Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

SUPPLEMENTARY INFORMATION

Sodium Insertion in $H_2Ti_3O_7$ for Na Ion Batteries

Aitor Eguía-Barrio[a,b] *, Elizabeth Castillo-Martínez* [a,*]*, Maider Zarrabeitia,*[a]

Miguel A. Muñoz-Márquez, [a] *, Montse Casas-Cabanas* [a,] *Teófilo Rojo* [a,b,*]

[a] CIC Energigune, C/Albert Einstein 48, 01510, Parque Tecnológico de Álava, Miñano, Spain.

[b] Departamento de Química Inorgánica, Universidad del País Vasco, UPV/EHU, Bilbao, Spain.

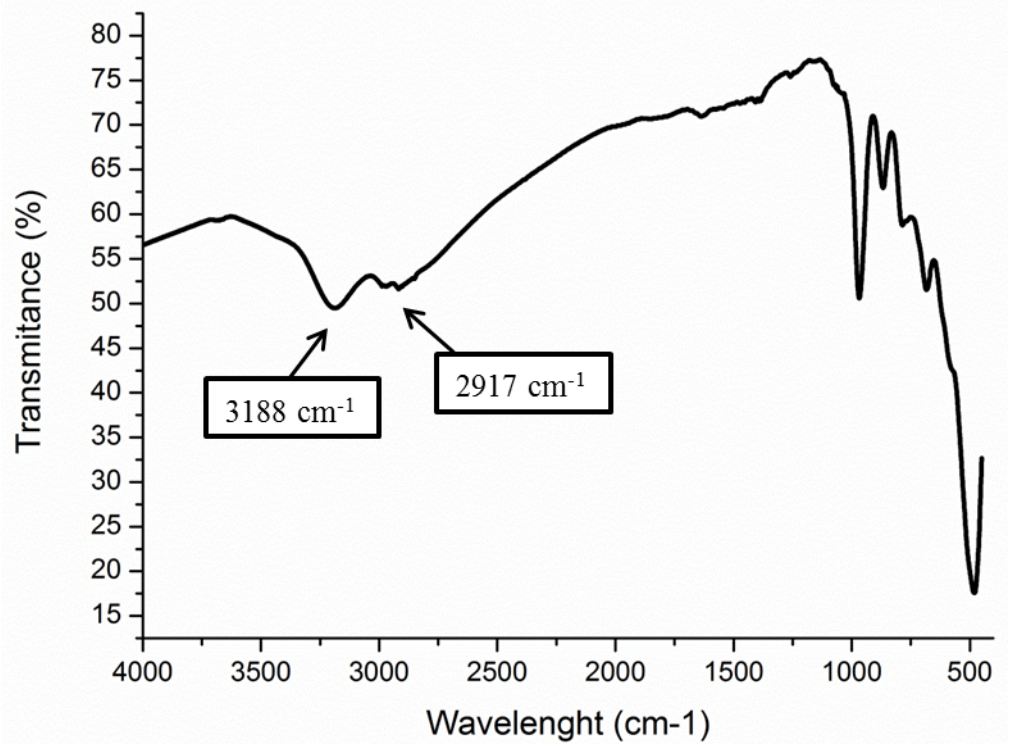

Figure S 1. Experimental FTIR spectra from 4000cm^{-1} to 450cm^{-1} of pristine $H_2Ti_3O_7$. It can be observed two signals from the different types of protons.

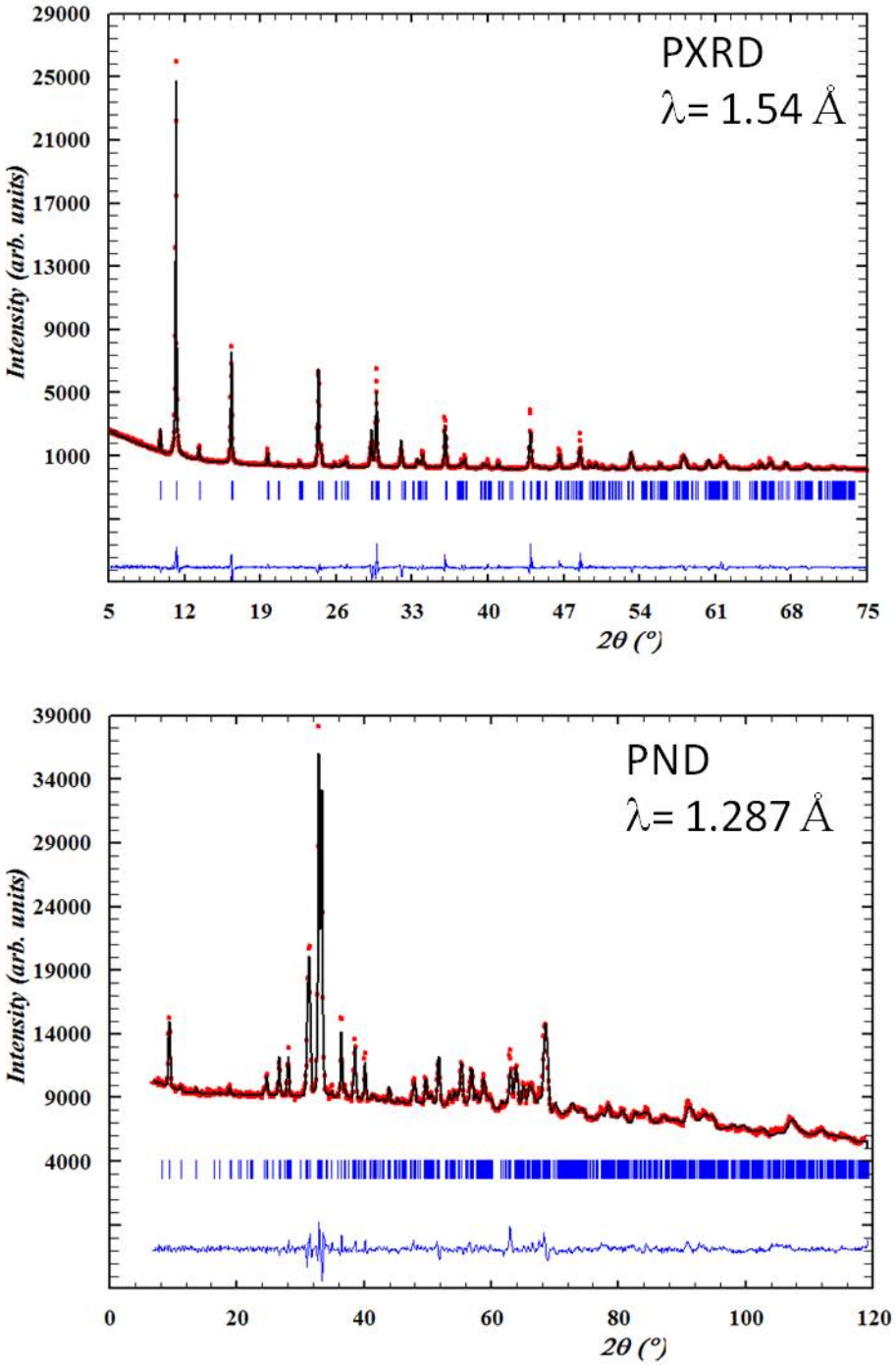

Figure S 2. Plot of the Rietveld refined X-ray (λ=1.54 Å) and neutron diffraction data collected at λ=1.287Å from the combined refinement of X-ray diffraction and neutron diffraction at two different wavelengths of $H_2Ti_3O_7$ at room temperature with space group *C*2/*m*. Experimental (red points) observed (black line) and difference (blue line) Bragg reflections are marked in Blue. Agreement factors, refined atomic position and interatomic distances are listed in Tables S1 and S2.

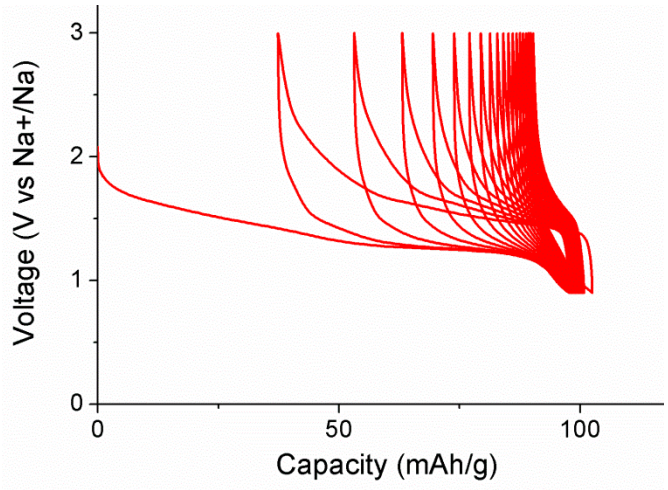

Figure S 3. Galvanostatic cycling of of $H_2Ti_3O_7$ in the 0.9-2.2V (cycles 1-10) at C/10.

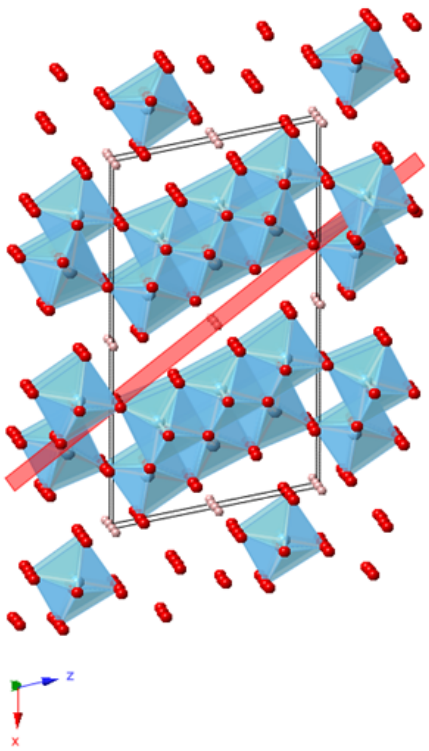

Figure S 4. Structure of $H_2Ti_3O_7$ with the 602 plane that shows the most pronounced changes during the initial states of sodiation indicated in red.

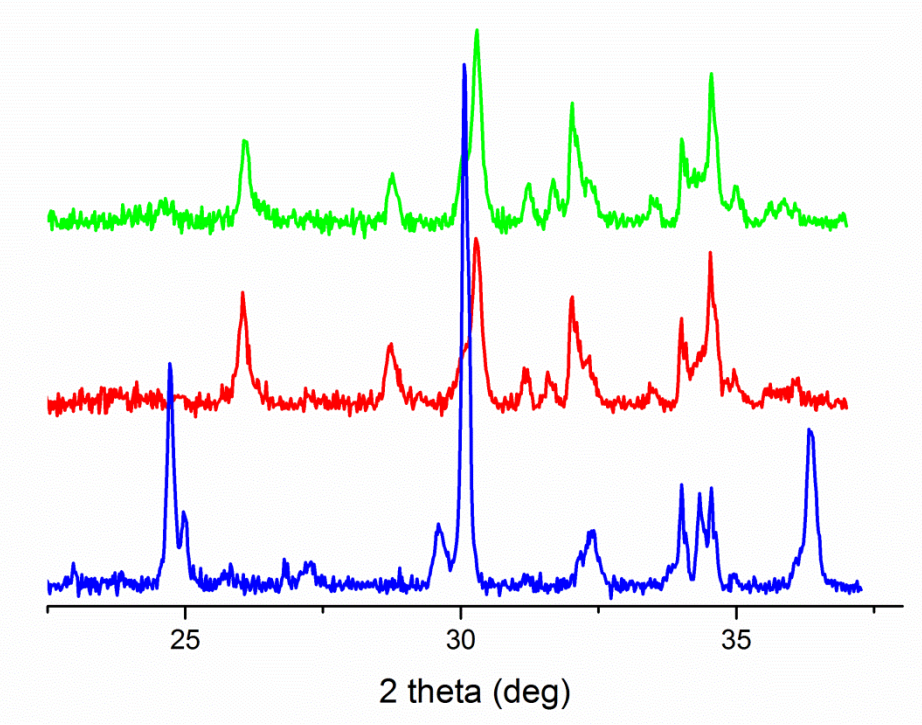

Figure S 5. Selected XRD patterns during the in-situ experiment. (background substracted). From bottom to top: Pristine $H_2Ti_3O_7$ (blue) reduced nominal "$H_2Na_{1.2}Ti_{1.8}^{IV}Ti^{III}_{1.2}O_7$" down to 0.9V (red), reoxidized material up to 2.2V (green).

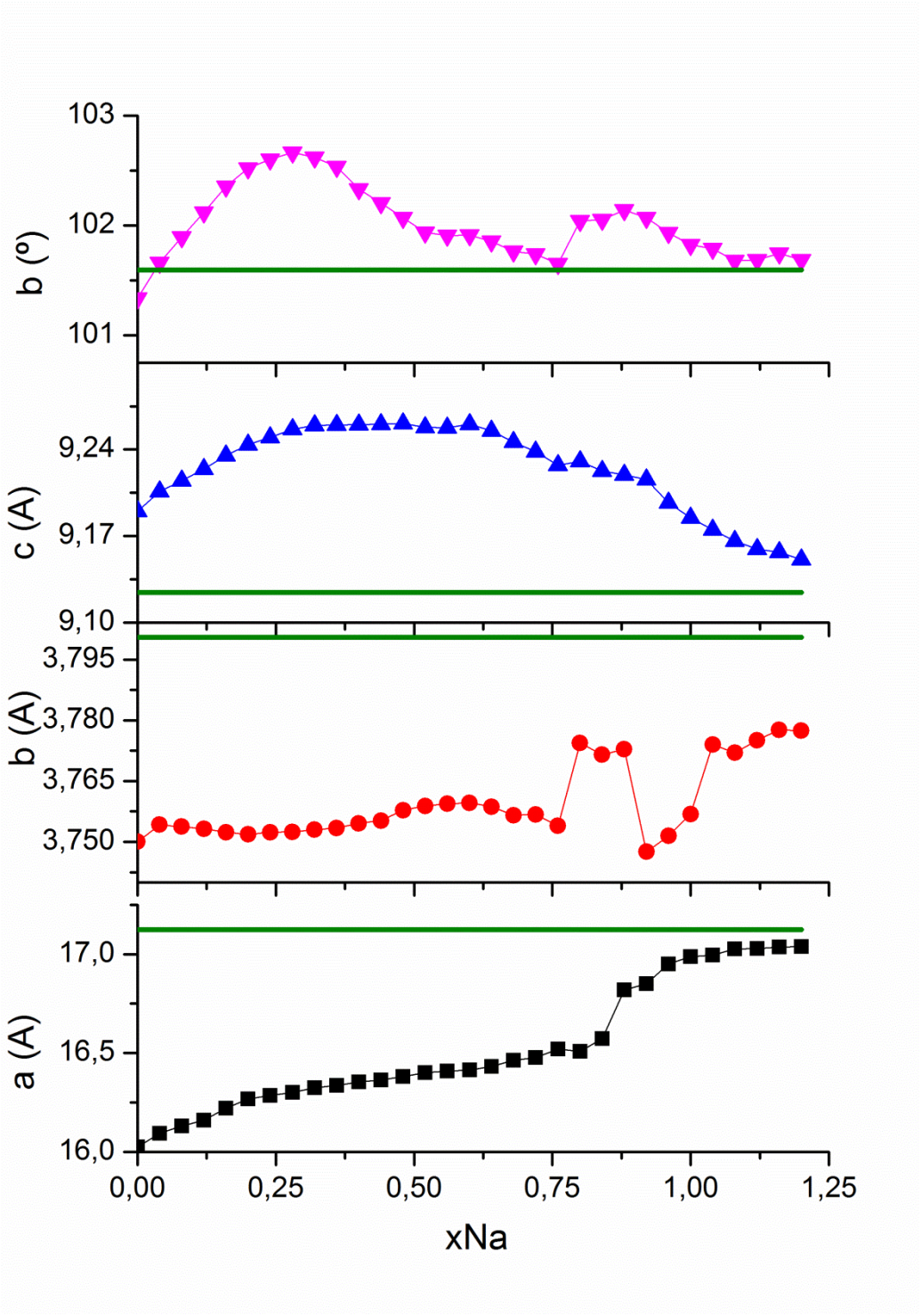

Figure S 6. Change in lattice parameters during the insertion of sodium ions in the first discharge. The parameters of pristine $Na_2Ti_3O_7$ are shown in the green line.

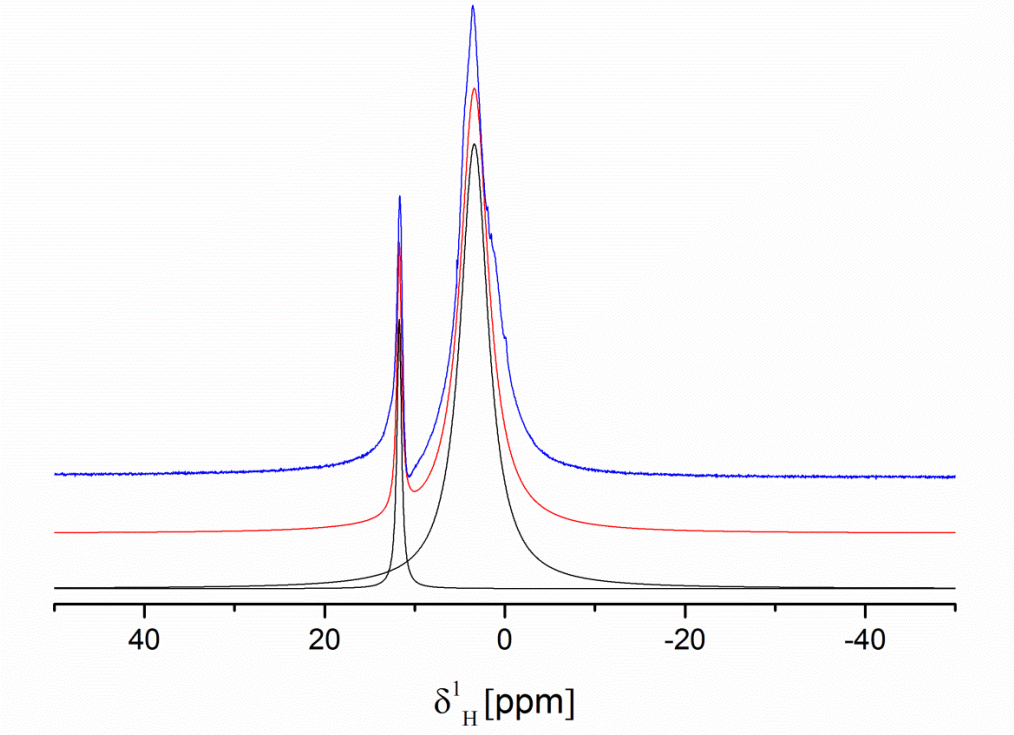

Figure S 7. Experimental and fitting NMR spectra of $H_2Ti_3O_7$ after two cycles in the 0.9V-2.2V range. Integrating the 11ppm signal about 0.2 mols of H/f.u. remain in the structure. The broad peak at 3.7 ppm might be the H signal for dimethyl carbonate from the electrolyte according to literature. 0.2 mol is a low limit considering that the whole sample is pure titanate, however the contribution from the carbonate component has not been considered.

Table S1. Reliability factors obtained from the combined refinement of PXRD and PND data without (left) and with protons (right) in the structure.

	Without protons			With protons		
	X-ray	**Neutron (λ=1.287 Å)**	**Neutron (λ=2.52 Å)**	**X-ray**	**Neutron (λ=1.287 Å)**	**Neutron (λ=2.52 Å)**
	Without H^+			With H^+		
Global χ2	26.7			7.03		
χ2	17.1	20.8	41.2	7.91	5.74	6.7
R_p	28.7	32.3	30.4	20.6	15.7	16.2
R_{wp}	32.3	29.2	27.5	21.9	14.4	11.0
R_B	19.5	25.6	22	7.95	7.36	7.55
R_F	11.6	17	17.9	6.87	4.88	8.06

	Global factors with protons
χ2	2.069
R_p	0.097
R_{wp}	0.083
R_B	0.032
R_F	0.022

Table S2. Atomic positions of $H_2Ti_3O_7$ as obtained from the combined refinement of PXRD and PND data with space group *C*2/*m* and the introduction of the 3 protons.

	Wyckoff position	x	y	z	Biso
Ti 1	4i	0.2288(6)	0	0.2140(10)	1.52(18)
Ti 2	4i	0.1715(7)	0	0.5107(11)	1.52(18)
Ti 3	4i	0.1254(6)	0	0.8297(10)	1.52(18)
O 1	4i	0.1684(9)	0	0.0330(19)	1.05(15)
O 2	4i	0.1339(10)	0	0.3161(18)	1.05(15)
O 3	4i	0.0813(11)	0	0.6076(18)	1.05(15)
O 4	4i	0.0096(10)	0	0.8606(18)	1.05(15)
O 5	4i	0.3505(8)	0	0.1763(15)	-0.14(11)
O 6	4i	0.2942(10)	0	0.4568(18)	-0.14(11)
O 7	4i	0.2355(9)	0	0.7456(17)	-0.14(11)
H 1	2c	0.00000	0	0.50000	5.8(7)
H 2	4i	0.036(2)	0	0.183(4)	5.8(7)
H 3	2a	0.50000	0.5	0.00000	5.8(7)

	d(Ti 1- O) (Å)	**d(Ti2-O) (Å)**	**d(Ti3-O) (Å)**	**d(H1-O) (Å)**	**d(H2-O) (Å)**	**d(H3-O) (Å)**
O1	1.75(2)	-	1.86(2)	-	-	-
O2	1.94(2)	1.78(2)	-	-	1.79(3)	-
O3	-	1.84(2)	2.03(2)	(2x) 1.48(2)	-	-
O4	-	-	1.93(2)	-	0.76(3)	(2x) 1.32(2)
O5	2.05(2)	-	(2x) 1.917(4)	-	-	-
O6	2.27(2)	(2x) 1.960(5) (1x) 2.12(2)	-	-	-	-
O7	(2x) 1.974(5)	2.20(2)	2.06(2)	-	-	-

Table S3. Agreement factors, atomic positions and distances of $H_2Ti_3O_7$ as obtained from the refinement of PND data of wavelength of 1.28 Å introducing the strain microstructural parameters with space group *C*2/*m*.

	Neutron (λ=1.287 Å)
χ2	2.29
R_p	0.106
R_{wp}	0.090
R_B	0.043
R_F	0.029

	Wyckoff position	x	y	z	Biso
Ti 1	4i	0.225(1)	0	0.211(2)	0.1 (2)
Ti 2	4i	0.173(1)	0	0.515(2)	0.4 (3)
Ti 3	4i	0.122(1)	0	0.824(2)	0.4 (2)
O 1	4i	0.1710(6)	0	0.035(1)	0.2 (2)
O 2	4i	0.1339(6)	0	0.316(1)	0.1 (2)
O 3	4i	0.0798(8)	0	0.604(2)	1.2 (2)
O 4	4i	0.0132(8)	0	0.865(2)	1.7 (2)
O 5	4i	0.3502(6)	0	0.180 (1)	0.5 (2)
O 6	4i	0.2951(6)	0	0.457(1)	0.1(2)
O 7	4i	0.2371(6)	0	0.744(1)	0.3 (2)
H 1	2c	0	0	0.5	4.4 (3)
H 2	4i	0.043(2)	0	0.193 (2)	4.4 (3)
H 3	2a	0.5	0.5	0	4.4 (3)

	d(Ti 1- O) (Å)	**d(Ti2-O) (Å)**	**d(Ti3-O) (Å)**	**d(H1-O) (Å)**	**d(H2-O) (Å)**	**d(H3-O) (Å)**
O1	1.68 (2)	-	1.94 (2)	-	-	-
O2	1.91 (2)	1.81 (2)	-	-	1.65 (2)	-
O3	-	1.84 (3)	2.00 (2)	(2x) 1.44 (1)	-	-
O4	-	-	1.86 (2)	-	0.96 (2)	(2x) 1.30 (2)
O5	2.08 (2)	-	(2x) 1.931 (4)	-	-	-
O6	2.31 (2)	(2x) 1.948 (5) (1x) 2.13 (2)	-	-	-	-
O7	(2x) 1.991 (5)	2.15 (2)	2.12 (2)	-	-	-

Table 4. Agreement factors, atomic positions and distances of $H_2Ti_3O_7$ as obtained from the refinement of PND data of wavelength of 1.28 Å introducing the strain microstructural parameters considering the splitting of H1 and the Baniso of H1 and H3 with space group *C*2/*m*.

	Neutron (λ=1.287 Å)
χ2	2.02
R_p	0.099
R_{wp}	0.084
R_B	0.034
R_F	0.023

	Wyckoff position	x	y	z	Biso
Ti 1	4i	0.227(1)	0	0.214(2)	1.0 (3)
Ti 2	4i	0.173(1)	0	0.510(2)	0.7 (3)
Ti 3	4i	0.1206(8)	0	0.827(2)	0.2 (2)
O 1	4i	0.1706(5)	0	0.034(1)	0.3 (2)
O 2	4i	0.1350(6)	0	0.317(1)	0.7 (2)
O 3	4i	0.0788(8)	0	0.602(2)	1.0 (2)
O 4	4i	0.0128(7)	0	0.863(2)	1.8 (2)
O 5	4i	0.3504(5)	0	0.182(1)	0.5 (2)
O 6	4i	0.2927(5)	0	0.454(1)	0.2(2)
O 7	4i	0.2390(6)	0	0.747(1)	0.4 (2)
H 1	4i	0.035(6)	0	0.522(2)	Aniso
H 2	4i	0.046(1)	0	0.195(2)	2.0 (3)
H 3	2a	0	0	0	Aniso

	d(Ti 1- O) (Å)	**d(Ti2-O) (Å)**	**d(Ti3-O) (Å)**	**d(H1-O) (Å)**	**d(H2-O) (Å)**	**d(H3-O) (Å)**
O1	1.72 (2)	-	1.91 (2)	-	-	-
O2	1.91 (2)	1.76 (2)	-	-	1.64 (2)	-
O3	-	1.88 (3)	2.04 (2)	0.91 (6) 1.95 (8)	-	-
O4	1.97 (5)	-	-	-	-	-
O5	-	-	1.82 (2)	-	0.98 (2)	(2x) 1.32 (2)
O6	2.06 (2)	-	(2x) 1.938 (4)	-	-	-
O7	(2x) 2.25 (2)	(2x) 1.964 (6)	-	-	-	-

Table 5. Agreement factors of the data collected by us of $H_2Ti_3O_7$ as obtained from the refinement of PND data of wavelength of 1.28 Å according to the model from CIF file reported by *Kataoka et al.* with space group *C*2/*m*.

Neutron

(λ=1.287 Å)

$\chi 2$	12.48
R_p	0.229
R_{wp}	0.225
R_B	0.125
R_F	0.082