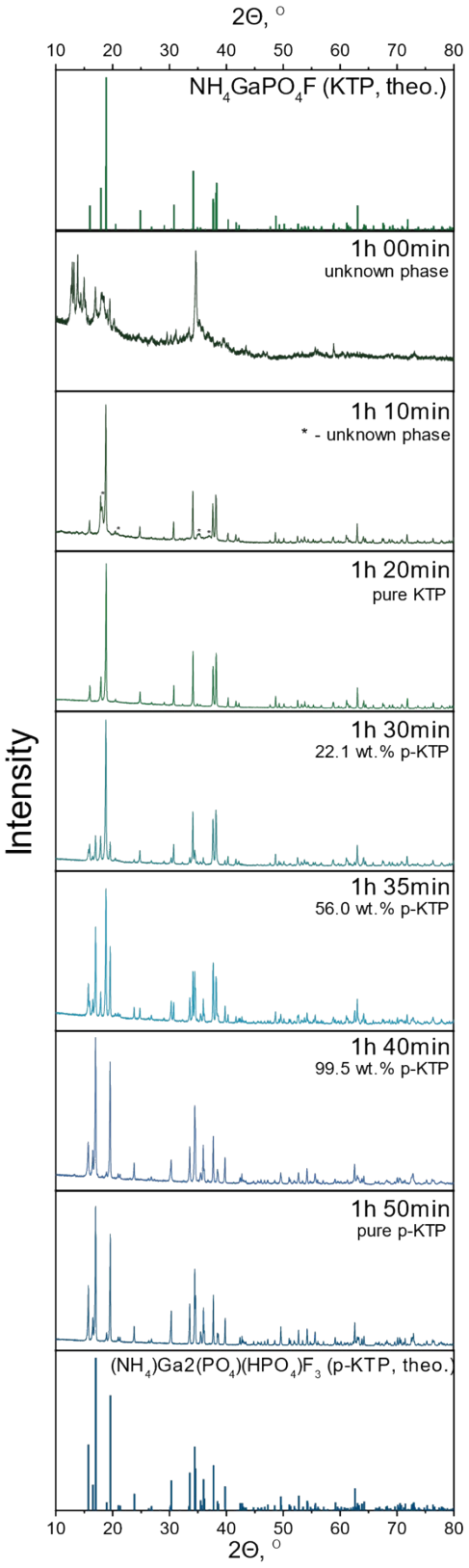
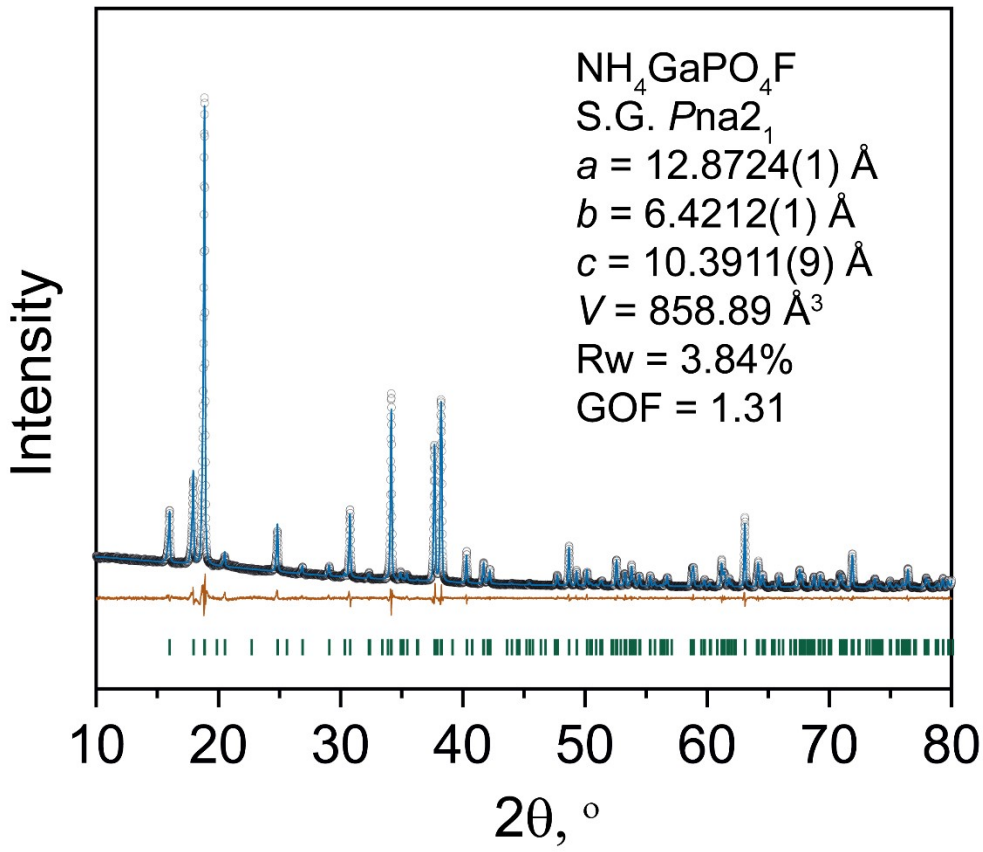
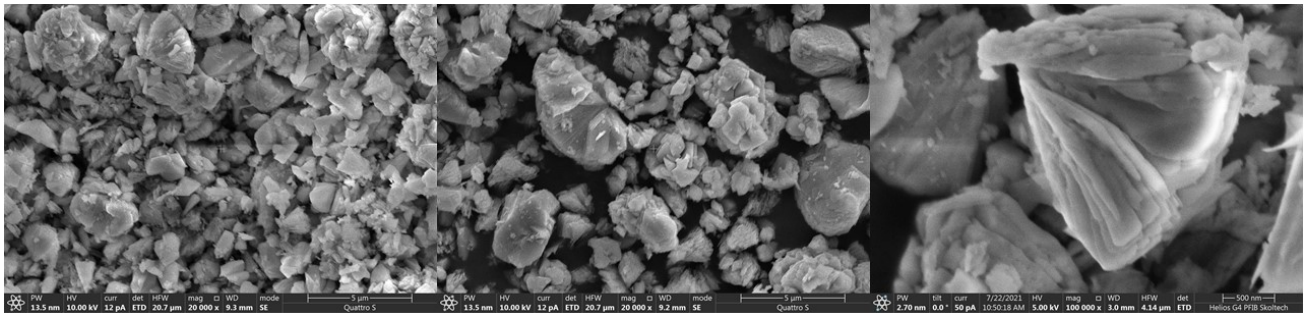


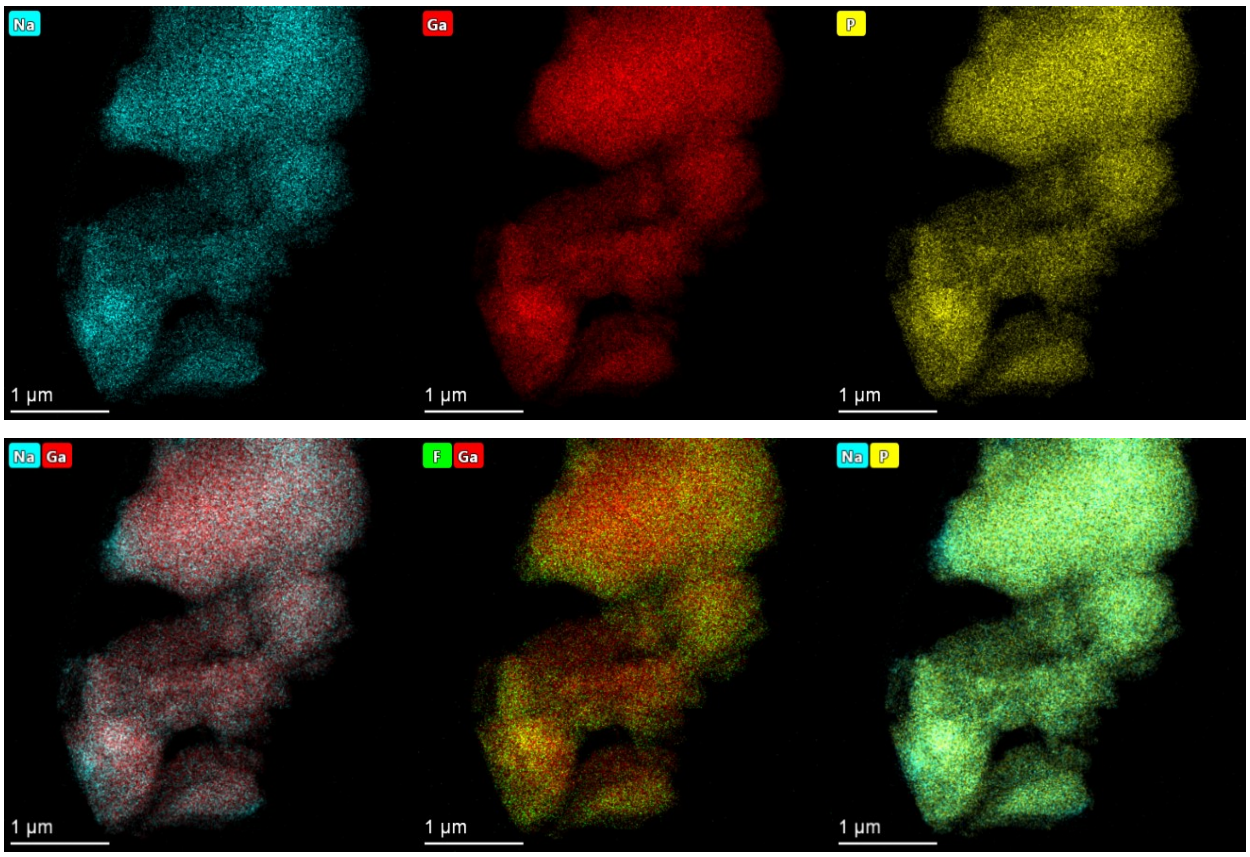
Supplementary Figure 1. XRD of different powders obtained with different heating time. The data collected using a Huber G670 Guinier diffractometer (CoKα_1 radiation (λ = 1.78892 Å), with Ge (111) monochromator and image plate detector. The patterns were measured at ambient temperature with a step of 0.005° within the 4-100° 2θ range. For better representation 10-80 2θ range is given. Phase fraction were determined via the Rietveld refinement.



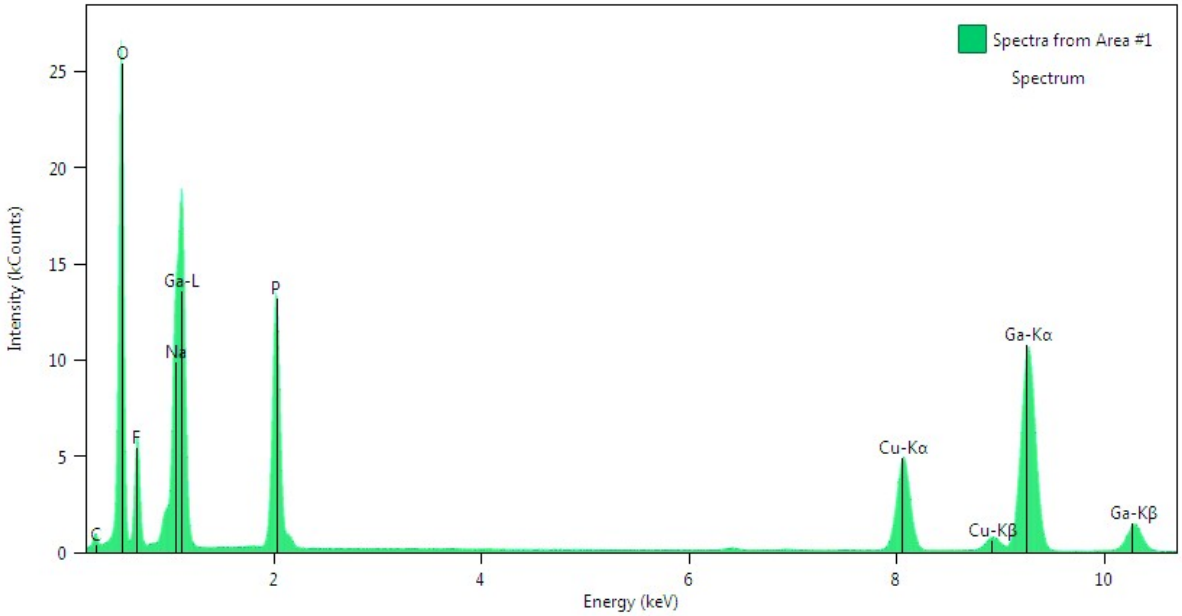
Supplementary Figure 2. Le Bail fitting of the X-ray powder diffraction pattern for NH_4GaPO_4F.



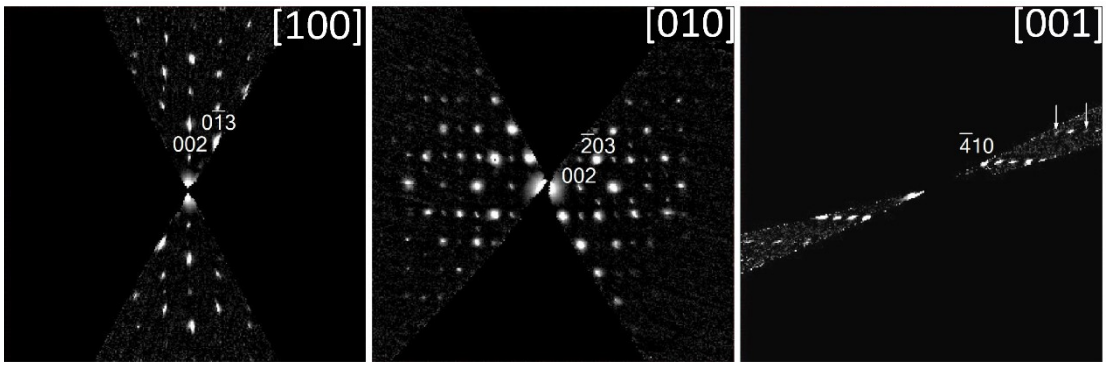
Supplementary figure 3. SEM images of NH_4GaPO_4F (left) and $NaGaPO_4F$ (middle and right) powders.



Supplementary figure 4. Elemental distribution maps of Na, Ga, F and P.



Supplementary figure 5. Typical EDX spectrum of $NaGaPO_4F$.



Supplementary figure 6. Electron diffraction tomography patterns of $NaGaPO_4F$

Supplementary table 1. Parameters of the Rietveld refinement.

Formula	$NaGaPO_4F$
Space Group	$Pna2_1$
a, Å	12.49296(15)
b, Å	6.10945(8)
c, Å	10.41321(13)
V, Å^3	794.789(17)
GOF	3.44
R_p, %	1.15
R_{wp}, %	1.53

Supplementary Table 2. Atomic coordinates and isotropic atomic displacement parameters.

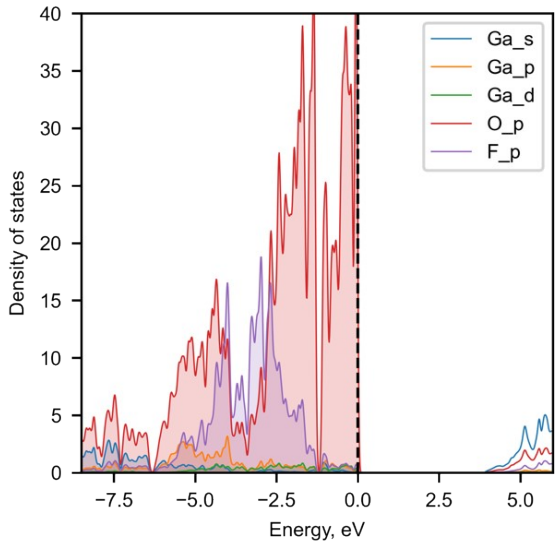
Atom	*x/a*	*y/b*	*z/c*	Occupancy	U_{iso}, Å^2
Na1	0.8582(4)	0.7151(7)	0.0480(4)	1.0	0.036(1)
Na2.1	0.8990(5)	0.2683(10)	0.3346(8)	0.7880	0.036(1)

Na2.2	0.9173(18)	0.323(5)	0.393(3)	0.2120	0.036(1)
Ga1	0.38928(8)	0.51449(17)	0.76610(18)	1.0	0.0054(1)
Ga2	0.23257(6)	0.26271(18)	0.000000	1.0	0.0054(1)
P1	0.4832(2)	0.3238(4)	0.0225(4)	1.0	0.0077(4)
P2	0.18708(16)	0.5166(5)	0.2568(4)	1.0	0.0077(4)
O1	0.4708(4)	0.5070(11)	-0.0774(5)	1.0	0.0062(4)
O2	0.4930(5)	0.4389(7)	0.1532(5)	1.0	0.0062(4)
O3	0.3829(4)	0.1783(8)	0.0221(7)	1.0	0.0062(4)
O4	0.5821(4)	0.1817(8)	-0.0024(8)	1.0	0.0062(4)
O5	0.1195(4)	0.3176(8)	0.2966(7)	1.0	0.0062(4)
O6	0.1115(4)	0.7137(8)	0.2456(5)	1.0	0.0062(4)
O7	0.2742(5)	0.5530(9)	0.3601(7)	1.0	0.0062(4)
O8	0.2501(4)	0.4978(15)	0.1303(7)	1.0	0.0062(4)
F1	0.2849(4)	0.5265(10)	0.6244(5)	1.0	0.0090(9)

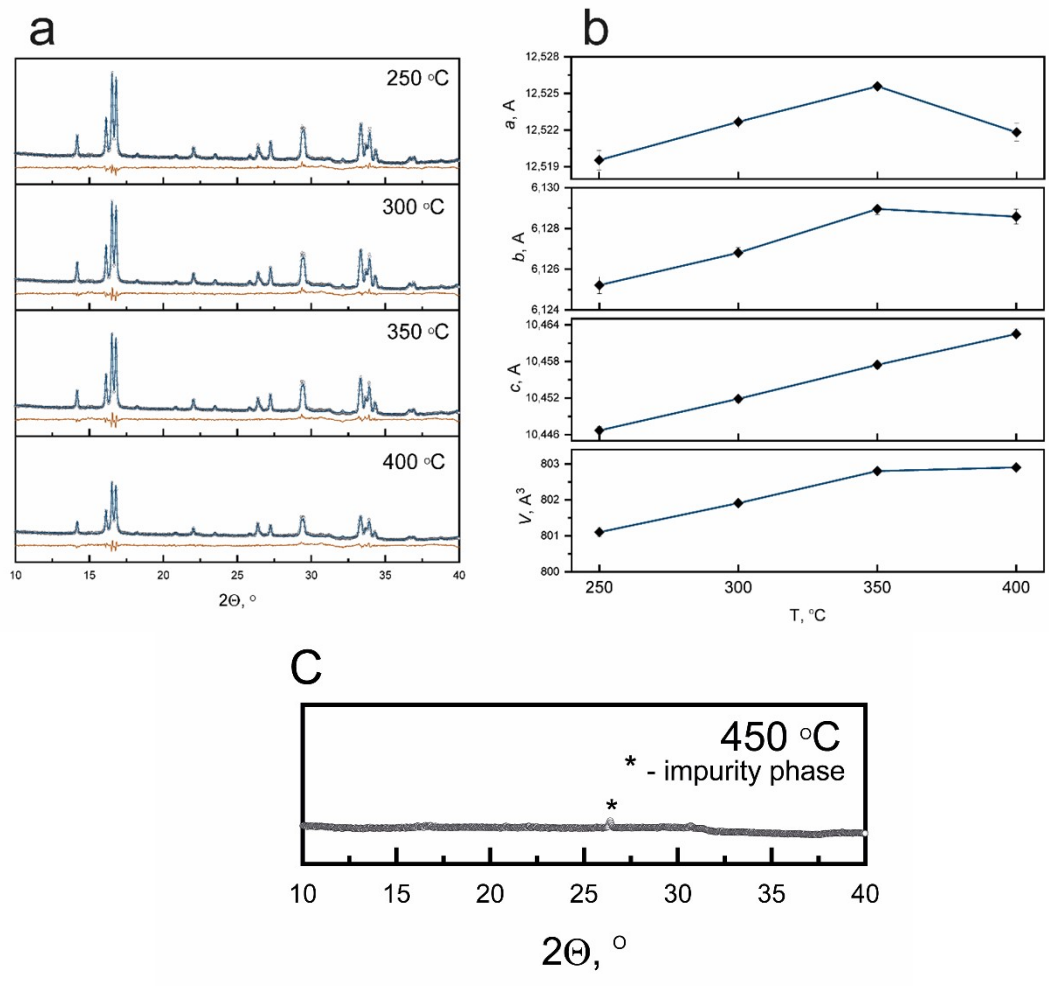
F2	0.2558(4)	0.4845(13)	0.8791(5)	1.0	0.0090(9)

Supplementary Table 3. Interatomic distances.

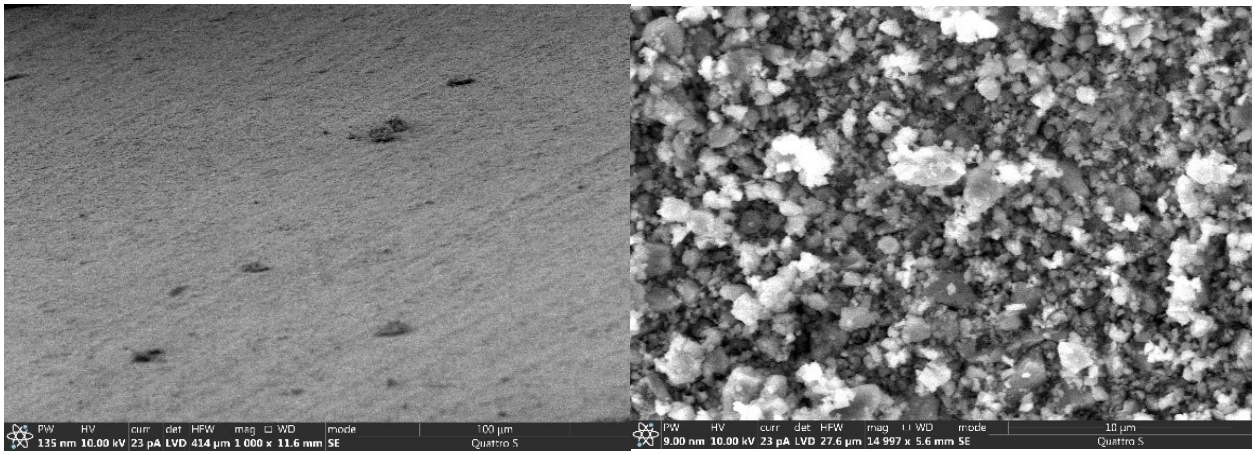
Bond	Distance, Å	Bond	Distance, Å
Ga1-O1	1.922(5)	P1-O1	1.536(6)
Ga1-O2	1.904(6)	P1-O2	1.537(6)
Ga1-O5	1.882(5)	P1-O3	1.536(5)
Ga1-O6	1.850(5)	P1-O4	1.532(5)
Ga1-F1	1.970(5)	P2-O5	1.537(6)
Ga1-F2	2.049(5)	P2-O6	1.535(6)
Ga2-O3	1.961(4)	P2-O7	1.546(7)
Ga2-O4	1.911(4)	P2-O8	1.540(7)
Ga2-O7	1.942(6)		
Ga2-O8	1.987(8)		
Ga2-F1	1.952(6)		
Ga2-F2	1.873(6)		



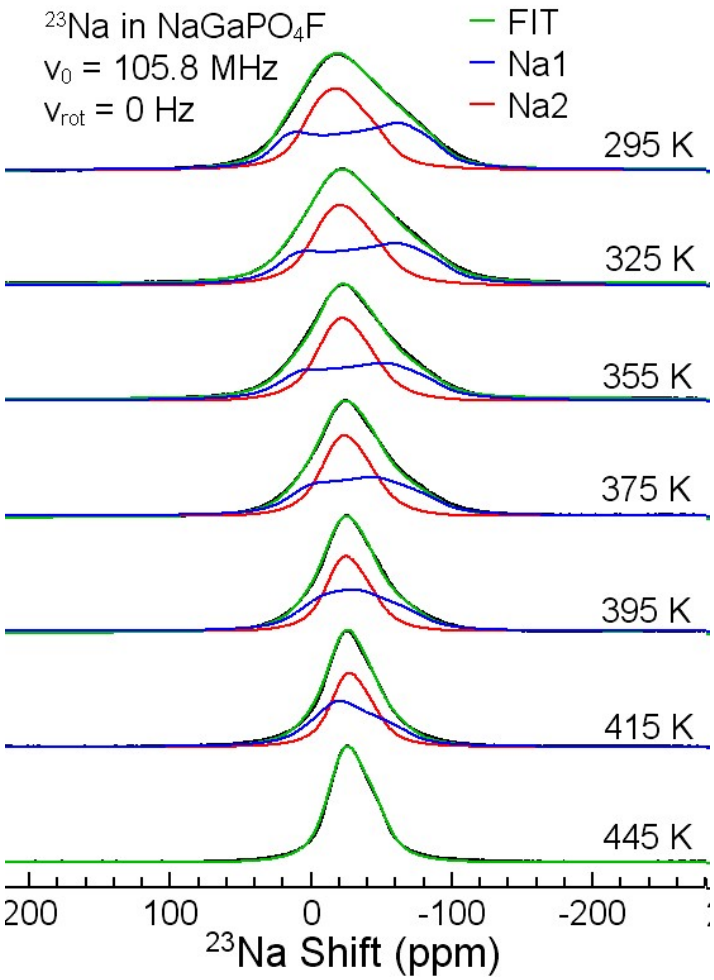
Supplementary figure 7. The orbital-projected density of states for Ga, O and F atoms in $NaGaPO_4F$ calculated with GGA PBE.



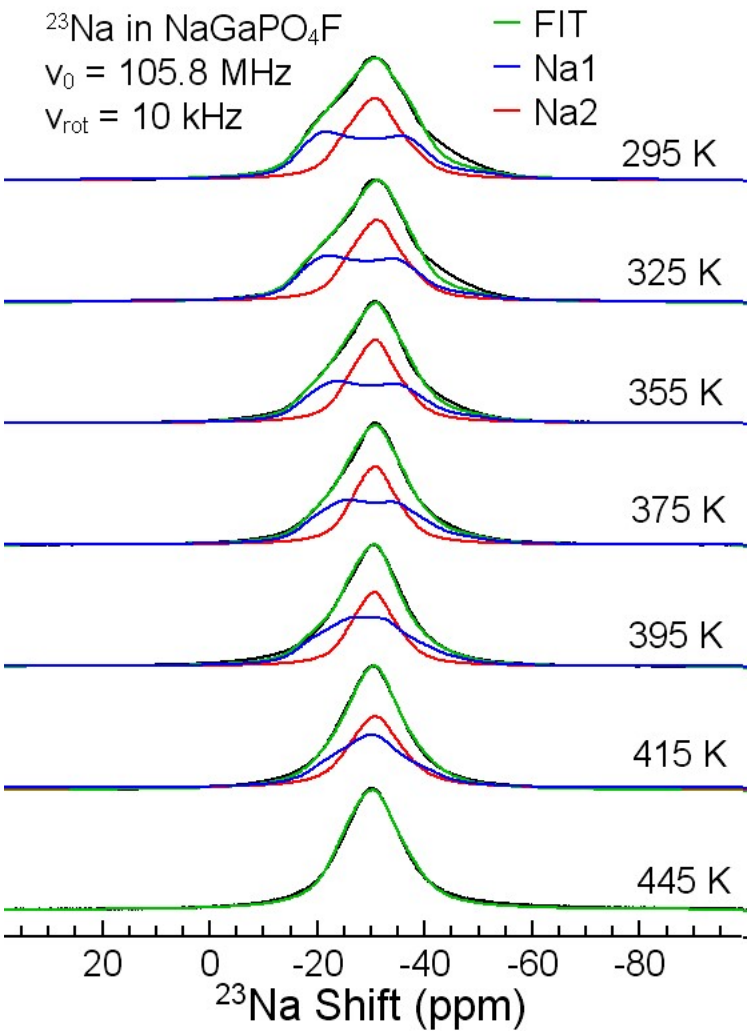
Supplementary Figure 8. High temperature XRD pattern of $NaGaPO_4F$ (a), unit cell parameters at different temperatures (b), and XRD pattern of $NaGaPO_4F$ at 450ºC (c)



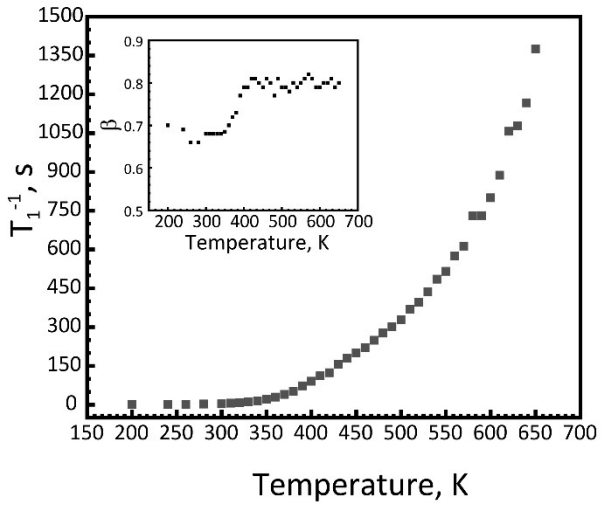
Supplementary figure 9. SEM images of cross-section $NaGaPO_4F$ pellet.



Supplementary figure 10. Typical ^{23}Na NMR spectra obtained at the resonance frequency ν_0 = 105.8 MHz with MAS speed, ν_{rot} = 0 Hz, in the temperature range 295-445 K for $NaGaPO_4F$. The colored lines show the results of spectra deconvolution (see text)



Supplementary figure 11. Typical ^{23}Na NMR spectra acquired at the resonance frequency ν_0 = 105.8 MHz with MAS speed, ν_{rot} = 10 kHz, in the temperature range 295-445 K for $NaGaPO_4F$. The colored lines show the results of spectra deconvolution (see text)



Supplementary figure 12. Spin-lattice relaxation rate of the ^{23}Na nuclei in $NaGaPO_4F$, measured at a resonance frequency ν_0 = 132.3 MHz in the temperature range 200-650 K. The inset shows the temperature behavior of the coefficient β

Supplementary table 4. Comparison of DFT relaxed and experimentally refined lattice parameters.

	SXRD	DFT	Diff, %
a, Å	12.49287(15)	12.67	-1.40
b, Å	6.10929(8)	6.21	-1.62
c, Å	10.41331(13)	10.56	-1.39
Volume, Å^3	794.772(17)	831.36	-4.40

Supplementary table 5. NEB calculated activation barriers for the selected Na vacancy-assisted hops. The hope distance was calculated as a sum of linear segments between images.

Na hop	Activation energy, eV	Pathway distance, Å	Hop distance, Å
P1	0.12	4.40	4.35
P2	0.22	4.04	3.86
P3	0.13	3.93	3.81