaxation and the initially monoclinic

structure converts into an orthorhombic one without topological changes. The tilting and twisting angles for monoclinic and orthorhombic structures do not differ substantially and have values:  $\tau = 156.9^\circ$ ,  $\rho = 7.53^\circ$  and  $\tau = 145.07^\circ$ ,  $\rho = 0^\circ$ , respectively. Similar structural behavior has been observed for  $\text{Na}_2\text{ZrSi}_2\text{O}_7 \cdot \text{H}_2\text{O}$  upon its acid-treatment. The crystal structures of the protonated samples exhibit pseudo-orthorhombic symmetry with  $\beta = 89.51(1)$  and  $89.87(1)^\circ$  for HM-2 and HM-1, respectively. Cell volume increase from  $673.56 \text{ \AA}^3$  (as-synthesized phase) to  $684.9 \text{ \AA}^3$  (partially protonated sample) is observed when the reaction's media concentration has been adjusted to  $0.2 \text{ N HNO}_3$ . The successful refinement of the structure of HM-2 confirms our initial assumption that the “mid channel located” sodium ( $\text{Na}_m$ ) is more susceptible to the protonation process than the stronger bound to the framework oxygen atoms “cavity located” ( $\text{Na}_p$ ) one. Leaching would hardly be possible on Na atoms of special position before this process has been totally completed for sodium placed in general position. Attempts to refine the structure with partial decrease of  $\text{Na}_p$  occupancy or total elimination of this position failed. When all of the sodium ions are leached ( $c \approx 0.1 \text{ N HNO}_3$ ) from the structure the cell volume decreases to  $660.8(1) \text{ \AA}^3$ . These data suggest a two-stage protonation mechanism for the studied material that could be controlled through adjustment of the reaction's media pH. The values of  $\tau = 179.18^\circ$ ,  $\rho = 27^\circ$  and  $\tau = 152.37^\circ$ ,  $\rho = 22^\circ$  for HM-2 and HM-1 respectively confirm the enlargement of the framework channels during the first protonation stage and subsequent relaxation upon further protonation. The obtained values for the twisting angles of both protonated samples characterizing the mutual rotation of the adjacent layers differ substantially from those ones found in the initial and dehydrated samples

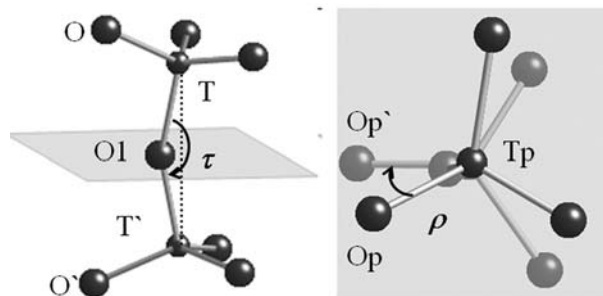


Fig. 4. Angles indicating the degree of pyrogroups deformation.  $\text{O}_p$ ,  $\text{O}_p'$  and  $\text{T}_p$  are projections of O, T, T' and O' on the plane perpendicular to T-T'

**Table 2.** Comparison of the values of the tilting and twisting angles of the as-synthesized compound and its dehydrated and protonated forms

Material	Tilting angle ( $\tau$ ) °	Twisting angle ( $\rho$ ) °
as-synthesized $\text{Na}_2\text{ZrSi}_2\text{O}_7 \cdot \text{H}_2\text{O}$	156.9	7.53
dehydrated $\text{Na}_2\text{ZrSi}_2\text{O}_7$	145.07	0
partially protonated HM-2	179.18	27
completely protonated HM-1	152.37	22

(Table 2). This suggests that protonation process causes higher degree of framework deformations as compared to the dehydration one. Although this process is accompanied with increase of the water content in the channels this could not compensate for the lack of “inner” stabilization caused by leaching of sodium from them.

## CONCLUSION

An experimental procedure for controlled protonation of a new small-pore microporous zirconosilicate is reported. The occurring compositional and structural changes have been studied and described by means of atomic absorption spectroscopy, TG-DTA, and Rietveld refinement routine. Two pH-dependent protonation stages of the  $\text{Na}_2\text{ZrSi}_2\text{O}_7 \cdot \text{H}_2\text{O}$  have clearly been defined. Crystal structures of the partially and completely protonated samples have been refined. Evaluation of the framework deformation in terms of tilting and twisting angles of the  $\text{Si}_2\text{O}_7$  groups has given evidence that the protonation process causes stronger deformations as compared to those ones occurring upon dehydration of the same structure. Apparently, sodium leaching deprives the channels from their “inner” stabilization causing substantial mutual shifting of the neighboring build-

ing layers, however without changing the initial topology of this material.

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## ДВУСТАДИЙНО ПРОТОНИРАНЕ НА МИКРОПОРЕСТ ЦИРКОНОСИЛИКАТ $\text{Na}_2\text{ZrSi}_2\text{O}_7 \cdot \text{H}_2\text{O}$

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(Резюме)

Изследвани са кристалохимичните промени настъпващи в процеса на протониране на микропорестия цирконосиликат  $\text{Na}_2\text{ZrSi}_2\text{O}_7 \cdot \text{H}_2\text{O}$ . Показано е, че степента на киселинност на първоначалния разтвор влияе върху степента на излужване на натрия от пробата. Уточнени са кристалните структури на частично и напълно протонирани проби и получените данни са сравнени с аналогичните за изходната фаза. В процеса на протониране кристалната структура запазва своята топология, но се наблюдава взаимно завъртане на съседните слоеве, което рефлектира съответно в промяна на параметрите на елементарна клетка. В първия етап обемът на елементарна клетка се увеличава от  $673.56 \text{ \AA}^3$  (синтезирана фаза) до  $684.9 \text{ \AA}^3$  (частично протонирана фаза) а при втория намалява до  $660.8(1) \text{ \AA}^3$  (напълно протонирана фаза). Доказано е, че в процеса на протониране, кристалната структура релаксира до псевдо-орторомбична със стойности за ъгъл  $\beta = 89.519(9)^\circ$  и  $89.872(3)^\circ$  съответно за частично и напълно протонираната фаза. Данните показват, че процесът на протониране води до по-значителни промени в кристалната структура от процеса на дехидратация на изследвания материал.