

Elastic behavior of the titanosilicate framework in Mn-ETS-4

L. Tsvetanova^{1*}, V. Kostov-Kytn¹, S. Ferdov², R. Nikolova¹

¹ Bulgarian Academy of Sciences, Institute of Mineralogy and Crystallography “Acad. Ivan Kostov”,
1113 Sofia, Akad. G. Bonchev Str., bl. 107, Bulgaria

² Department of Physics, University of Minho, 4800-058 Guimarães, Portugal

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Microporous titanosilicate Na-K-ETS-4 has been synthesized and subsequently exchanged on Mn²⁺. The crystal structures of the as-synthesized and the exchanged forms have been analyzed by single crystal X-ray diffraction at 290 K and 150 K, correspondingly. The elasticity and stability of the titanosilicate framework have been investigated as important characteristics of the studied material with impact on its ion-exchange and sorption properties. The obtained results reveal that the crystal structure of ETS-4 is stable at temperatures of 150 K and well adapts to the new conditions through non-destructive, mutually compensating each other deformations of the pores and the channel systems within the titanosilicate framework. The exchange on Mn²⁺ ions affects the degree of structural deformation at low temperature conditions.

Keywords: synthetic zeolites, crystal structure, low temperature studies.

INTRODUCTION

ETS-4 (Engelhard titanium silicate – 4) is a microporous titanosilicate built up of silicon tetrahedra and titanium octahedra which interconnect in a way to produce a framework structure with an electronegative charge. This charge is compensated by positively charged ions residing in the cavities of the channel systems within the framework. Three types of channel systems have been formed as two of them run along the [010] direction being constructed by 6- and 8-membered rings, correspondingly. The third channel built by 7-membered rings is parallel to the [001] (Fig. 1) [1].

The position of the cations in the cavities and the channel systems depends on their ionic radius, the charge, the physico-chemical exchange conditions, etc. The 6-membered ring is inhabited by ions with a smaller ionic radius generally presented by e.g. Na⁺, Mg²⁺, Ni²⁺. The occupancy of this position is predominantly about 50% and varies from 16 to 85%. Compensating cations of bigger ionic radius such as Ag⁺, Cs⁺, Sr²⁺, Ba²⁺, Y³⁺, Mn²⁺, Cu²⁺ and Zn²⁺ are localized within the channels built by 7-membered rings as the occupancy in this position according to the published results is about 75% but

also varies widely (10 to 84%) [2–8]. The channels formed by 8-membered rings typically contain a different number of water molecules as well as ions with a large ionic radius such as Cs⁺. The occupancy of the position is usually less than 50%. [2]. There is a trend according to which the exchange of divalent ions results in a more significant reduction of elemental cell volume and higher thermal stability, compared to monovalent ions exchange [1, 4, 5, 9, 10]. The high degree of elasticity of the titanosilicate framework of ETS-4 allows reversibility of the deformations occurring upon dehydration at temperatures below 250 °C [9]. This peculiarity provides opportunity for varying of the effective pore sizes of the studied material and subsequently for control of its sorption and separation properties [9–12].

Our studies are aimed at assessing the elasticity of ETS-4 titanosilicate framework by comparing the results obtained by single crystal X-ray diffraction measurements on as-synthesized and Mn-exchanged form at 290 K (RT) and 150K (LT) and taking into consideration the fact that at low temperature conditions dehydration and consequently significant change in cell volume cannot be expected.

EXPERIMENTAL

The Na-K ETS-4 samples were prepared hydrothermally (sol-gel method) from a starting batch of

* To whom all correspondence should be sent:
E-mail: lilicvetanova79@abv.bg

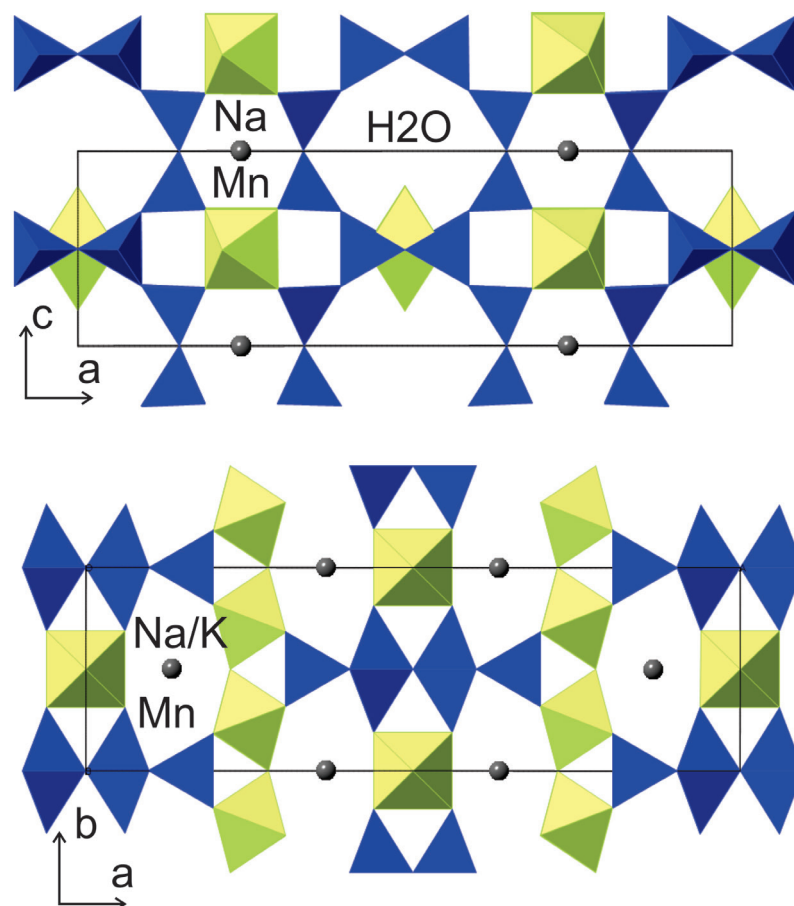


Fig. 1. Schematic representation of the ETS-4 structure.

the following molar composition: $5\text{Na}_2\text{O}-0.6\text{K}_2\text{O}-0.29\text{TiO}_2-5.4\text{SiO}_2-675\text{H}_2\text{O}$. The crystallization was performed under static conditions at 200°C and for 24 hours. The run products were cooled, the samples washed with distilled water and dried at room temperature [13].

The **Mn-ETS-4** samples were obtained by ion exchange from a 1M solution of MnCl_2 .

Single crystal X-ray diffraction (XRD)

Single crystals of **Na-K ETS-4** and **Mn ETS-4** have been investigated. Each of the samples has been measured at room temperature – 290 K (RT) and at 150 K (LT). The Mn exchanged sample has been additionally measured at room temperature after a two-month period of tempering and structure relaxation after the low-temperature experiment. Data collections were performed by ω -scan technique on an Agilent Diffraction SuperNova Dual four-circle diffractometer, equipped with Atlas CCD detector using mirror-monochromatized $\text{MoK}\alpha$ radiation from micro-focus source ($\lambda = 0.7107 \text{ \AA}$). During the LT data collection the sam-

ples were kept at 150 K with an Oxford Instruments Cobra controller device and in nitrogen atmosphere. The determination of unit cell parameters, data integration, scaling and absorption corrections were carried out using the CrysAlis Pro program package [14]. The structures were solved by direct methods (SHELXS-97/2013) and refined by full-matrix least-square procedures on F^2 (SHELXL-97/2013) [15]. The structure visualization was performed by Crystal Maker (version 2.6.2, SN2080) [16]. Further details of the crystal structure investigation may be obtained from Fachinformationszentrum Karlsruhe, 76344 Eggenstein-Leopoldshafen, Germany (fax: (+49)7247 808 666; e-mail: crysdata@fiz-karlsruhe.de, http://www.fizkarlsruhe.de/request_for_deposited_data.html on quoting the CSD-1880698, CSD-1881336, CSD-1881337.

RESULTS AND DISCUSSION

Crystal data and structure refinement parameters for Na-K-ETS-4 and Mn-ETS-4 samples measured at different temperature conditions are given in

Table 1.

Sample	Na-K-ETS-4		Mn-ETS-4	
	RT	LT	RT	LT
Chemical composition	$H_{2.36}K_{0.72}Na_{5.92}Si_{12}Ti_5O_{38}(OH) \times 11.28 H_2O$	$H_{2.38}K_{0.96}Na_{5.66}Si_{12}Ti_5O_{38}(OH) \times 11.04 H_2O$	$H_{0.08}Mn_{4.46}Si_{12}Ti_5O_{38}(OH) \times 8.73 H_2O$	$H_{0.44}Mn_{4.72}Si_{12}Ti_5O_{38}(OH) \times 8.42 H_2O$
Temperature (K)	RT	LT	RT	RT
Crystal system/ space group			Orthorhombic/ <i>Cmmm</i>	
unit cell (Å)				
a	23.226(2)	23.214(1)	23.13(1)	23.086(14)
b	7.2103(9)	7.1932(6)	7.182(2)	7.156(2)
c	6.9610(8)	6.9584(6)	6.884(3)	6.874(3)
Volume (Å ³)/Z	1165.7(2)	1161.9(1)	1143.4(8)	1135.7(9)
Dx [Mg m ⁻³] (Crystal density)	2.201	2.208	2.302	2.332
μ [mm ⁻¹]	1.381	1.404	2.452	2.457
Tmin – Tmax	0.1928 – 1.00	0.8942/1	0.887 – 1.000	0.486 – 1.000
Reflections collected	2614	2673	1581	1854
Independent reflections	847	844	601	591
Parameters	78	88	80	88
Final R indices ($I > 2\sigma(I)$)	$R_1 = 0.0772$ $wR_2 = 0.1703$	$R_1 = 0.0584$ $wR_2 =$	$R_1 = 0.0971$ $wR_2 = 0.2370$	$R_1 = 0.0873$ $wR_2 = 0.2239$
$\theta_{min} - \theta_{max}$	2.926/29.216	2.927/29.521	3.513 - 24.369	2.963 - 26.157
F_{000}	759	759	771	775
R indices (all data)	$R_1 = 0.1217$ $wR_2 = 0.2019$	$R_1 = 0.0875$ $wR_2 = 0.1575$	$R_1 = 0.1390$ $wR_2 = 0.2692$	$R_1 = 0.1465$ $wR_2 = 0.2764$
R_{int}	0.104	0.0913	0.0913	0.1219
Goodness-of-fit on F^2	1.085	1.113	1.051	0.949
				1.169
				$R_1 = 0.1238$ $wR_2 = 0.2900$
				3.529 - 23.338
				751
				$R_1 = 0.1967$ $wR_2 = 0.3467$
				0.1054

Table 1. Schematic presentation of the 6-, 7-, and 8-membered rings constructing the pores in the channel systems is given in Fig. 1.

Certain small deviations in the contents of compensating cations and water molecules have been noted for each of the studied ETS-4 forms during the refinement of their crystal structures at RT and LT, correspondingly. Whereas differences in the water molecules contents can be explained through partial dehydration, obtained during the nitrogen blowing procedure these differences for the compensating cations can only originate as a result of statistical error. Nevertheless, during the refinement we have not fixed the occupancies of the compensating ions positions because there is no criterion according to which to choose one of the experiments as more plausible than the other. The obtained results for the positions of the compensating ions and their occupancies are presented in Table 2. Both ETS-4 forms have their extra-framework cations residing within the 6- and the 7-membered rings, while the 8-membered ones contain only water molecules. The manganese ions replace the sodium and potassium ones as a result of the exchange procedure.

However, similarly to the as-synthesized material no full charge compensation has been achieved for the Mn-ETS-4 structure (Table 1). The occupancies of the compensating ions positions in the exchanged form are smaller than those observed for the (Na, K)-ETS-4, however being divalent the Mn that has entered the structure provides higher charge compensation (Table 1). During the low temperature experiments certain differences have been noted in the behavior of the extra-framework cations residing in the 7-membered rings. Although, no essential positional changes have been detected for the as-synthesized form, a shift has been registered for the manganese ions along the [001] direction and the new position has been preserved in the structure after its relaxation for a two-month period of tempering at room temperature. This fact suggests mobility of the Mn^{2+} ions facilitating optimal adaptation of the structure towards the occurring temperature changes. Similar mobility has been reported previously for thermally treated Sr-ETS-4 [9].

Selected interatomic distances, characterizing the titanosilicate framework flexibility are reported in Table 3. These data indicate that the variations of

Table 2. Atomic position of the charge compensation cations in the studied samples (RT – 270 K and LT – 150 K)

Sample	Atom name	RT			Occu-pancy	LT			Occu-pancy	RT			Occu-pancy
		x	y	z		x	y	z		x	y	z	
Na/K ETS-4	Na1	0.25	0.25	0.5	0.50(2)	0.25	0.25	0.5	0.49(1)	–	–	–	–
	Na/K	0.3631	0	0.7751	0.49	0.3634	0	0.7778	0.46	–	–	–	–
		0.3631	0	0.7751	0.09	0.3634	0	0.7778	0.12	–	–	–	–
Mn- ETS-4	Mn1	0.25	0.25	0	0.29(1)	0.25	0.25	0	0.26(1)	0.25	0.25	0	0.30(1)
	Mn2	0.3680	0	0.280	0.41(2)	0.375	0	0.252	0.32(5)	0.37	0	0.228	0.31(3)
	Mn3	–	–	–	–	0.3643	0	0.301	0.14(3)	0.3627	0	0.331	0.06(1)

Table 3. Framework interatomic distances (Å) the studied samples (RT – 270 K, LT – 150 K)

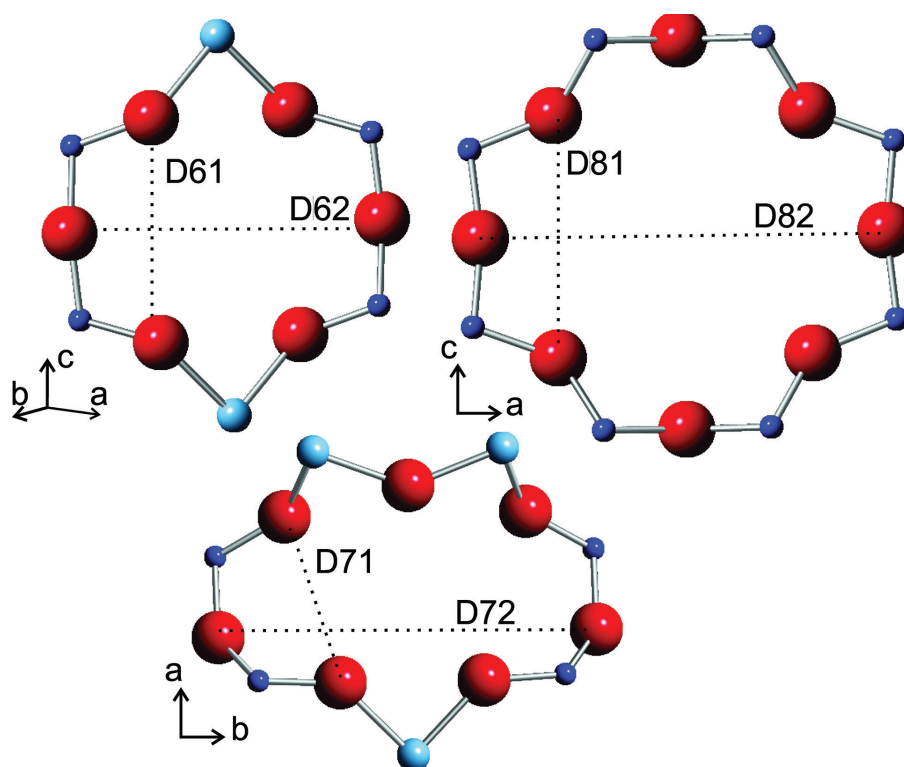
Bond length, Å	Na-K-ETS-4		Mn-ETS-4		
	RT	LT	RT	LT	RT
Si1–O1	1.615 (2)	1.615(2)	1.579 (4)	1.570 (4)	1.571 (3)
Si1–O2(x2)	1.607 (4)	1.610 (3)	1.580 (8)	1.576 (8)	1.582 (7)
Si1–O3	1.644 (6)	1.643 (4)	1.60(1)	1.60(1)	1.607 (9)
Si2–O3(x2)	1.656 (6)	1.656 (4)	1.66(1)	1.64(1)	1.66(1)
Si2–O4	1.635 (4)	1.636 (3)	1.624 (7)	1.639 (7)	1.633 (6)
Si2–O5	1.62(1)	1.61(1)	1.55 (2)	1.56 (2)	1.61 (2)
Mean Si–O	1.636 (6)	1.636 (7)	1.605 (8)	1.601 (8)	1.615(1)
Ti1–O2(x4)	1.965 (4)	1.963 (3)	1.962 (8)	1.968 (8)	1.949 (7)
Ti1–O6(x2)	1.935 (3)	1.931 (2)	1.920 (4)	1.919 (5)	1.935 (4)
Ti2–O5(x4)	1.96(1)	1.958 (9)	1.95 (2)	1.92 (2)	1.91 (2)
Ti2–O7(x2)	1.69 (4)	1.70 (3)	2.20 (10)	2.10 (8)	1.95(1)
	2.47 (4)	2.46 (3)	–	–	–
Mean Ti–O	2.00 (5)	2.00 (4)	1.99 (6)	1.97 (6)	1.93 (6)

Table 4. Interatomic distances (Å) defining the 6-, 7-, and 8-membered rings geometry (RT – 270 K, LT – 150 K)

	RT	LT	RT	RT	LT	RT
<i>6-membered ring</i>		D61			D62	
Na-K-ETS-4	2.809	2.804		4.366	4.374	
Mn-ETS-4	2.725	2.696	2.762	4.332	4.336	4.243
<i>7-membered ring</i>		D71			D72	
Na-K-ETS-4	2.175	2.179		5.86	5.843	
Mn-ETS-4	2.179	2.212	2.182	5.832	5.806	5.837
<i>8-membered ring</i>		D81			D82	
Na-K-ETS-4	2.977	2.97		5.827	5.9	
Mn-ETS-4	2.925	2.905	2.886	5.81	5.797	5.911

these parameters are wider for the exchanged form than for the as-synthesized sample. This is most likely due to the smaller atomic radius of manganese ions as compared to those of sodium and potassium, the lower occupancy of positions in the 6- and 7-membered rings and the smaller amount of water molecules. The recorded changes in the lengths of the interatomic distances correspond to the changes of the unit cell parameters, both after the ion exchange and in the low temperature conditions. The unit cell volume decreases by about 2% due to the ion exchange with manganese and up to 1% under the low temperature conditions, with Mn ETS-4

deformation being comparatively greater than that of the parent sample (Table 1). To investigate the degree and direction of deformation for the three channel systems, the distances between the oxygen atoms constituting the 6-, 7- and 8-membered rings have been measured. In Table 4, the longest and shortest distance values for each of the rings are presented and designated as in Figure 2. The figure also shows the directions of shrinkage and expanding of the rings. The size of the 6- and 8-membered rings decreases after the manganese ion exchange, the most significant being the change in direction [001] by about 6%, whereas the deformations at

**Fig. 2.** Schematic representation of ETS-4 framework channels. The distances shown on Table 4 are marked.

the 7-membered ring are insignificant and are carried out in the directions [100] and [010]. The low-temperature conditions influence differently the two tested samples. In the initial (Na, K)-ETS-4 no difference is observed for the distances at room and low temperature and the largest one is for D82 – 0.09 Å (Table 4). The Mn ETS-4 exhibits deformation of all rings, which is expressed in the extension of the ring in one direction and compensating it shrinkage in the other. The process is reversible and, when the temperature is recovered from low to room, there are opposite restoring changes in the size of the rings.

CONCLUSIONS

The ability of the ETS-4 titanosilicate framework to deform under the influence of various physicochemical effects (e.g. ion exchange, high temperature or pressure) is a subject of study by many authors. Knowing the directions and degree of deformation of the channel systems and the behavior of the compensating ions in these processes are important for the evaluation and control of the separating properties of the studied material.

The described results complement the already known facts about the behavior of ETS-4, namely how this material deforms in a low-temperature environment, and the influence of manganese ions on the extent of these deformations.

The structure of Na-K-ETS-4 has been shown to be less susceptible to deformation at 150 K than that one of Mn-ETS-4, mainly due to the lower occupancy of the compensating ion positions.

In the case of manganese samples, a mobility of the compensating ions from the 7- towards the 6-membered ring is observed and a relatively high degree of deformation is recorded in the 7-membered ring, correspondingly.

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