Supplementary Material for

Unraveling the structural features of Dion-Jacobson-type layered perovskite-related material $HCa_2Nb_3O_{10}\cdot 1.5H_2O$

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Table S1 Fractional atomic coordinates and isotropic atomic displacement parameters of dehydrated HCNO with space group $P4_22_12$. These parameters were obtained by Rietveld refinement.

Dehydrated HCNO ($HCa_2Nb_3O_{10}$) tetragonal $P4_22_12$
$a = 7.7114(7)$, $c = 28.7960(8)$

Atom	Site	x	y	z	B (^{2})
H1	4*f*	1/4	3/4	0	0 (fixed)
H2	4*e*	3/4	3/4	0	0 (fixed)
Ca1	8*g*	0.247(2)	0.2301(17)	0.1688(2)	0.02(6)
Ca2	8*g*	0.2285(15)	0.7540(19)	0.1772(2)	0.02(-)
Nb1	4*d*	1/2	0	0.1037(9)	0.11(7)
Nb2	4*d*	1/2	0	0.2504(10)	0.11(-)
Nb3	4*d*	1/2	0	0.3968(9)	0.11(-)
Nb4	4*c*	0	0	0.1027(5)	0.46(8)
Nb5	4*c*	0	0	0.2497(5)	0.46(-)
Nb6	4*c*	0	0	0.3973(5)	0.46(-)
O1	8*g*	0.255(16)	-0.009(10)	0.380(5)	2.07(16)
O2	8*g*	0.001(10)	0.260(15)	0.381(5)	2.07(-)
O3	8*g*	0.276(6)	-0.051(6)	0.251(5)	2.07(-)
O4	8*g*	-0.058(5)	0.264(8)	0.251(5)	2.07(-)
O5	8*g*	-0.006(10)	0.260(18)	0.117(5)	2.07(-)
O6	8*g*	0.258(17)	-0.010(10)	0.118(5)	2.07(-)
O7	4*d*	1/2	0	0.046(11)	5.68(117)
O8	4*d*	1/2	0	0.316(8)	5.68(-)
O9	4*d*	0	1/2	0.046(11)	5.68(-)
O10	4*d*	0	1/2	0.316(8)	5.68(-)
O11	4*c*	0	0	0.043(3)	5.41(116)
O12	4*c*	0	0	0.315(4)	5.41(-)
O13	4*c*	1/2	1/2	0.046(4)	5.41(-)
O14	4*c*	1/2	1/2	0.314(4)	5.41(-)

$R_{wp} = 8.93$, $S = 1.19$

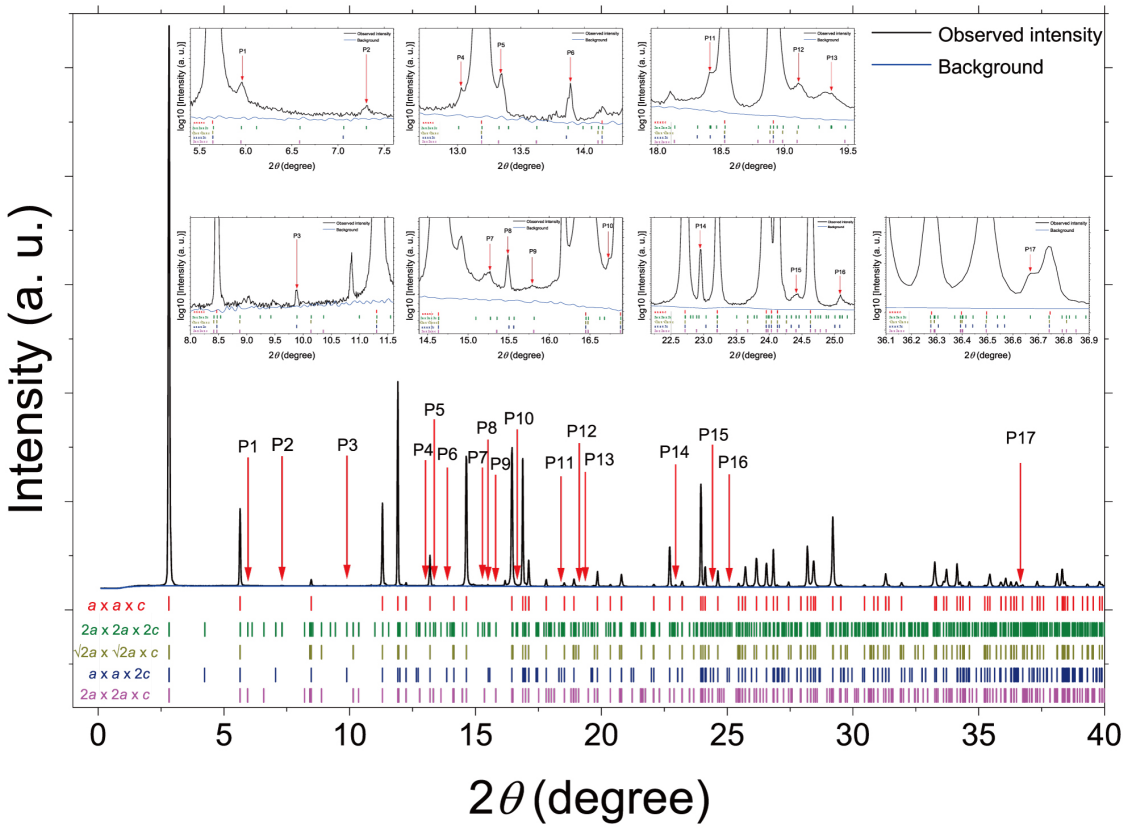

Fig. S1 The comparison is based on the parent-cell whole-pattern Le Bail analysis in the space group *P*4/*mmm*. Cell sizes have been changed to $a \times a \times c$, $2a \times 2a \times 2c$, $\sqrt{2}a \times \sqrt{2}a \times \sqrt{2}c$, $a \times a \times 2c$, and $2a \times 2a \times c$ for comparison. Red arrows (P1−P17) mark additional weak reflections not indexed by the parent cell; the insets show enlarged views of selected regions. The $2a \times 2a \times 2c$ supercell provides the best overall match to these weak reflections.

A reduction in symmetry generally increases the number of refined parameters and often decreases the *R* factors. It is important to determine if the apparent improvement in the Rietveld refinement is statistically significant. To do this, Hamilton's *R*-factor ratio test was applied to the refinement results.[1] This test provides a quantitative criterion for assessing whether an improved fit truly indicates a better structural model or simply results from having more refined parameters. Following Hamilton's formulation,[1] the test statistic $F_{\text{statistic}}$ is given by

$$F_{statistic} = \left[\left(\frac{R_Q}{R_0}\right)^2 - 1\right]\frac{n-m}{b}$$

where $R_Q = R_{wp1}$ and $R_0 = R_{wp2}$ are the weighted profile *R* factors for the restricted (simpler) and unrestricted (more complex) models, respectively. Following Hamilton's original notation, the variables *n*, *m*, and *b* correspond to the total number of data points, the number of refined parameters in the unrestricted model, and the increase in the number of refined parameters, respectively. In the present Rietveld refinement context, these quantities are expressed as $n = N$, $m = P_2$, and $b = P_2 - P_1$. In the present analysis, all SR-XRD data used for the Hamilton test contain 9460 profile points, giving $dfn = P_2 - P_1$ and $dfd = N - P_2$. The calculated $F_{\text{statistic}}$ values were compared with the critical values of the corresponding $F_{(dfn,\ dfd)}$ distribution at one-sided significance levels of $\alpha = 0.05$ and 0.01.[2,3] The numerical results are summarized in Table S2, and the corresponding $F_{(dfn,\ dfd)}$ distributions are shown in Fig. S2. In all six comparisons, the calculated $F_{\text{statistic}}$ values exceed the corresponding critical values even at the $\alpha = 0.01$ level. The associated *p-values* were obtained from the upper tail of the same *F* distribution and are reported as $-\log_{10}(p)$ because of their extremely small values. These results confirm that the improvements obtained with the lower-symmetry models are statistically significant and cannot be attributed simply to the increase in the number of refined parameters.

Table S2 Statistical significance of the improvements in the Rietveld refinement results evaluated by Hamilton's *R*-factor ratio test.

Comparison	*N*	P_1	P_2	*dfn*	*dfd*	$F_{statistic}$	F_{crit} 0.05	F_{crit} 0.01	$-\log_{10}(p)$
Fig. 2 — Framework-only model (O omit)									
$P4/mmm \rightarrow P4_2/nbc$	9460	120	136	16	9324	254.771	1.645	2.002	715.964
$P4/mmm \rightarrow P4_22_12$		120	146	26	9314	176.185	1.497	1.757	779.435
$P4_2/nbc \rightarrow P4_22_12$		136	146	10	9314	35.406	1.832	2.323	67.900
Fig. 3 — Framework model with interlayer water-oxygen sites included									
$P4/mmm \rightarrow P4_2/nbc$	9460	144	146	2	9314	1205.023	2.997	4.607	465.426
$P4/mmm \rightarrow P4_22_12$		144	167	23	9293	201.496	1.530	1.812	790.037
$P4_2/nbc \rightarrow P4_22_12$		146	167	21	9293	84.354	1.557	1.856	330.845

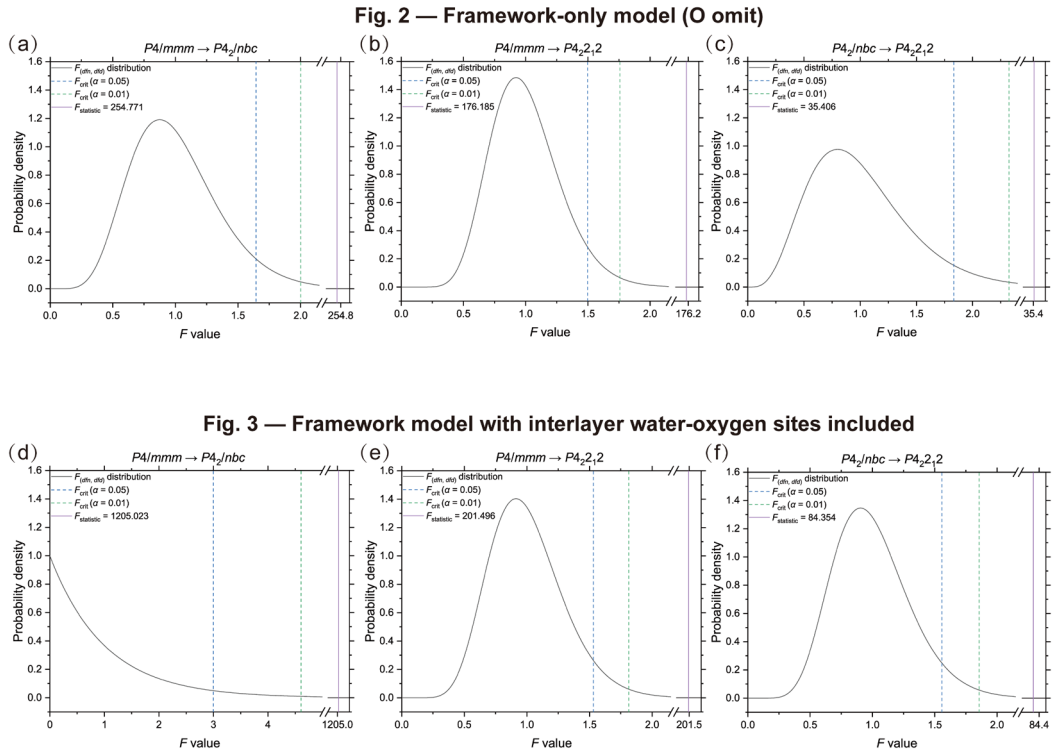

Fig. S2 $F_{(dfn,\, dfd)}$ distributions for the six Hamilton-test comparisons summarized in Table S2. The upper panels show the framework-only model (O omit): (a) *P*4/*mmm* → *P*4$_2$/*nbc*, (b) *P*4/*mmm* → *P*4$_2$2$_1$2, and (c) *P*4$_2$/*nbc* → *P*4$_2$2$_1$2. The lower panels correspond to the framework model including interlayer water-oxygen sites: (d) *P*4/*mmm* →*P*4$_2$/*nbc*, (e) *P*4/*mmm* → *P*4$_2$2$_1$2, and (f) *P*4$_2$/*nbc* → *P*4$_2$2$_1$2. In each panel, the dashed vertical lines mark the critical values (F_{crit}) at α = 0.05 and 0.01, and the solid vertical line indicates the calculated $F_{\mathrm{statistic}}$. Broken *x*-axes are used where necessary because some $F_{\mathrm{statistic}}$ values fall far outside the main range of the corresponding *F* distributions.

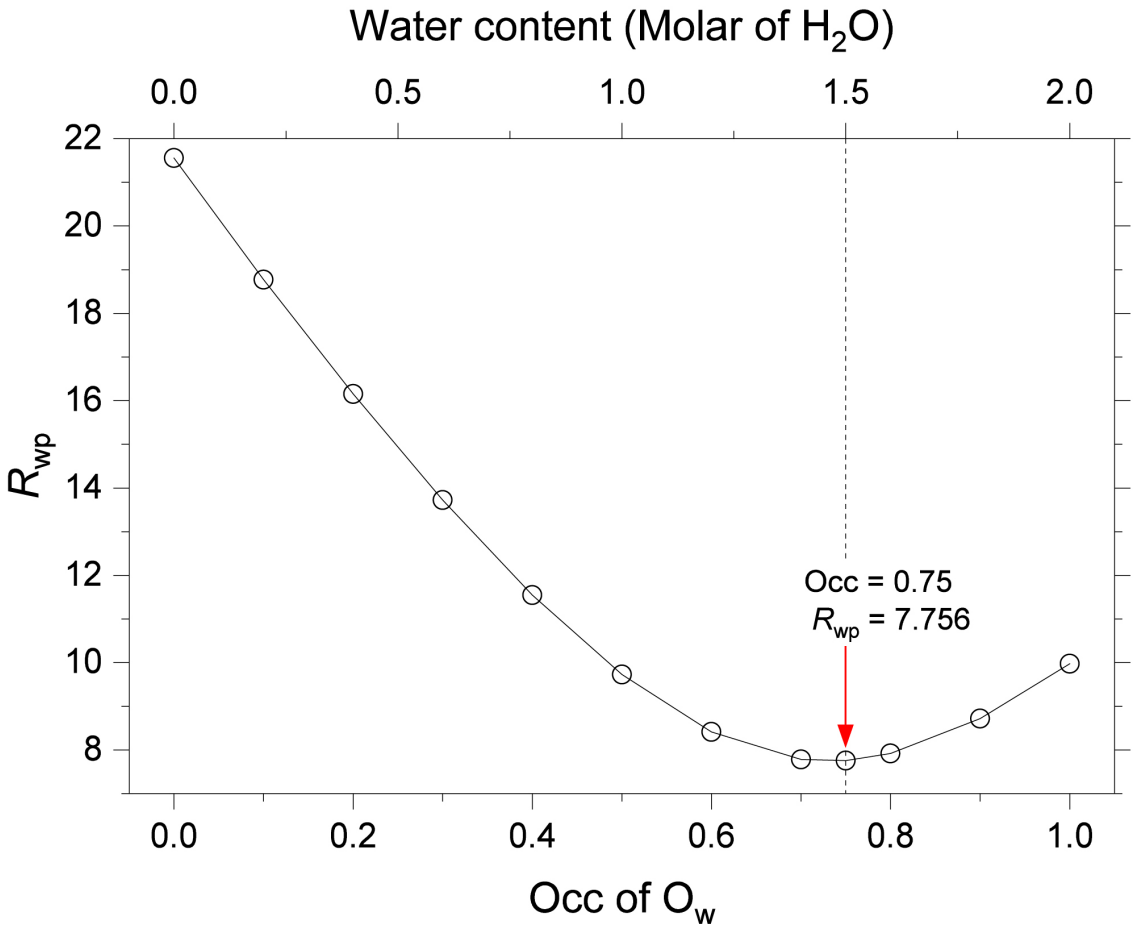

Fig. S3 R_{wp} versus the constrained O_w occupancy from a series of Rietveld refinements for the SR-XRD data of HCNO hydrate. The same occupancy parameter *g* was applied to both interlayer water-oxygen sites, O_w1 and O_w2. Therefore, Occ = 0.75 corresponds to $HCa_2Nb_3O_{10}\cdot 1.5H_2O$.

References

[1] W. C. Hamilton, *Acta Cryst.*, 1965, **18**, 502－510.

[2] NIST/SEMATECH, *Upper Critical Values of the F Distribution*, NIST/SEMATECH e-Handbook of Statistical Methods, n.d., https://www.itl.nist.gov/div898/handbook/eda/section3/eda3673.htm, accessed 2026-03-05).

[3] J. Chable, B. Dieudonné, M. Body, C. Legein, M.-P. Crosnier-Lopez, C. Galven, F. Mauvy, E. Durand, S. Fourcade, D. Sheptyakov, M. Leblanc, V. Maisonneuve and A. Demourgues, *Dalton Trans.*, 2015, **44**, 19625－19635.