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Crystal structure of Ag^+ exchanged ETS-4 at room temperature and 150 K

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Single crystals of microporous titanosilicate Na-K-ETS-4 are synthesized and exchanged to Ag^+ form. Crystal structures of the as-synthesized and ion exchanged samples are analyzed by single crystal X-ray diffraction at room temperature and 150K. The material characterization is supplemented by SEM, DTA/TG-DTA, and powder XRD. Our studies show that Na^+ and K^+ ions are completely removed from the ETS-4 structure during the ion exchange procedure and the framework charge is almost entirely compensated by Ag^+ ions. The occurring structural deformations upon the applied ion exchange have been thoroughly analyzed. The low temperature measurements ensure precise determination of atomic positions and minimize the effects of atomic thermal vibration and positional disorder.

Key words: ETS-4, single crystal X-ray diffraction, low temperature experiment.

INTRODUCTION

ETS-4 (Engelhard titanium silicate-4) is a mixed tetrahedral-octahedral molecular sieve synthesized for the first time in 1990 [1]. Based on ^{29}Si MAS NMR analyses and powder XRD data it was assumed that ETS-4 structure is related to that of the mineral zorite [1–4]. Later on, many authors performed studies on ETS-4 structure in order to clarify the tetrahedral-octahedral arrangement of its "highly faulted framework" [5–7]. The conventional explanation of the ETS-4 structure was proposed by Braunbarth et al. in 2000 who described the framework as a superposition of four hypothetical polymorphs differing in the arrangement of the bridging units [6]. The first single crystal structure solvation was reported by Nair et al. in 2001 [7]. The common understanding for the ETS-4 structure is that it exhibits three-dimensional microporous framework built of silicon tetrahedra and titanium octahedra and semioctahedra. Within the framework there are three types of channels: **6**- and **8**-membered ones running parallel to **b** axis and **7-**membered one along **c** axis. It is interesting to note that each of the suggested theoretical polymorphs allows the existence of additional unbroken channels running along **c** axis built up of **12**-membered rings. Unfortunately, the superposition of the polymorphs within the structure precludes the formation of these potentially very interesting channels. The search of appropriate synthetic conditions for obtaining singular polymorphs still goes on. Anyway, the ETS-4 materials suppose good ion exchange properties, which have been extensively studied by many authors [8–17]. While the exchange capacity of monovalent Li^+, Na^+, K^+, Cs^+ and Ag^+ has been reported there is still lack of information concerning the positions of these ions within the ETS-4 channels [12–15]. Recently, we published results on the structural characterization of Cs^+ exchanged ETS-4 and the elastic behavior of the structure under ion exchange and low temperature conditions [16, 17].

Here we present results on the structure solution of Ag^+ exchanged ETS-4 and compare the flexibility of the framework before and after the ion exchange. Crystal structures of the as-synthesized and ion exchanged samples were analyzed by single crystal X-ray diffraction at room temperature (RT) and low temperature (LT) conditions. The material characterization has been performed by SEM, DTA/TG-DTA, and powder XRD.

EXPERIMENTAL

Sample preparation: The Na-K-ETS-4 samples were synthesized using the procedure described by Nikolova et all. [16]. In our synthesis, 5 g SiO_2 (Aldrich) were added to a solution of 6.3 g NaOH

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and 1 g KOH (Aldrich) in 150 ml distilled water. Subsequently, 0.5 ml $TiCl_4$ (Fluka) hydrolyzed in 40 ml distilled water was added to the above solution. The mixture was homogenized and transferred into Teflon-lined stainless autoclave. The crystallization was performed under static conditions at 200 °C for 24 h. The ion exchange was performed by immersing the as-synthesized ETS-4 in 1 M solutions of $AgCl_2$ (Aldrich) for 3 days at 80 °C. Finally, the samples were washed with distilled water and dried at room temperature.

SEM analysis of the single crystal samples was performed using a JEOL JSM 6390 scanning electron microscope. The technique was equipped with Oxford INCA Energy 350 – EDS. The device was connected to INCA Energy software for data processing. The data were collected at accelerating voltage 20kV and been current of 65 nA. 30 s of integration time were used to perform EDS analysis on single crystals of as-synthesized NaK ETS-4 and the Ag exchanged ETS-4 samples.

DTA/TG experiments were conducted by Setsys Evolution apparatus (SETERAM, France) in the temperature range from room temperature to 550 °C, in air environment. The rate of heating was 10 °C min^{-1}, and the weight of the measured samples was 10 mg.

Powder XRD experiments were carried on a diffractometer D2 PHASER AXS - Bruker, equipped with Bragg-Brentano horizontal goniometer (2θ) and scintillation counter using Ni-filtred CuKα radiation (λ = 1.5406 Å). The data were recorded at room temperature in the interval of 4–55° 2θ with a step at of 0.05 2θ and scanning time 1s.

Single-crystal X-ray diffraction data were collected for the as-synthesized Na-K-ETS-4 and Ag$^+$ exchanged samples. The same crystals were used for the RT and LT experiments. 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 MoKα radiation from micro-focus source (λ = 0.7107 Å). During the LT data collection the samples were kept at 150K 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 [18]. The structures were solved by direct methods (SHELXS-97/2013) [19] and refined by full-matrix least-square procedures on F^2 (SHELXL-97/2013) [19]. The structure visualization was performed by Crystal Maker (version 2.6.2, SN2080) [20]. 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-429019, 429026, 429027 and 429028. The structural data obtained at room and low temperature measurements and the structure refinement indicators for the studied compounds are presented in Table 1.

STRUCTURE SOLUTION

The crystal structures have been solved in an orthorhombic space group *Cmmm* and refined using similar procedure for all studied samples. Each of the Si and Ti atoms occupies two crystallographic positions marked as Si1, Si2 and Ti1 and Ti2, respectively. The superposition *Cmmm* model suggests that the framework atoms positions are of two types. First one belongs to the non-bridging units and should be refined as a fully occupied (in our structures Si1, Ti1 and the adjacent O atoms). The second type is of the bridging unit and should be refined with ½ occupancy (Si2, Ti2 and the adjacent O atoms). In addition, the Ti2 atom could lie on the (001) mirror plane and in that case will have exactly ½ occupancy. If Ti2 is slightly outside of the (001) mirror plane, as it has been reported by Nair et al. [7], its position and that of the corresponding oxygen atoms should be refined as ¼ occupied. Following the described conditions, first the atomic positions of the framework atoms with isotropic displacement parameters have been refined. Concerning the Ti2 position, both of the possible arrangements have been observed. In the as synthesized Na-K ETS-4 sample Ti2 lies at a distance of 0.06Å apart from the mirror plane, while in the Ag exchanged sample Ti2 is exactly on the mirror plane. That is why the Ti2 occupancy has been fixed as ¼ in the Na-K ETS-4 sample and ½ in the Ag ETS-4 one. After the refinement of the framework atoms the positions of compensating ions and water oxygens have been found from difference Fourier maps. Their occupancies have been refined simultaneously with the atomic coordinates and isotropic displacement parameters. Subsequently, a refinement of the anisotropic displacement parameters has been performed. The experimental data do not allow anisotropic refinement for all of the atoms. This is because of the disparity between the number of measurable intensities and the number of refinement parameters, which is due to the size and quality of the single crystal samples. For the as-synthesized Na-K-ETS-4 sample the water oxygens (O21, O22, O23) and O4 oxygen (part of the framework bridging unit) have been refined only isotropically at RT while the LT measurement allows refinement of the anisotropic displacement parameters for all of the atoms. In the case of Ag$^+$

Table. 1. Crystal data and structure refinement parameters for Na-K- ETS-4and Ag-ETS-4 samples measured at different temperature conditions – 290 K (RT) and 150 K (LT)

Samples	Na-K-ETS-4		Ag-ETS-4	
Temperature (K)	290	150	290	150
Space group	Cmmm	Cmmm	Cmmm	Cmmm
a (Å)	23.226(2)	23.2140(18)	23.252(2)	23.235(4)
b (Å)	7.2103(9)	7.1932(6)	7.2477(10)	7.2034(9)
c (Å)	6.9610(8)	6.9584(6)	6.9169(9)	6.9153(9)
V (Å^3)	1165.7(2)	1161.93(17)	1165.6(2)	1157.4(3)
Z	1	1	1	1
Dx [Mg m^{-3}]	2.201	2.208	2.832	2.821
μ [mm^{-1}]	1.381	1.404	3.634	3.587
Tmin–Tmax	0.1928/1	0.8942/1	0.716/1	0.5499/1
measured reflections	2614	2673	1639	1979
independent reflections	847	844	599	635
parameters	78	88	83	85
reflections with $I > 2\sigma(I)$	554	634	429	447
θmin–θmax	2.926/29.216	2.927/29.521	3.419/26.434	3.421/24.964
F000	759	759	943	933.4
T (K)	290	150	290	150
$R\ [F^2 > 2\sigma(F^2)]$	0.0772	0.0584	0.0746	0.0876
wR (F^2)	0.2019	0.1575	0.216	0.254
Rint	0.104	0.0539	0.0755	0.0805
S	1.085	1.113	1.073	1.298

exchanged sample water oxygens has been refined isotropically only for both the RT and LT experiments. The two very close to each other positions of water oxygens (O23 and O24) at RT conditions turn into one position at LT conditions. The chemical composition of the studied samples obtained after the structure refinement are presented in Table 2. The bond distances within the framework and the compensating cation coordination environment are summarized in Table 3 and Table 4, respectively.

RESULT AND DISCUSSION

The EDS analysis shows lower Si/Ti ratio than the expected one for the model framework (12/5). The Si deficiency differs from crystal to crystal and is found to be up to 10% for some of the exchanged samples. This is most likely due to the highly disordered framework of ETS-4. It should be noted that our analyses show chemical composition of isolated single crystals, while the published till now chemical compositions are based on ICP analyses of powder samples. For simplification of the structure refinement we use the ideal Si/Ti ratio of 12/5.

DTA /TG analysis were used for determination of the type and quantity of the water molecules. The results show three types of water molecules for the studied samples – one physisorption and two crystallization ones. The Ag$^+$ exchanged ETS-4 sample contains one water molecule less than the as-synthesized one.

Powder XRD analyses of the samples after DTA-TG analyses confirm that the ETS-4 structure has completely been destroyed upon heating it to 350 °C.

Table. 2. Chemical composition of Na-K- ETS-4 and Ag-ETS-4 samples calculated after the structure refinement

Sample	Data from structure refinement at 290 K (RT)	Data from structure refinement at 150 K (LT)
Na-K-ETS-4 – as synthesized	$Na_{5.92}K_{0.72}H_{2.36}Si_{12}Ti_5O_{38}(OH)$ x 11.28 H_2O	$Na_{5.66}K_{0.96}\ H_{2.38}Si_{12}Ti_5\ O_{38}(OH)$ x 11.04 H_2O
Ag-ETS-4 – ion exchanged	$Ag_{5.83}H_{3.17}Si_{12}Ti_5O_{38}(OH)$ x 9.92 H_2O	$Ag_{.5.68}\ H_{3.32}Si_{12}Ti_5O_{38}(OH)$ x 9.55 H_2O

Table 3. Framework interatomic distances (Å) for Na-K- ETS-4 and Ag- ETS-4 samples

Bond length	Na-K-ETS-4 290 K (RT)	Na-K-ETS-4 150 K(LT)	Ag-ETS-4 290 K (RT)	Ag-ETS-4 150 K(LT)
Si1-O1	1.615(2)	1.615(19)	1.612(3)	1.6110(3)
Si1-O2(x2)	1.607(4)	1.610(3)	1.596(6)	1.603(7)
Si1-O3	1.644(6)	1.643(4)	1.620(8)	1.613(10)
Si2-O3(x2)	1.656(6)	1.656(4)	1.649(9)	1.654(10)
Si2-O4	1.635(4)	1.636(3)	1.627(5)	1.608(7)
Si2-O5	1.621(13)	1.611(10)	1.57(3)	1.62(3)
Mean Si-O	1.63(6)	1.63(7)	1.61(6)	1.62(7)
Ti1-O2(x4)	1.965(4)	1.963(3)	1.964(6)	1.9587(7)
Ti1-O6(x2)	1.935(3)	1.931(2)	1.943(4)	1.925(5)
Ti2-O5(x4)	1.964(11)	1.958(9)	1.93(2)	1.87(3)
Ti2-O7	1.69(4)	1.70(3)	2.01(4)(x4)	2.05(5)(x4)
	2.47(4)	2.46(3)		
Mean Ti-O	2.00(5)	2.00(4)	1.96(4)	1.95(5)

Table 4. Selected bond lengths (Å) for Na-K-ETS-4 and Ag-ETS-4 samples

Na-K-ETS-4	Distance 290 K (RT)	Distance 150 K (LT)	Ag-ETS-4	Distance 290 K (RT)	Distance 150 K (LT)
Na1 – O21(x2)	2.429(13)	2.423(11)	Ag1 – O22	2.59(9)	2.38(3)
Na1 – O1(x2)	2.859(6)	2.862(5)	Ag1 – O24	2.13(5)	–
Na1 – O2(x4)	2.495(4)	2.490(3)	Ag1 – O2(x2)	2.669(6)(x1)	2.661(7)
			Ag1 – O5(x2)	2.68(2)(x1)	2.62(19)
Na2/K – O21(x2)	2.539(14)	2.576(12)	Ag1 – O6	2.40(10)	2.380(13)
Na2/K – O22(x2)	2.46(2)	2.447(17)	Ag1 – O7	2.61(4)	2.55(5)
Na2/K – O2(x2)	2.626(6)	2.619(5)			
Na2/K – O5(x2)	2.693(14)	2.682(11)	Ag2 – O22	2.60(9)	2.89(5)
Na2/K – O6	2.479(11)	2.472(8)	Ag2 – O24	2.24(14)	–
			Ag2 – O1	2.872(9)	2.857(10)
			Ag2 – O2(x4)	2.419(7)(x2)	2.393(7)
				2.656(6)(x2)	2.635(7)
			Ag3 – O2(x2)	2.526(12)	2.520(9)
			Ag3 – O6	2.523(25)	2.569(16)

IMPACT OF THE ION EXCHANGE AND LOW TEMPERATURE CONDITIONS ON FRAMEWORK

The elastic properties of ETS-4 structure are manifested by the variations of the unit cell parameters upon ion exchange and upon applying low temperature conditions. The structural parameters of the studied compounds are compared with the previously reported results for Cs^+ exchanged ETS-4 in order to check how the ionic radii and amount of the compensating ions influence the elasticity [17] (Table 5). The results show that in contrast to Cs^+ the Ag^+ exchange does not cause increase of the unit cell volume of ETS-4, most probably because of the smaller size of Ag^+ cations (ionic radius of Cs^+ – 1.85Å and Ag^+ – 1.22Å). The LT conditions cause structure contraction being more pronounced for the ion exchanged forms than for the as-synthesized one. The framework topology remains stable and only some of the atomic positions are slightly shifted in order to adapt the topology to the temperature conditions (Table 3.) It should be noted that the position of the Ti2 atom remains the same at RT and LT conditions for both of the studied samples. Such a behavior was reported for Mg^{2+} and Cs^+ exchanged forms, but not for the Ba^{2+} exchanged one, where LT conditions shift the Ti2 atom from outside the mirror plane to exactly the plane itself [16, 17]. It will be interesting to provide more detailed study

Table 5. Unit cell parameters (Å) and volume (Å^3) of Na–K-ETS-4, Ag-ETS-4 and Cs-ETS-4 [ ] samples

Sample	Ionic radii of charge compensating ion [Å]	Unit cell parameters 290 K (RT)	Unit cell parameters 150 K (LT)	Volume 290 K (RT)	Volume 150 K (LT)
Na–K-ETS-4	1.12/1.38	a = 23.226(2) b = 7.210(9) c = 6.961(8)	a = 23.214(9) b = 7.193(6) c = 6.958(6)	1165.7(2)	1161.9(8)
Ag-ETS-4	1.22	a = 23.252(2) b = 7.247(9) c = 6.9169(9)	a = 23.235(4) b = 7.203(9) c = 6.915(9)	1165.6(2)	1157.4(3)
Cs-ETS-4	1.85	a = 23.214(10) b = 7.258(2) c = 6.9416(19)	a = 23.123(2) b = 7.213(4) c = 6.930(3)	1169.6(7)	1156.9(2)

on how the ion exchange and different temperature or pressure conditions influence the Ti2 position in the structure, because exactly the Ti2 position was one of the reasons for Nair et al. to propose five coordinated environment of this atom [7]. According to our results the Ti2 position is more appropriate to expect both five and six coordinated titanium in the bridging part. Moreover, the refinement of the O7 position (oxygen connected only to Ti2 atom) occupancy indicates that almost half of the Ti2 atoms should be six coordinated.

The framework structure of ETS-4 is presented on Figure 1. The channel systems are built by 6-, 7- and 8-membered rings and are marked as A1 (mixed

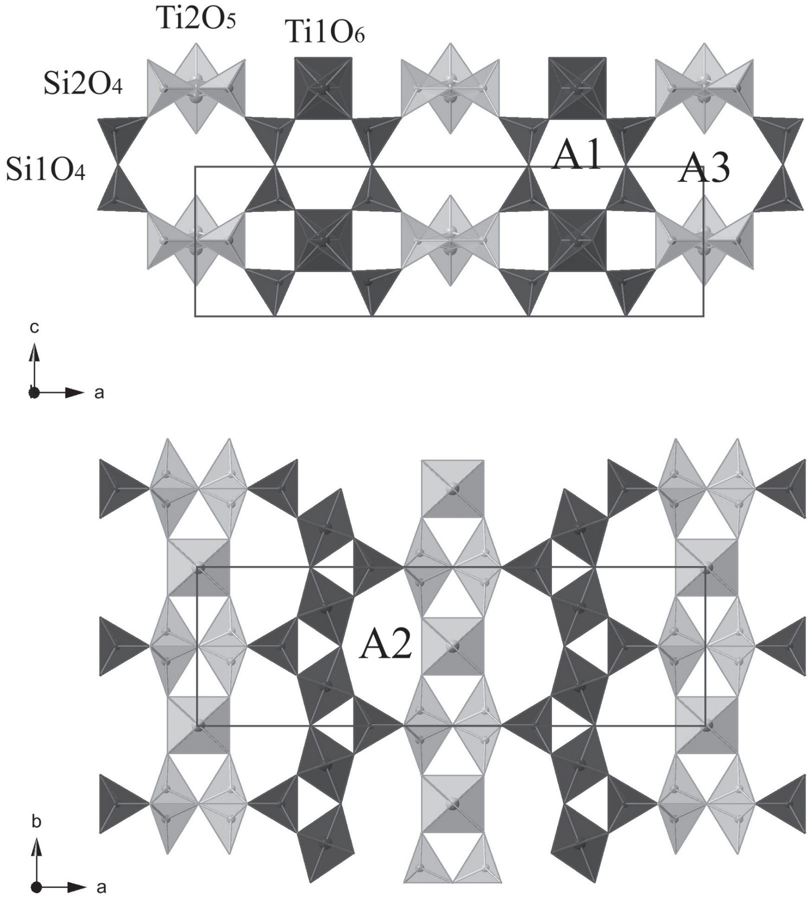

Fig. 1. Model of ETS-4 framework showing the channel systems: a) in direction [010] and b) in direction [001]. The six, seven and eight-membered ring channels are marked as A1, A2, and A3, respectively. The Ti1O$_6$ and Si1O$_4$ polyhedrons are dark grey colored. The Ti2O$_5$ and Si2O$_4$ bridging units are light grey colored.

terahedra-octahedra 6-membered rings), A2 (mixed tetrahedra-octahedra-semioctahedra 7-membered rings) and A3 (8-membered rings only tetrahedra), respectively. The structure refinement of the Ag^+ exchanged form shows that all of the Na^+ and K^+ ions are released from the structure during the ion exchange procedure. This is also confirmed by the chemical composition based on EDS analysis. The framework charge is entirely compensated by Ag^+ ions, which occupy three crystallographically non-equivalent positions – one within A1 channel and two within the A2 one. Refinement of the occupancy of the exchangeable cations positions shows that the Ag^+ ions in A1 channel are less than the released Na^+ ions, while Ag^+ ions in A2 channel have almost the same quantity as the sum of K^+ and Na^+ ions released during the ion exchange procedure. The A3 channel is occupied only by water molecules similarly to the as-synthesized sample. The coordination spheres of the charge compensating ions are built of framework oxygens and water molecules (Table 3). The polyhedra within the ion exchanged sample are more irregular and distorted comparing to those in the as-synthesized sample.

CONCLUSIONS

The crystal structure of Ag^+ exchanged ETS-4 was solved using RT and LT single crystal diffraction data. The structure refinement showed that all of the Na^+ and K^+ ions are released from the ETS-4 structure during the Ag^+ ion exchange procedure and the framework charge is almost entirely compensated by Ag^+ ions. The Ag^+ exchange does not cause changes of the unit cell parameters of ETS-4. The LT conditions on the other side causes structure contraction of higher degree compared to that of the as- synthesized ETS-4 and the structure deformation affects mainly the bridging units of the framework.

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КРИСТАЛНА СТРУКТУРА НА Ag$^+$ ЙОНООБМЕНЕНИ МОНОКРИСТАЛИ НА ETS-4 ПРИ СТАЙНА (290 K) И НИСКА (150 K) ТЕМПЕРАТУРА

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(Резюме)

Синтезиран е микропорест титаносиликат Na-K-ETS-4 във вид на монокристали, които са обменени със Ag$^+$ йони. Кристалните структури на изходната и йонно-обменена форми са изследвани чрез монокристална рентгенова дифракция при стайна 290 K и ниска 150 K температура. За допълнителна характеристика на изследваните кристали са използвани методите: SEM, DTA/TG и прахова XRD. Изследването показва, че Na$^+$ и K$^+$ йони са напълно обменени от Ag$^+$ йони. Йонообменът и нискотемпературните условия водят до деформации в структурата на скелета, проявено в промяна на параметрите на елементарната клетка. Нискотемпературните изследвания позволяват по-прецизно уточняване на атомните параметри, минимизиране на ефекта на температурните трептения и позиционната неподреденост на атомите.