$\text{Na}_3[\text{Ti}_2\text{P}_2\text{O}_{10}\text{F}]$: an new titanium fluorophosphate with ionic conductive property

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Supporting Information

1 Rietveld plots of X-ray diffraction data for $\text{Na}_3(\text{H}_2\text{O})_x\text{Ti}_2\text{FO}_2(\text{PO}_4)_2$ ($x < 1$) in the space group $I4/mmm$.

Figure S1 Rietveld Plot of the x-ray diffraction data for $\text{Na}_3[\text{Ti}_2\text{P}_2\text{O}_{10}\text{F}] \cdot x\text{H}_2\text{O}$ (1).

2. Selected bond distances for $\text{Na}_3[\text{Ti}_2\text{P}_2\text{O}_{10}\text{F}]\cdot x\text{H}_2\text{O}$ (1)

Table s1 Selected bond distances for $\text{Na}_3[\text{Ti}_2\text{P}_2\text{O}_{10}\text{F}]\cdot x\text{H}_2\text{O}$ (1)

Bonds	Distances (Å)	Bonds	Distances(Å)
Ti1—F1	2.143(1)	Na/Ow1—F1	2.526(1)
Ti1—O2	1.611(1)	Na/Ow1—O2	2.563(1)
Ti1—O3	2.056(1)	Na/Ow1—O3	2.496(1)
P1—O3	1.522(1)		

3. The details on the structure determination

The structure solution was initially established in the space group $I4/m$ by using the direct method, where titanium, phosphorus, sodium and part of oxygen positions were located. The rest of the oxygen positions were obtained by subsequent difference Fourier analysis. The structure was refined using the Rietveld method with isotropic displacement parameters for all atoms by cooperative use of the powder X-ray diffraction data and the neutron diffraction data. The structure refinement of the $I4/m$ model resulted in a reasonable profile fitting as shown for the neutron diffraction data in Figure S2. All of the atomic positions are well defined in the structure refinement, except the Na/Ow1.

Figure s2 Rietveld fit of the powder neutron diffraction pattern of **1** in the $I4/m$ (left) and $I4/mmm$ (right) models.

According to the result of chemical analysis and TG-MS analysis, and charge balance, this position should not be occupied merely by Na ions, but together with water molecules. The occupancy factor of Na ions was fixed to 0.75 based on the chemical analysis. From the atomic parameters shown in Table S2, one could clearly see that the structure framework can also be well described in the space group $I4/mmm$, if the O3 position moves slightly to a special position $16n$ (0, y, z) in the space group $I4/mmm$, and the Na/Ow1 position moves to a special position $8h$ (x, x, 0). The $I4/mmm$ model also gave a reasonable profile fitting as shown in Figure S2. However, as shown in figure S3, the electron

densities at Na/Ow1 position are very similar for both the I4/m model and the I4/mmm model. It is easy to see that there two mirror plane for the distribution of electron density. This strongly suggests that the structure of **1** is of I4/mmm symmetry. The distributions of the corresponding atoms are also shown in figure 2. It is clearly that the I4/mmm model is better. Therefore, **1** is considered to crystallize in the space group I4/mmm.

Table 2 Rietveld refinement details of $\text{Na}_3(\text{H}_2\text{O})_x\text{Ti}_2\text{FO}_2(\text{PO}_4)_2$ ($0 < x < 1$) in the space group I4/m and I4/mmm^a

atom	site	I4/m	I4/mmm	Occupy
Ti	4e	0,0, 0.8001(1)	0,0, 0.7993(1)	1
P	4d	0, 0.5, 0.75	0, 0.5, 0.75	1
F1	2a	0, 0, 0	0, 0, 0	1
O2	4e	0, 0, 0.6484(1)	0, 0, 0.6484(1)	1
O3	16i/16n ^b	0.0024(1), 0.3131(1), 0.8345(1)	0, 0.3137(1), 0.8381(1)	1
Na/Ow1	8h	0.2988(1), 0.2559(1), 0	0.2782(1), 0.2782(1), 0	0.75/0.09
		$R^X_p=0.042$, $R^X_{wp}=0.064$, $R^N_p=0.036$, $R^N_{wp}=0.050$	$R^X_p=0.039$, $R^X_{wp}=0.059$, $R^N_p=0.036$, $R^N_{wp}=0.049$	

^aThe corresponding lattice parameters are $a=6.4207(1)\text{\AA}$, $c=10.6762(2)\text{\AA}$.

^bThe site symbol 16i is for I4/m, and 16h for I4/mmm. The other symbols are same for both I4/m and I4/mmm. R^X_p and R^X_{wp} are R factors for X-ray diffraction data, and R^N_p and R^N_{wp} for neutron diffraction data.

The water molecular may be located around the sodium position. However, it is difficulty to find the exact position of them for the occupation is just about 0.1. To simplify the question, we just assume that the water is located at the sodium position, and then the occupation of water may be suggested by GSAS.

Fig.s3 Electron density of the Na/Ow1 position calculated from difference Fourier maps for the I4/m model (a) and the I4/mmm model (b), and the distribution of atoms around the Na/Ow1 position for the I4/m model (c) and the I4/mmm model (d). The Fourier map calculation was carried out by including all atoms except Na/Ow1.

4. The weight loss for two samples.

Figure S4a TG-MS spectra of Sample A

Figure S4b TG-MS spectra of Sample B