

Crystal structures of Cs⁺, Mg²⁺, Ba²⁺ ion exchanged ETS-4 at RT and 150 K

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Ion exchanged ETS-4 samples by Cs⁺, Mg²⁺, and Ba²⁺ cations were analyzed by single crystal X-ray diffraction at 150 K. Structural data obtained from low temperature (LT) experiment are compared with the room temperature (RT) ones obtained from the same samples. The study shows that the low temperature conditions ensure precise determination of atomic positions and minimize the effects of atomic thermal vibration and positional disorder.

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

INTRODUCTION

ETS-4 (*Engelhard* titanium silicate – 4) is a mixed tetrahedral-octahedral molecular sieve related to the mineral zorite [1–4]. Due to its highly disordered structure various studies aiming at elucidation of ETS-4 framework have been reported [5–7]. The first structural data providing evidence for the framework similarity between Na-ETS-4 and zorite have been published in 1996 [5]. Later reports described ETS-4 as an intergrowth of four hypothetical polymorphs which differ in the arrangement of part of the titano-silicate units [6]. The ETS-4 framework exhibits orthorhombic *Cmmm* symmetry and each of the Ti and Si atoms has two symmetrically independent positions. The Ti1 atom is six coordinated and takes part in –O–Ti–O– chains running parallel to [010]. In the [001] direction the chains are interconnected by Si1 tetrahedra to build layers parallel to (100). The layers are identical for all of the hypothetical polymorphs. The latter differ in the arrangement of the titano-silicate bridging units formed by Ti2 and Si2 polyhedra. The position of the Ti2 atom with respect to the mirror plane perpendicular to *c* axis is supposed to predetermine its coordination environment and has been of significant interest for most of the authors. In earlier structural studies based on powder diffraction data six-coordination environment was suggested for this atom as it was positioned exactly on the mirror plane. The coordination

octahedron is built of four oxygen atoms from four Si2O₄ tetrahedra and two oxygens (usually marked as O7) symmetrically related to each other with respect to the mirror plane where the Ti2 atom is positioned. [5–6]. Single crystal X-ray diffraction analysis of Na-ETS-4 and Sr-exchanged ETS-4 indicated that the Ti2 atom in the studied samples is situated close to but not on the mirror plane and as a consequence the Ti2 octahedron suffers some distortion expressed in terms of the Ti2–O7 distances (1.70 vs. 2.23 Å). The performed refinement of the Ti2 and O7 atoms occupancy gave evidence that Ti2 atom in the studied samples is five-coordinated [7]. However, interpretation of the Ti2 coordination is rather controversial because the low occupancy of the O7 ligand position in it can be due to various reasons e.g. structural defects *etc.* Recently the crystal structures of Cs⁺, Mg²⁺, and Ba²⁺ exchanged forms of as-synthesized Na-K-ETS-4 have been reported [8]. The performed single crystal analyses confirmed that Ti2 in the initial Na-K-ETS-4 is situated outside the mirror plane. It was also found that the incorporation of Cs⁺ and Mg²⁺ ions do not provoke significant distortion of the ETS-4 framework, but the Ti2 atom is shifted closer to the mirror plane. In contrast, Ba²⁺ inclusion in the pore system of ETS-4 causes substantial framework contraction, splitting of some of the positions of the framework atoms and shifting of the Ti2 atom to a position lying exactly on the mirror plane perpendicular to the *c* axis. It has been suggested that the coordination of the Ti2 atom remains the same in the Na-K-ETS-4 and its exchanged forms. This puts the question to what extent the position of the Ti2 atom with respect to the mirror plane, defines its coordination.

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The present study aims at structural investigation of the same Cs⁺, Mg²⁺, Ba²⁺ exchanged ETS-4 samples performed at low temperature in order to minimize the effects of atomic thermal vibration and positional disorder. The elastic behavior of the unit cell and the positions of the framework and extra-framework cations from room temperature (RT) and low temperature (LT) experiments are compared. The framework distortion, position and coordination of the Ti2 atom are also discussed.

EXPERIMENTAL

Single-crystal X-ray diffraction data have been collected at low temperature conditions using the same single crystal samples of Cs⁺, Mg²⁺, Ba²⁺ exchanged ETS-4 for which RT experimental data have been published in [8]. LT (150 K) data collection was performed by ω -scan technique, on an Agilent Diffraction SuperNova Dual four-circle diffractometer equipped with Atlas CCD detector using mirror-monochromatized MoK α radiation from micro-focus source ($\lambda = 0.7107 \text{ \AA}$). During the low temperature data collection the samples were kept

at 150 K with an Oxford Instruments Cobra controller device and a nitrogen atmosphere. The determination of cell parameters, data integration, scaling and absorption corrections were carried out using the CrysAlis Pro program package [9]. The structures were solved by direct methods (SHELXS-97) [10] and refined by full-matrix least-square procedures on F^2 (SHELXL-97) [10]. 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-425730, 425731. The crystal data obtained by the low temperature experiment and the structure refinement indicators for the studied compounds are presented in Table 1.

RESULTS AND DISCUSSION

Chemical composition of the studied Cs- Mg- Ba-ETS-4 samples obtained after the data refinement for RT and LT experiments are presented in Table 2. The discrepancies in the calculated chemi-

Table 1. LT crystal data and structure refinement indicators for Cs- Mg- Ba-ETS-4

Sample	Cs-ETS-4	Mg-ETS-4	Ba-ETS-4
Space group	Cmmm	Cmmm	Cmmm
a (Å)	23.123(2)	23.198(4)	22.939(3)
b (Å)	7.213(4)	7.177(2)	7.169(3)
c (Å)	6.930(3)	6.948(2)	6.721(2)
V (Å ³)	1156.9(2)	1157.0(1)	1105.5(5)
Z	1	1	1
D _x [Mg m ⁻³]	273.5	2.123	2.824
μ [mm ⁻¹]	4.42	1.54	5.16
T _{min} -T _{max}	0.261 – 1	0.916–1	none
measured reflections	2196	2212	2067
independent reflections	723	728	695
parameters	85	75	83
reflections with $I > 2\sigma(I)$	381	479	490
θ_{\min} - θ_{\max}	2.9°–28.3°	2.9°–28.3°	3.0°–28.2°
F ₀₀₀	648	728	874
T (K)	150(2)	150(2)	150(2)
$R[F^2 > 2\sigma(F^2)]$	0.113	0.077	0.083
wR(F ²)	0.332	0.212	0.222
R _{int}	0.186	0.088	0.086
S	1.105	1.08	1.04

Table 2. Chemical composition of Cs-, Mg-, Ba-ETS-4 calculated after the structure refinement

Compound	RT – structural data	LT – structural data
Cs-ETS-4	K _{1.18} Na _{1.20} Cs _{4.01} H _{2.61} Si ₁₂ Ti ₅ O ₃₈ (OH) × 7.12 H ₂ O	K _{0.86} Na _{1.12} Cs _{3.96} H _{3.06} Si ₁₂ Ti ₅ O ₃₈ (OH) × 7.36 H ₂ O
Mg-ETS-4	K _{2.63} Mg _{1.44} H _{3.49} Si ₁₂ Ti ₅ O ₃₈ (OH) × 7.92 H ₂ O	K _{2.81} Mg _{1.52} H _{3.15} Si ₁₂ Ti ₅ O ₃₈ (OH) × 8.24 H ₂ O
Ba-ETS-4	Ba _{4.31} H _{0.39} Si ₁₂ Ti ₅ O ₃₈ (OH) × 4.52 H ₂ O	Ba _{4.41} H _{0.18} Si ₁₂ Ti ₅ O ₃₈ (OH) × 4.6 H ₂ O

cal compositions for the RT and LT data are most probably due to statistical reasons of the experimental conditions used. It is also notable that there is no partial dehydration of the samples with N_2 gas flow – an effect observed by other authors performed LT experiments of water containing porous materials [11, 12].

A model obtained by superposition of the four hypothetical polymorphs models of the ETS-4 framework (see Introduction) is presented in Figure 1. The complex pore system of the presented framework includes three different kinds of channels. The six-membered-ring channel, where smaller ions as Na^+ and Mg^{2+} reside, is marked with A1. This channel is formed within the titano-silicate layer formed by Ti1O_6 and Si1O_4 polyhedra. The A2 channel is the one formed between the layer and the titanosilicate bridging units built by Ti2O_5 and Si2O_4 polyhedra. The channel consists of seven-membered rings and is occupied by bigger cations. In the studied samples K^+ , Ba^{2+} or Cs^+ ions are situated there. The eight-membered ring made by four Si1O_4 and four Si2O_4 tetrahedra is marked as A3. It has been found that water molecules and Cs^+ ions reside in the channels formed by the eight-membered rings and running parallel to [010]. It should be noted that the accessibility of A2 and A3 channels depends on

the orientation of the titano-silicate bridging units formed by the Ti2O_5 and Si2O_4 polyhedra.

Unit cell behavior at LT conditions

The unit cell parameters variation of the studied samples as a function of the cation exchange and low temperature conditions are shown in Figure 2. The elastic behavior of ETS-4 structure is studied by comparing the unit cell parameters in the following order: Na-K-ETS-4 → ETS-4 exchanged samples at RT → ETS-4 exchanged samples at LT. The ion exchange by Cs^+ and Mg^{2+} do not cause significant changes of the ETS-4 unit cell volume. The unit cell parameters of the initial Na-K-ETS-4 and the exchanged samples at RT are almost the same. Interestingly the unit cell volume of ETS-4 decrease by 60 \AA^3 after the ion exchange of Na-K-ETS-4 by Ba^{2+} . This notable contraction observed at RT measurements is most probably due to the higher ionic potential of barium ion. The low temperature conditions affect differently the structural parameters of the ion exchanged samples. In the Ba-ETS-4 the compression capability of the ETS-4 structure is realized after the ion exchange and no additional contraction is possible with temperature lowering (Fig. 2). However a structural adjustment

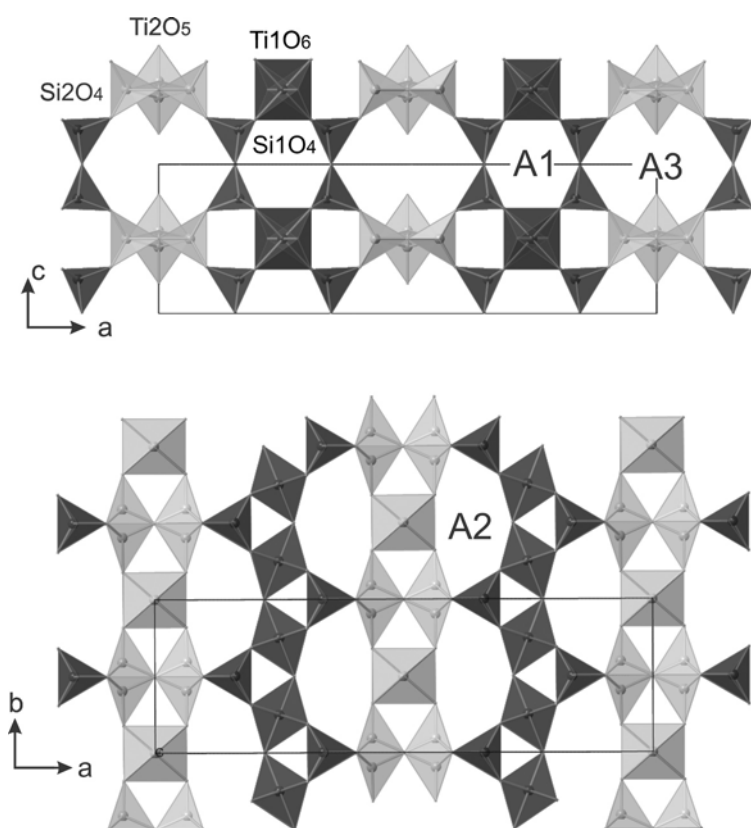


Fig. 1. Superposition model of the ETS-4 framework. The six, seven and eight – membered-ring channels are marked by letters as A1, A2 and A3 respectively. The Ti1O_6 and Si1O_4 polyhedra, building the layers are dark grey colored. The Ti2O_5 and Si2O_4 bridging units are marked by light grey color

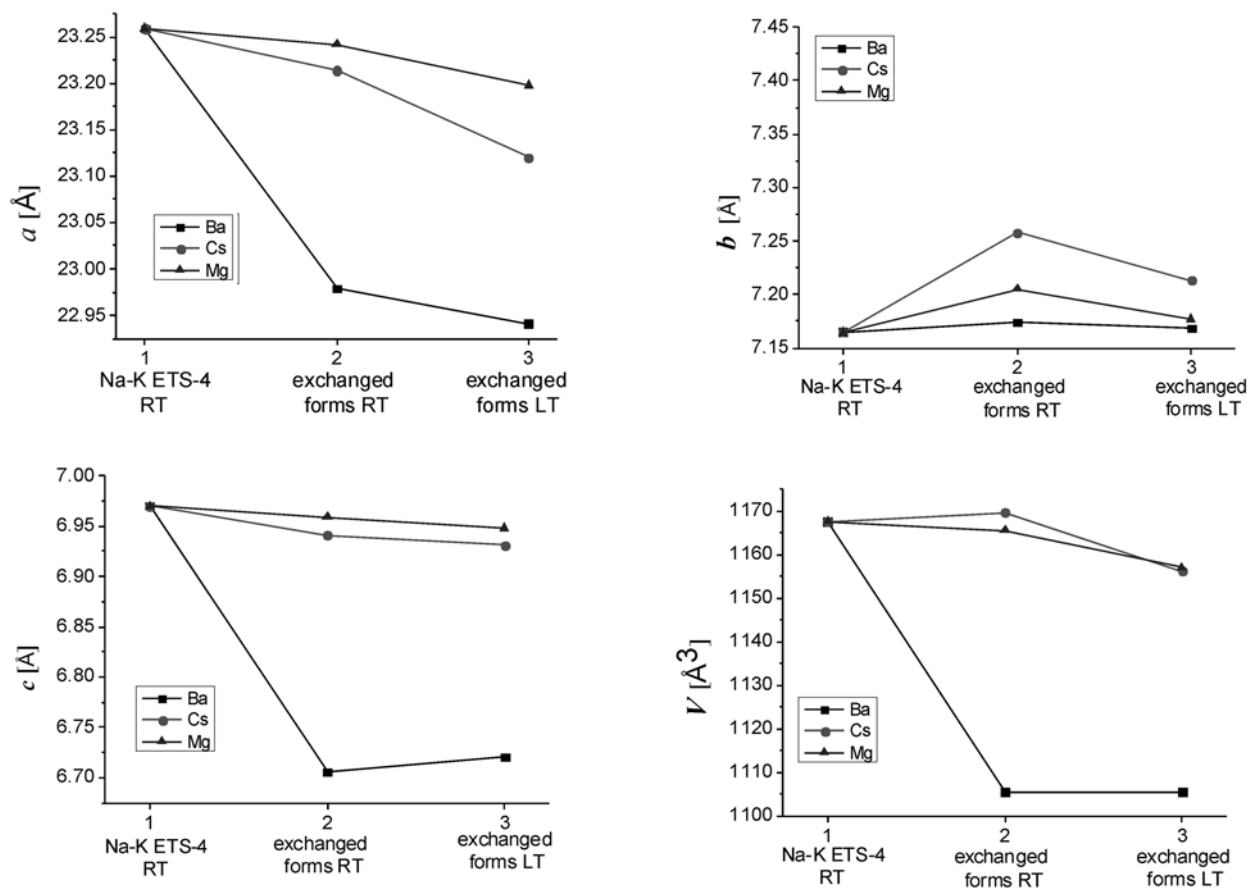


Fig. 2. Unit cell parameters of K-Na-ETS-4 and exchanged forms at RT and LT

to the LT conditions is realized by altering of the deformation directions. This process is expressed by slight increase of the c parameter compensated by decreasing of a and b parameters thus the cell volume remains the same. Although a lowering of the Cs- and Mg-ETS-4 volumes at LT conditions is observed these structures remain less compressed than that one of the Ba-ETS-4 one (Fig. 2).

Framework atoms position at LT conditions

The framework topology of the studied compounds remains stable but some of the fractional coordinates of the framework atoms shift from their positions found for RT experiments in order to adapt the structure to the low temperature conditions (Table 3). Thus the structures contraction accompanied by atom positions shifts influence the bond distances (Table 4) and angles in all the studied compounds.

In the Cs-ETS-4 sample all framework positions remain almost unchanged most probably because all of the channels are occupied by cations (A1 – Na^+ , A2 – K^+ and Cs^+ and A3 – Cs^+) and the coordination

bonding between the framework oxygens and the extra-framework cations stabilize the structure. The Mg-ETS-4 sample behaves similarly and the framework atoms remain at the same positions except the Ti2 one which shifts along the c axis to a position lying exactly on the mirror plane perpendicular to it (Table 3.). Such a shift of the Ti2 atom from general to a special position was reported for Ba-ETS-4 after the ion exchange and a possible change of the Ti2 coordination from five to six was previously suggested [8]. In the case of Mg-ETS-4 the shift of the Ti2 position is most probably due to readjustment of the framework occurring upon the LT conditions of the experiment. In the most distorted Ba-ETS-4 framework the atomic positions of Si1, Ti2 and most of the framework oxygen atoms remain unchanged. In this case the framework responds to the temperature lowering by a cooperative rotation of Si_2O_4 and Ti_1O_6 polyhedra. This is expressed by shift of the Si2 and Ti1 atoms from the special positions in [001] direction and split of the O1 and O2 atomic positions. In order to preserve the framework topology and chemical stoichiometry these new positions have been refined as half occupied.

Table 3. Atomic parameters of the studied compounds at RT and LT conditions

ETS sample	x (RT)	x (LT)	y (RT)	y (LT)	z (RT)	z (LT)	Occupancy (RT)	Occupancy (LT)	U _{eq} ² (RT)	U _{eq} ² (LT)
Cs ETS-4	0.337(2)	0.337(1)	0	0	0.230(2)	0.230(2)	1	1	0.0147(12)	0.0143(16)
Mg ETS-4	0.338(2)	0.338(1)	0	0	0.229(2)	0.230(2)	1	1	0.0144(6)	0.0090(7)
BaETS-4	0.337(2)	0.337(1)	0	0	0.228(2)	0.228(1)	1	1	0.0180(12)	0.0183(12)
Cs ETS-4	0.063(1)	0.064(1)	0.402(2)	0.406(1)	0.5	0.5	0.5	0.5	0.0139(19)	0.014(3)
Mg ETS-4	0.063(2)	0.063(1)	0.408(1)	0.407(1)	0.5	0.5	0.5	0.5	0.0161(11)	0.0113(11)
BaETS-4	0.064(1)	0.064(1)	0.410(2)	0.410(1)	0.5	0.5	0.5	0.25	0.055(5)	0.018(5)
Cs ETS-4	0.25	0.25	0.25	0.25	0.5	0.5	1	1	0.0197(12)	0.0159(16)
Mg ETS-4	0.25	0.25	0.25	0.25	0.5	0.5	1	1	0.0215(7)	0.0157(7)
BaETS-4	0.25	0.25	0.25	0.25	0.5	0.461(2)	1	0.5	0.0421(18)	0.0111(19)
Cs ETS-4	0	0	0	0	0.450(3)	0.460(3)	0.25	0.25	0.037(9)	0.06(5)
Mg ETS-4	0	0	0	0	0.468(3)	0.5	0.25	0.5	0.014(4)	0.034(2)
BaETS-4	0	0	0	0	0.5	0.5	0.5	0.5	0.021(3)	0.023(2)
Cs ETS-4	0.155(2)	0.155(2)	0.5	0.5	0	0	1	1	0.023(4)	0.020(5)
Mg ETS-4	0.154(2)	0.154(2)	0.5	0.5	0	0	1	1	0.032(3)	0.024(2)
BaETS-4	0.125(2)	0.127(2)	0	0.5	0	0	0.34(4)	0.48(4)	0.007(8)	0.042(12)
O12	0.187(1)	0.184(2)	0	0.5	0	0	0.32(4)	0.52(5)	0.007(8)	0.051(13)
O13	0.343(2)	–	0.074(8)	–	0	–	0.17(2)	–	0.007(8)	–
Cs ETS-4	0.305(1)	0.305(1)	0.184(2)	0.181(2)	0.299(2)	0.299(2)	1	1	0.026(2)	0.025(3)
Mg ETS-4	0.306(2)	0.305(1)	0.186(2)	0.185(3)	0.297(2)	0.298(3)	1	1	0.0250(12)	0.0183(12)
BaETS-4	0.304(2)	0.304(2)	0.180(1)	0.180(1)	0.291(2)	0.291(2)	1	–	0.11(2)	–
O21	0.310(2)	0.310(2)	0.183(2)	0.183(2)	0.350(3)	0.350(3)	0.44	0.44	0.013(5)	0.013(5)
O22	0.300(2)	0.300(2)	0.177(2)	0.177(2)	0.246(3)	0.246(3)	0.56	0.56	0.022(5)	0.022(5)
Cs ETS-4	0.404(2)	0.405(2)	0	0	0.309(1)	0.309(1)	1	1	0.037(3)	0.036(5)
Mg ETS-4	0.404(1)	0.404(2)	0	0	0.313(2)	0.311(1)	1	1	0.0327(19)	0.0240(17)
BaETS-4	0.402(2)	0.403(2)	0	0	0.309(3)	0.313(3)	1	1	0.065(6)	0.064(5)
Cs ETS-4	0	0	0.5	0.5	0.5	0.5	1	1	0.020(5)	0.016(6)
Mg ETS-4	0	0	0.5	0.5	0.5	0.5	1	1	0.018(3)	0.011(3)
BaETS-4	0	0	0.5	0.5	0.559(4)	0.44(1)	0.5	0.5	0.015(8)	0.010(5)
Cs ETS-4	0.058(1)	0.059(2)	0.184(4)	0.192(4)	0.5	0.5	0.5	0.5	0.039(7)	0.036(9)
Mg ETS-4	0.059(2)	0.059(2)	0.184(2)	0.185(2)	0.5	0.5	0.5	0.5	0.054(5)	0.060(7)
BaETS-4	0.060(1)	0.059(1)	0.187(4)	0.186(3)	0.5	0.5	0.5	0.5	0.069(10)	0.064(8)
Cs ETS-4	0.218(2)	0.220(1)	0	0	0.5	0.5	1	1	0.025(4)	0.016(4)
Mg ETS-4	0.220(2)	0.220(1)	0	0	0.5	0.5	1	1	0.0170(19)	0.0093(18)
BaETS-4	0.219(2)	0.219(2)	0	0	0.451(3)	0.452(2)	0.5	0.5	0.009(6)	0.007(4)
Cs ETS-4	0	0	0	0	0.185(3)	0.186(2)	0.25	0.25	0.25(14)	0.04(2)
Mg ETS-4	0	0	0	0	0.218(3)	0.216(2)	0.25	0.25	0.032(10)	0.036(11)
BaETS-4	0	0	0	0	0.215(2)	0.218(3)	0.25	0.25	0.034(17)	0.039(16)

Table 3 (continued)

ETS sample	x (RT)	x (LT)	y (RT)	y (LT)	z (RT)	z (LT)	Occupancy (RT)	Occupancy (LT)	U _{eq} ^{Å²} (RT)	U _{eq} ^{Å²} (LT)
Cs ETS-4	0.25	0.25	0.25?	0.25	0	0	0.30(4)	0.28(5)	0.031(5)	0.025(17)
Mg ETS-4	0.25	0.25	0.25	0.25	0	0	0.36(2)	0.38(2)	0.047(15)	0.033(6)
BaETS-4	–	–	–	–	–	–	–	–	–	–
Cs ETS-4	0.128(1)	0.131(3)	0	0	0.328(6)	0.668(5)	0.14(1)	0.10(2)	0.060(16)	0.004(12)
Mg ETS-4	0.134(2)	0.133(6)	0	0	0.260(3)	0.266(3)	0.32(2)	0.35(2)	0.113(8)	0.109(8)
BaETS-4	0.139(3)	0.138(1)	0	0	0.236(2)	0.237(1)	0.20(2)	0.21(1)	0.014(3)	0.017(3)
	0.116(3)	0.116(1)	0	0	0.333(7)	0.340(5)	0.08(1)	0.07(1)	0.038(10)	0.028(7)
Cs ETS-4	0	0	0.387(9)	0.440(4)	0	0	0.89(6)	0.15(9)	0.076(2)	0.05(7)
Cs3	0	0	0.361(1)	0.361(1)	0	0	0.22(14)	0.22(14)	0.045(8)	0.045(8)
Mg ETS-4	0	0.009(4)	0.337(5)	0.338(5)	0	0.170(2)	0.80(7)	0.50(3)	0.173(19)	0.17(2)
BaETS-4	0	0	0.374(8)	0.374(8)	0	0	0.49(2)	0.49(2)	0.11(2)	0.11(2)
	0	0	0.372(8)	0.372(8)	0	0	0.69(8)	0.69(8)	0.013(5)	0.013(5)
Cs ETS-4	0.086(5)	0.090(5)	0	0	0	0	0.43(4)	0.21(7)	0.13(6)	0.17(8)
Mg ETS-4	0.078(2)	0.084(2)	0.112(6)	0	0	0	0.23(5)	0.63(9)	0.17(4)	0.17(5)
BaETS-4	–	–	–	–	–	–	–	–	–	–
Cs ETS-4	0.190(2)	0.189(2)	0	0	0	0	0.51(2)	0.50(2)	0.0442(15)	0.0336(18)
Mg ETS-4	0.206(2)	0.206(2)	0	0	0	0	0.86(6)	0.85(6)	0.127(14)	0.123(15)
BaETS-4	0.200(1)	0.200(1)	0	0	0	0	0.50(2)	0.53(2)	0.0114(8)	0.0145(8)
Cs ETS-4	0.094(1)	0.095(2)	0	0	0.466(4)	0.5	0.58(4)	1	0.044(9)	0.053(10)
BaETS-4	0	0	0.173(5)	0.174(5)	0.272(6)	0.276(5)	0.23(4)	0.23(4)	0.008(14)	0.012(14)

Table 4. Framework interatomic distances (Å) for structure refinements at RT and LT

Bond length	Cs ETS-4 RT	Cs ETS-4 LT	Mg ETS-4 RT	Mg ETS-4 LT	Ba ETS – 4 RT	Ba ETS – 4 LT
Si1-O1	1.609(4)	1.605(6)	1.607(3)	1.605(3)	O11 1.761(19) O12 1.632(15) O13 1.63(2)	O11 1.725(16) O12 1.617(12)
Si1-O2 (x2)	1.605(8)	1.588(10)	1.603(5)	1.605(5)	1.555(10)	O21 1.669(15) O22 1.539(13)
Si1-O3	1.644(12)	1.648(16)	1.636(7)	1.626(7)	1.589(15)	1.603(14)
Si2-O3 (x2)	1.673(11)	1.652(15)	1.638(7)	1.648(7)	1.625(19)	1.84(2)
Si2-O4	1.640(9)	1.631(12)	1.620(5)	1.620(5)	1.660(11)	1.728(12)
Si2-O5	1.59(3)	1.54(3)	1.619(16)	1.598(15)	1.60(4)	1.63(3)
mean Si-O	1.63(1)	1.61(1)	1.62(1)	1.617	1.62(4)	1.66(8)
Ti1-O2 (x4)	1.952(8)	1.951(11)	1.961(5)	1.962(4)	1.949(12)	O21 1.651(14)(x2) O22 1.925(15)(x2)
Ti1-O6 (x2)	1.953(6)	1.932(7)	1.925(3)	1.924(3)	1.955(6)	1.930(5)
Ti2-O5 (x4)	1.94(3)	1.97(4)	1.927(15)	1.917(15)	1.93(4)	1.91(3)
Ti2-O7 (x2)	1.87(13)	1.9(2) 2.4(2)	1.74(4)	1.97(4)	O71 1.91(7) O23 1.97(4)	1.89(2)
mean Ti-O	1.93(1)	2.03(1)?	1.88(9)	1.94(3)	1.94(6)	1.86(1)

Extra-framework cations and water molecules positions at LT conditions

The extra-framework atoms positions remain almost unchanged at LT conditions for all of the studied samples. The LT structure refinements confirm a significant reduction of the thermal vibration effects of the extra-framework population, as shown by the magnitude of the thermal displacement ellipsoids at RT (290 K) and LT (150 K) in Table 3. Only in Cs-ETS-4 the Cs1 position splits into two ones – Cs1 and Cs3 thus allowing more isometric displacement ellipsoids to be obtained (Table 3).

CONCLUSIONS

The LT conditions enhance the structure contraction of Mg- and Cs-ETS-4, as the contraction potential of these structures is not fully realized during the ion exchange process. In Ba-ETS-4 the compression ability of the structure is manifested already upon the ion exchange procedure and the structure response to the LT conditions acts mainly through changing of the deformation direction. At 150 K the Cs- and Mg-ETS-4 structures remain less compressed than that one of the Ba-ETS-4.

The LT structure refinements confirm a significant reduction of the thermal vibration effects of the extra-framework population.

The flexibility of the ETS-4 framework is most pronounced for the titano-silicate bridging unit in-

cluding the T2O₅ and Si2O₄ polyhedra. Both ion exchange and temperature lowering shift the Ti2 atom to a position closer to or placed on the mirror plane, giving evidence that the position of the Ti2 atom with respect to the mirror plane does not define explicitly its coordination.

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КРИСТАЛНИ СТРУКТУРИ НА Cs⁺, Mg²⁺, Ba²⁺ ЙОННО ОБМЕНЕНИ
ОБРАЗЦИ НА ETS-4 ПРИ СТАЙНА (290 К)
И НИСКА ТЕМПЕРАТУРА (150 К)

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(Резюме)

Обменени с Cs⁺, Mg²⁺, and Ba²⁺ катиони образци от титано-силиката ETS-4 са изследвани чрез монокристален рентгеноструктурен анализ при температура от 150 К. Получените структурни данни са сравнени с тези от рентгеноструктурния анализ на същите образци при стайна температура 290 К. Получените резултати потвърждават, че нискотемпературните изследвания позволяват прецизно уточняване на атомните параметри и минимизиране на ефекта на температурните трептения и позиционната неопределеност на атомите.