SUPPLEMENTARY INFORMATION

Structure-properties relationship in the hydronium-containing pyrochlores $(H_3O)_{1+p}Sb_{1+p}Te_{1-p}O_6$ with catalytic activity in the fructose dehydration reaction.

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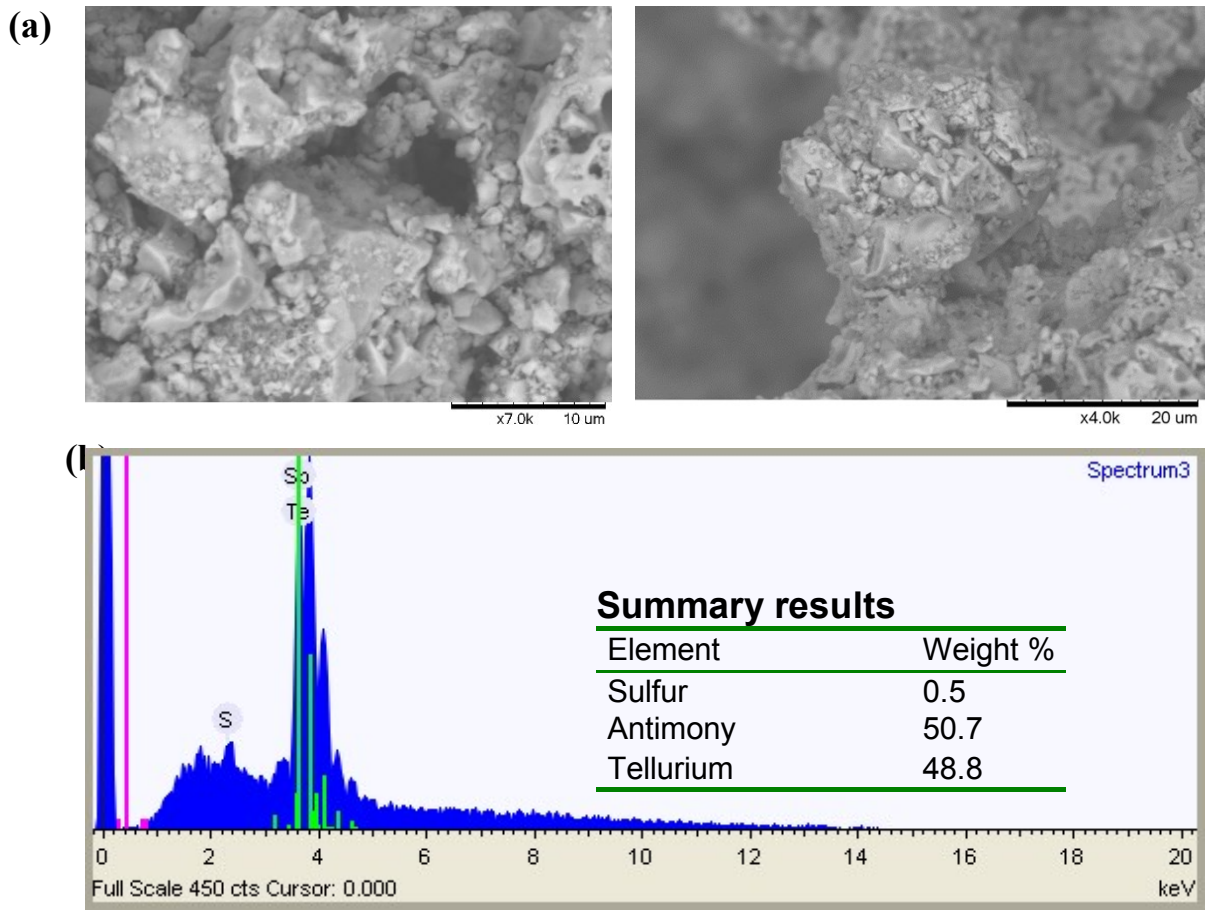

Fig. S1 (**a**) SEM micrographs of the H_3O-1.25 sample. A rough, heterogeneous texture defines its surface, with grains sized up to 10 μm. Bigger clusters may be found, conformed by smaller catalyst particles. (**b**) EDX composition analysis. No measurable K quantities were detected on its surface, but only slight amounts of sulfur, proceeding from the sulfuric acid ion-exchange treatment.

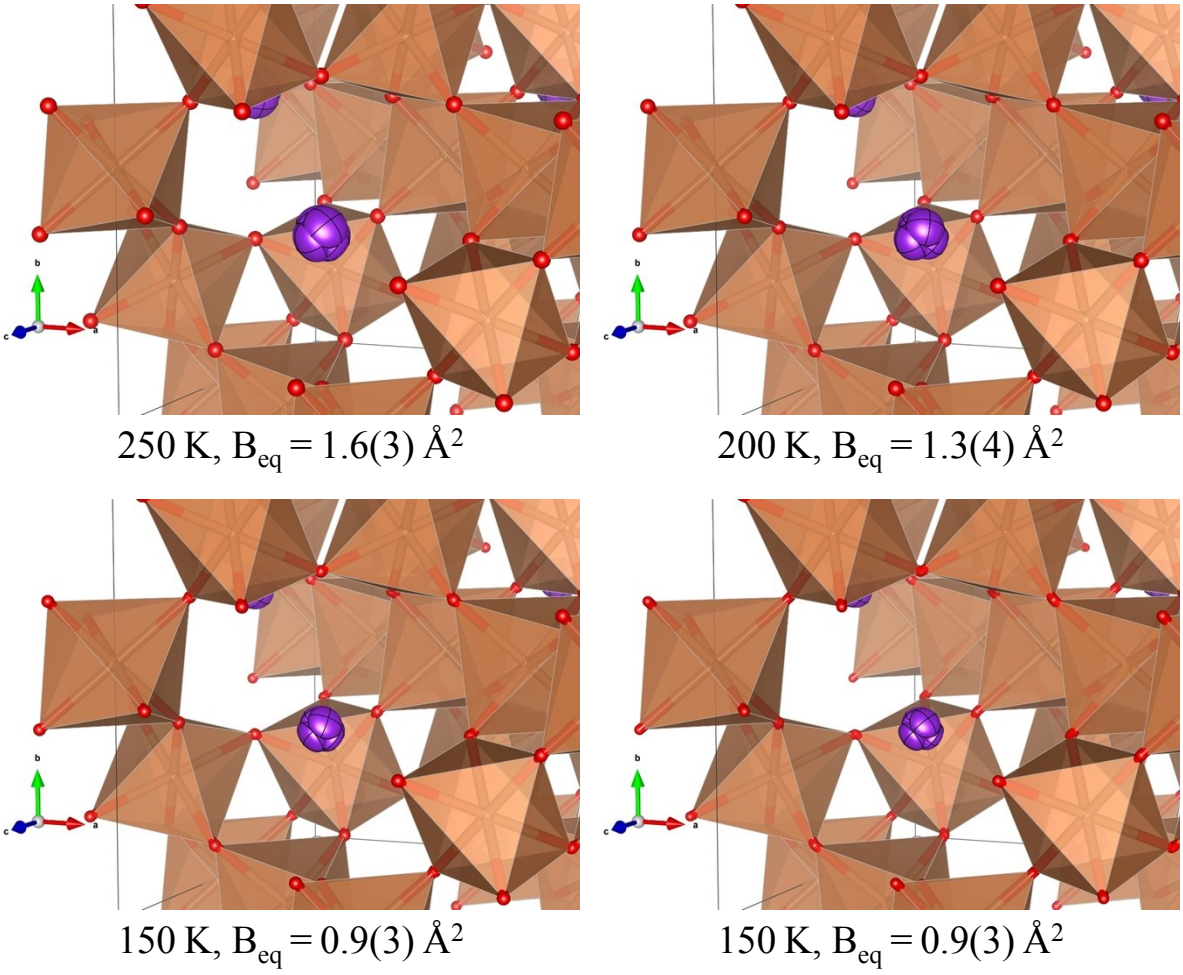

Fig. S2 Close up of a single cavity of the $KSbTeO_6$ pyrochlore oxide, obtained from SXRD data Rietveld refinements at different temperatures. The Sb and Te (brown) at 16*d* and the O1 (red) at 48*f* Wyckoff sites conform a framework that creates the hollow space wherein the K^+ ions (purple) are located off-center at 32*e* Wyckoff sites, where all displacement ellipsoids are presented with a 95 % probability. Nominally, only 1 out of 4 potassium atoms here displayed are present. The temperatures at which each SXRD data were collected, together with the atomic equivalent isotropic displacement ellipsoids (B_{eq}) of the K^+ ions are labeled below each corresponding picture.

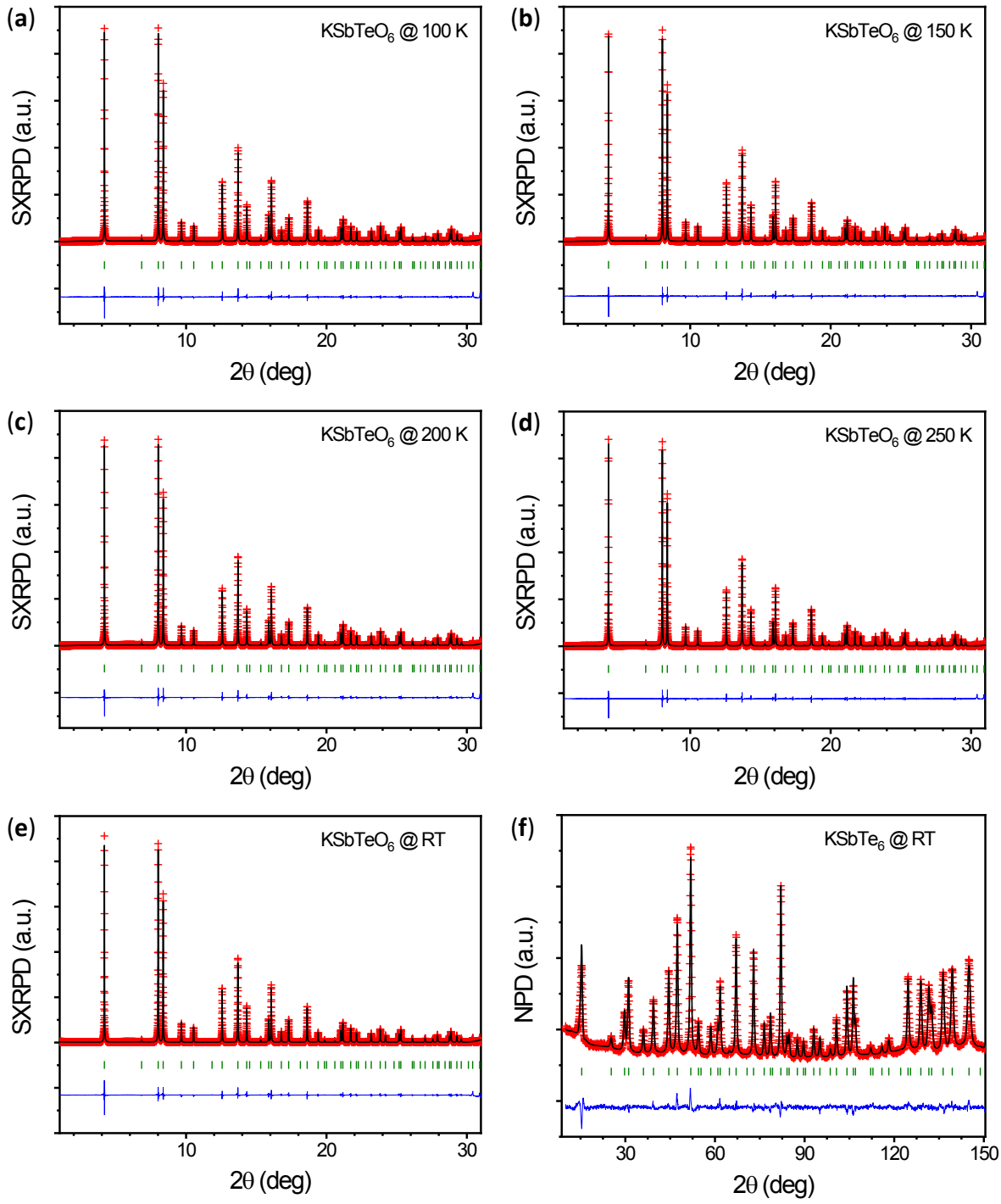

Fig. S3 Rietveld refinement from SXRD data of the $KSbTeO_6$ defect pyrochlore, collected at (**a**) 100 K, (**b**) 150 K, (**c**) 200 K, (**d**) 250 K and (**e**) RT. Also, Rietveld refinement from NPD data collected at RT is presented (from Ref. 14) (**f**). In the graph, experimental (red crosses), theoretical (solid black line), and difference (solid blue line at the bottom) powder SXRD/NPD pattern, with Bragg reflection positions marked by vertical green bars are shown.

Table S1 Unit-cell parameter (*a*) and volume (V), fractional atomic coordinates (*x*), atomic equivalent isotropic displacement parameters (B_{eq}) for the $KSbTeO_6$ defect pyrochlore precursor, defined in the cubic $Fd\bar{3}m$ (# 227) space group (Origin Choice # 2), Z = 8, refined from SXRD data collected at 100, 150, 200, and 250 K (λ_{SXRD} = 0.42640 Å). RT sample was refined with combined data from SXRD (λ_{SXRD} = 0.42640 Å) and NPD (λ_{NPD} = 1.5947 Å). The agreement factors after the refinements are also included.

$KSbTeO_6$	**100 K**	**150 K**	**200 K**	**250 K**	**298 K**	
***a* (Å)**	10.11186(3)	10.11276(3)	10.11457(3)	10.11677(3)	10.11897(4)	
V(Å^3)	1033.935(6)	1034.212(6)	1034.766(6)	1035.441(6)	1036.116(7)	
K 32*e* (*x*,*x*,*x*)						
x	0.1116(12)	0.1111(11)	0.1111(13)	0.1109(12)	0.1089(9)	
B_{eq} (Å^2)	0.8(3)	0.9(3)	1.3(4)	1.6(3)	1.4(3)	
(Sb, Te) 16*d* (½,½,½)						
B_{eq} (Å^2)	0.209(8)	0.237(8)	0.251(8)	0.283(9)	0.32(1)	
O1 48*f* (*x*,⅛,⅛)						
x	0.4265(2)	0.4265(2)	0.4265(2)	0.4266(2)	0.42718(13)	
B_{eq} (Å^2)	0.10(5)	0.15(5)	0.20(5)	0.26(5)	0.70(5)	
Reliability factors	SXRD	SXRD	SXRD	SXRD	SXRD	NPD
R_p (%)	7.33	7.22	7.33	7.23	7.76	5.27
R_{wp} (%)	9.21	9.10	9.32	9.24	9.63	6.97
R_{exp} (%)	3.64	3.68	3.69	3.71	5.12	3.92
χ^2	6.39	6.13	6.37	6.22	4.73	3.16
R_{Bragg} (%)	1.79	1.83	2.42	1.99	2.10	1.97

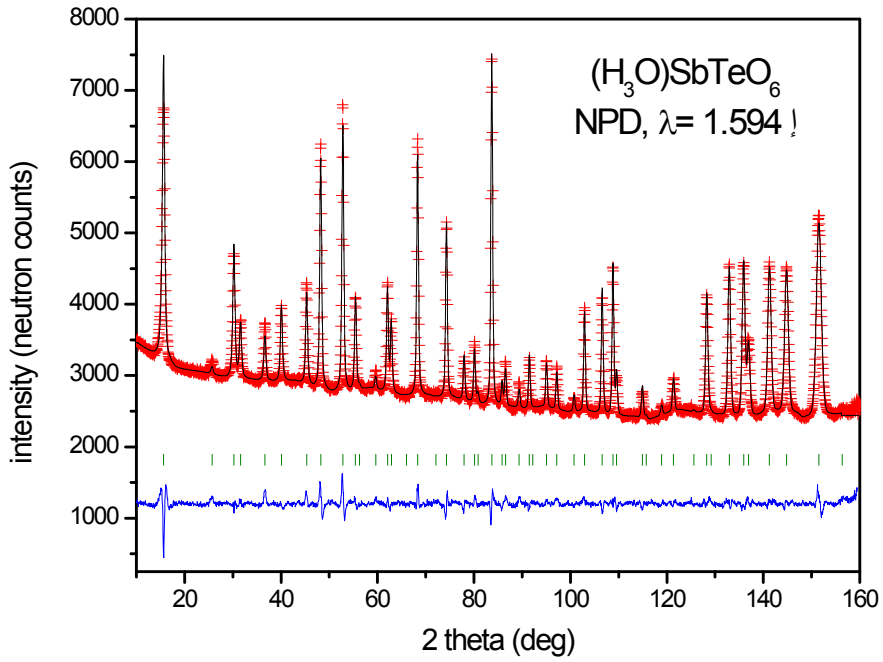

Fig. S4 Rietveld refinement from neutron powder diffraction data for $(H_3O)SbTeO_6$ sample, collected at RT in a wide 2θ range from 10° to 160°. In the graph, experimental (red crosses), theoretical (solid black line), and difference (solid blue line at the bottom) powder SXRD pattern, with Bragg reflection positions marked by vertical green bars are presented.

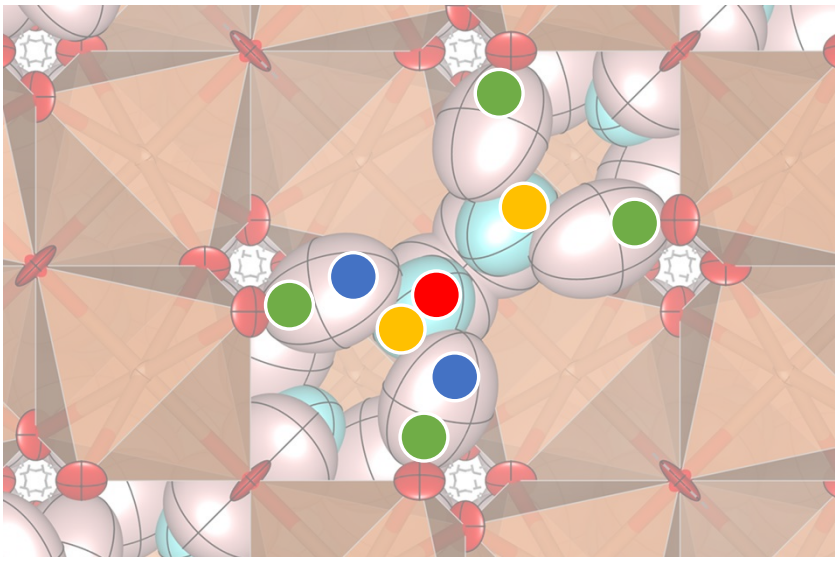

Fig. S5 Representation for the H3O-1.25 sample of how one or two hydronium groups could fit properly within a single cavity generated by the B_2O_6 covalent framework. The atomic anisotropic displacement ellipsoids, here presented with a 95 % probability, represent a mean, statistical distribution of O2 (light blue) and H (pearl) atoms of the hydronium units. When only one acid group fits within the cavity, O2 atom can be centered at the red circle, while H atoms at the blue points. When two H3O+ units are located in a single cavity, O2 and H atoms could adopt the yellow and green positions, respectively. This way, O2–O2 would adopt distances further than 1.4 $Å^2$.