

Thermally activated multistep alteration of Fe²⁺-bearing fluorophlogopite revealed by in situ Raman spectroscopy

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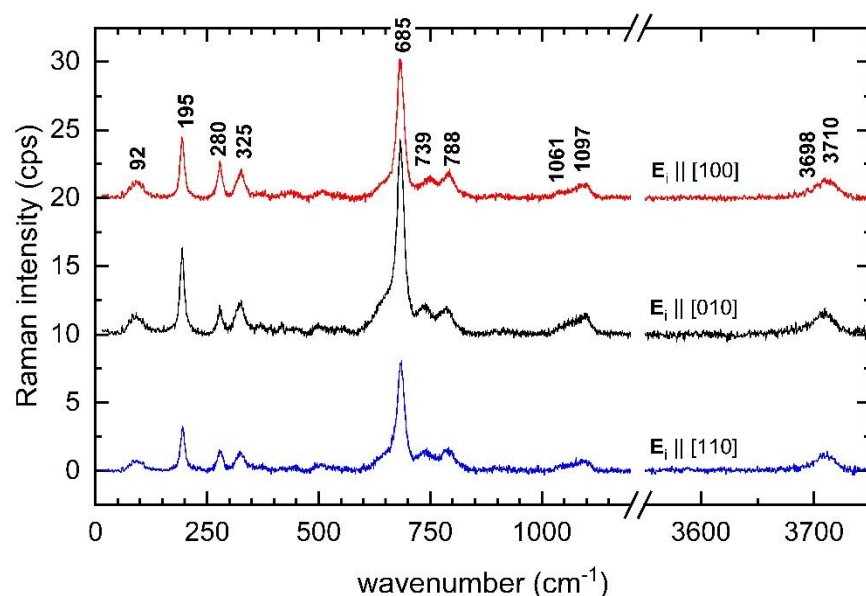


Figure S1: Comparison of the initial room-temperature Raman spectra of fluorophlogopite measured in the three scattering geometries described in the main text. The spectra are vertically offset for clarity.

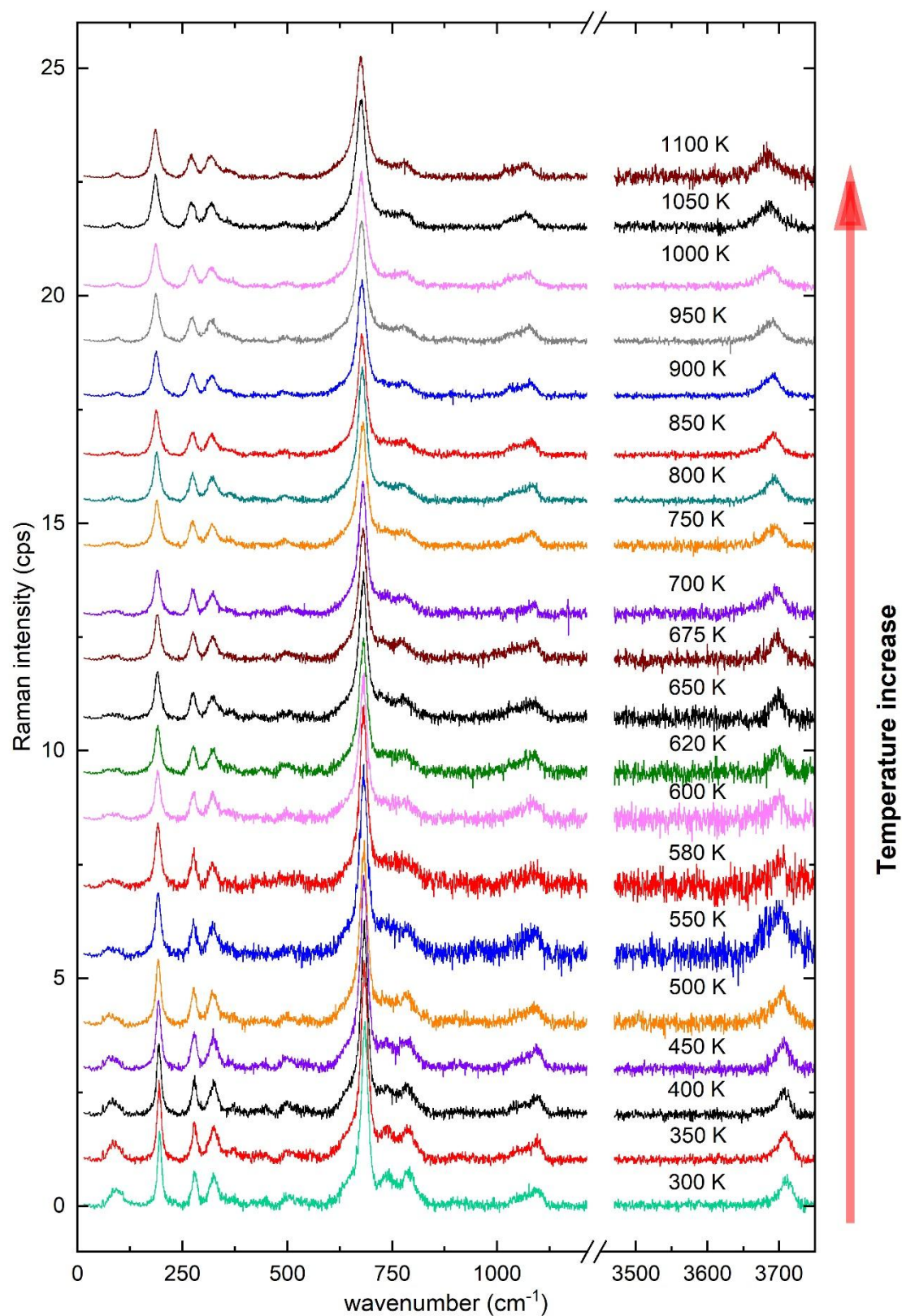


Figure S2: Raman spectra of the B27 single crystal measured with $E_i \parallel [110]$ during heating in the range 300-1100 K (run 1). For better comparison the spectra are vertically offset.

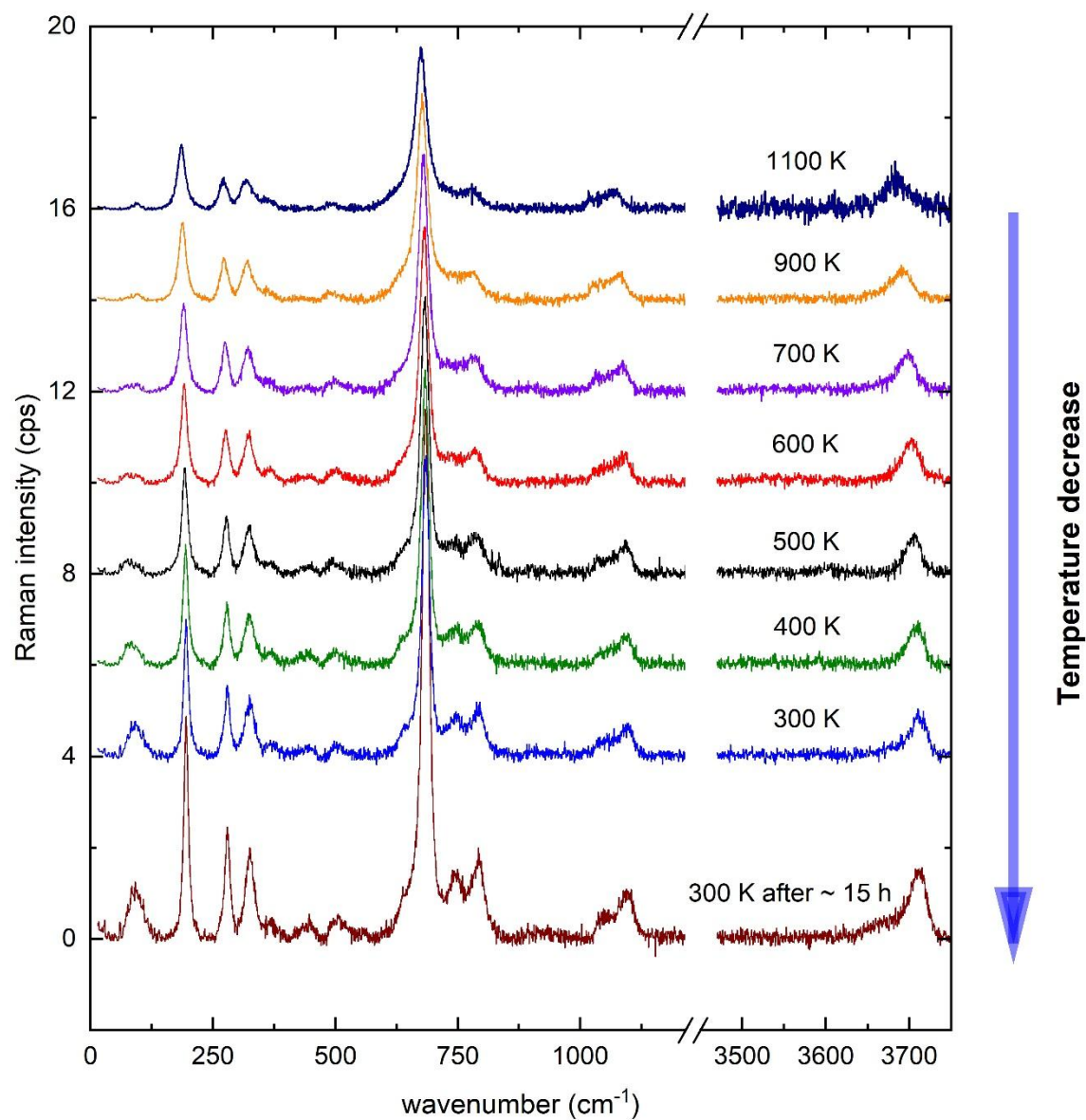


Figure S3: Raman spectra of the B27 single crystal measured with $E_i \parallel [110]$ during cooling in the range 1100-300 K (run 1). The spectra are vertically offset for clarity.

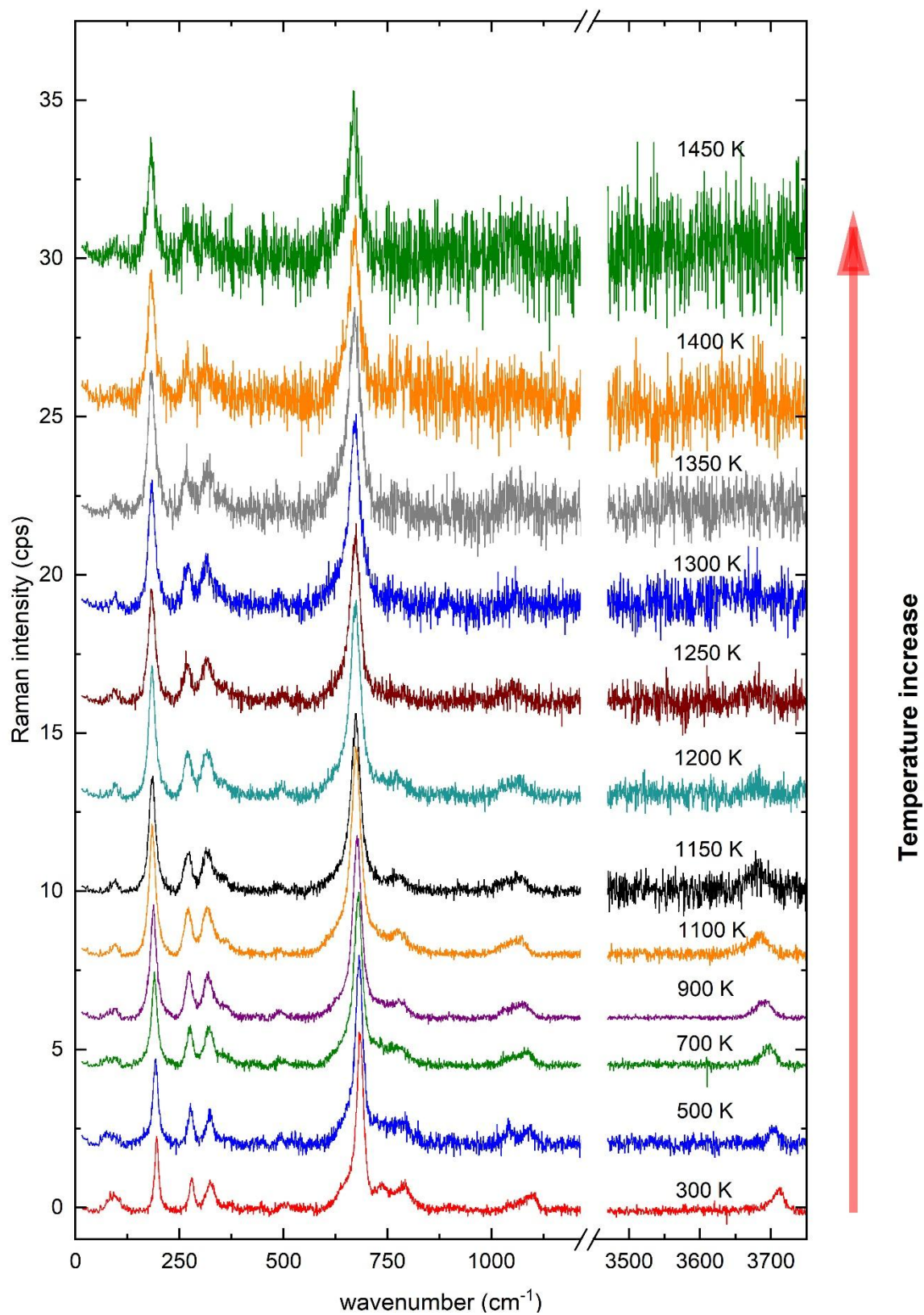


Figure S4: Raman spectra of the B27 single crystal measured with $E_i \parallel [110]$ during heating at temperature between 300 and 1450 K (run 2). For better comparison the spectra are vertically offset.

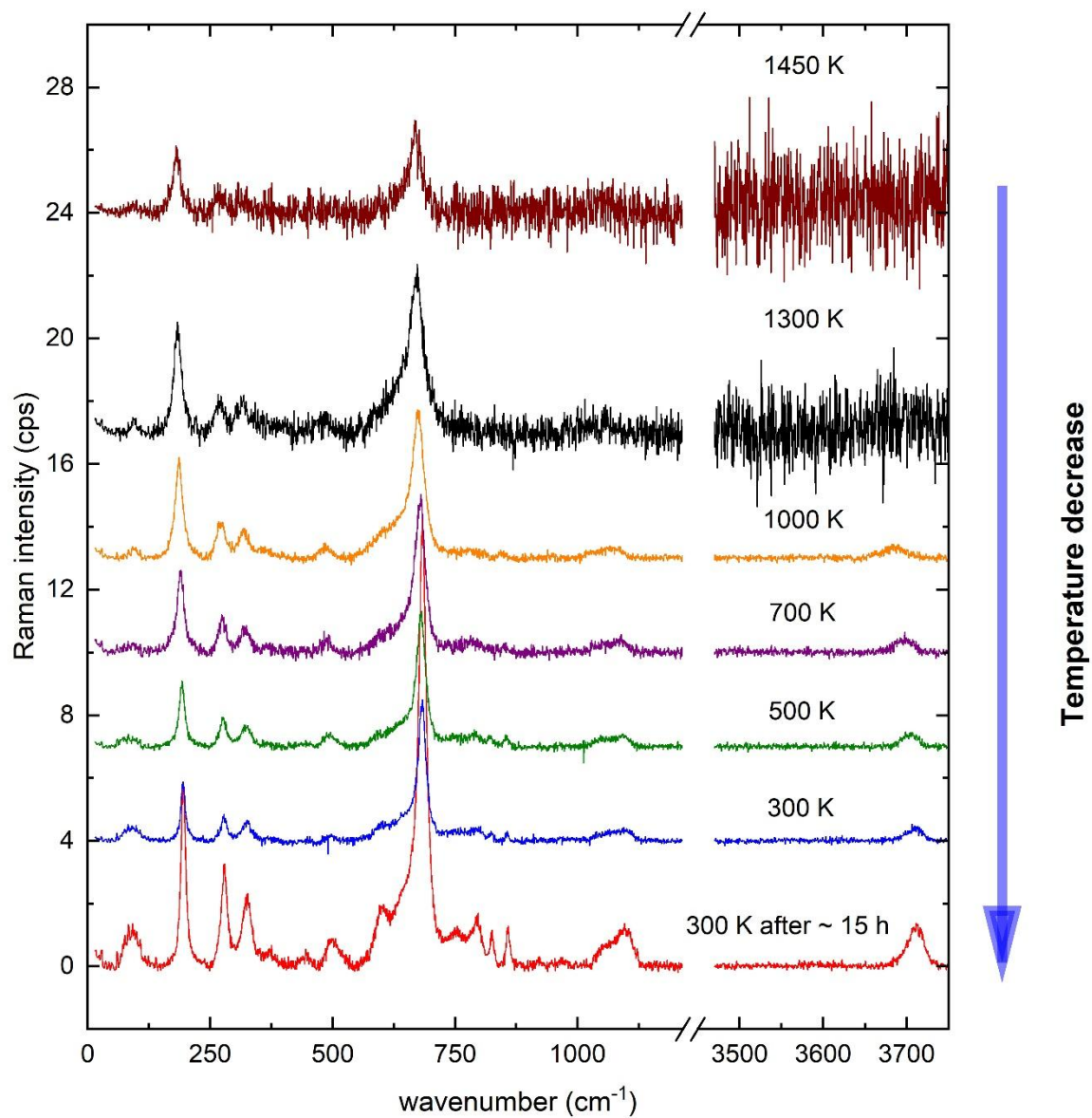


Figure S5: Raman spectra of the B27 single crystal measured with $E_i \parallel [110]$ during cooling at temperature between 1450 and 300 K (run 2). The spectra are vertically offset for clarity.

Table S1: Average chemical composition (wt. %), chemical formulae (in apfu), and statistical standard deviation (σ) of the studied fluorophlogopite crystal, as determined by EMPA, before and after the *in situ* high-temperature Raman scattering experiments up to 1450 K. FeO, H₂O, and Fe₂O₃ were calculated following the guidelines of the charge balance approach of Li et al. (2020). Abbreviations in the table: b.d.l.: below detection limit; apfu: atoms per formula units; O_{exc.} = O excess; X_F = F/(F+OH).

	Untreated		Heat-treated (1450 K)		Untreated		Heat-treated (1450 K)	
	Av. (wt.%)	σ	Av. (wt.%)	σ	apfu	σ	apfu	σ
SiO ₂	40.3	0.4	40.4	0.3	^T Si = 2.99	0.03	^T Si = 2.99	0.02
TiO ₂	0.54	0.03	0.45	0.01	^T Ti = 0.020 ^M Ti = 0.010	0.002	^T Ti = 0.0250 ^M Ti = 0.0	0.0006 0.0
Al ₂ O ₃	11.3	0.3	11.35	0.08	^T Al = 0.99	0.03	^T Al = 0.99	0.01
FeO _{total}	2.38	0.07	2.33	0.08	-	-	-	-
MnO	0.09	0.04	0.11	0.01	^M Mn = 0.006	0.003	^M Mn = 0.007	0.001
MgO	25.4	0.4	25.7	0.3	^M Mg = 2.81	0.04	^M Mg = 2.84	0.03
CaO	b.d.l.	-	b.d.l.	-	-	-	-	-
Na ₂ O	0.38	0.02	0.42	0.01	^A Na = 0.055	0.003	^A Na = 0.060	0.001
K ₂ O	9.83	0.11	9.91	0.05	^A K = 0.93	0.01	^A K = 0.930	0.005
Cr ₂ O ₃	b.d.l.	-	b.d.l.	-	-	-	-	-
NiO	b.d.l.	-	b.d.l.	-	-	-	-	-
CuO	b.d.l.	-	b.d.l.	-	-	-	-	-
ZnO	b.d.l.	-	b.d.l.	-	-	-	-	-
SrO	b.d.l.	-	b.d.l.	-	-	-	-	-
BaO	0.15	0.02	0.18	0.03	^A Ba = 0.0050	0.0005	^A Ba = 0.005	0.001
Cl	b.d.l.	-	b.d.l.	-	-	-	-	-
F	6.8	0.8	7.6	0.7	^X F = 1.60	0.19	^X F = 1.78	0.16
-O=F+Cl	2.9	0.3	3.2	0.3	-	-	-	-
Sum _{initial}	94.2	0.8	95.3	0.7	-	-	-	-
FeO _{calculated}	2.38	0.07	1.87	0.06	^M Fe ²⁺ = 0.148	0.004	^M Fe ²⁺ = 0.116	0.004
Fe ₂ O ₃ _{calculated}	0.00	-	0.52	0.02	^M Fe ³⁺ = 0.0	0.0	^M Fe ³⁺ = 0.029	0.001
H ₂ O _{calculated}	0.86	0.05	0.39	0.05	^X OH = 0.40	0.02	^X OH = 0.19	0.02
Sum _{calculated}	95.1	0.8	95.6	0.7	-	-	-	-
					^X O _{exc.} = 0.0	-	^X O _{exc.} = 0.03	-
X _F	0.79	0.09	0.90	0.08	-	-	-	-

Table S2. Crystal parameters and refinement details from single-crystal XRD analysis at room temperature of untreated and heat-treated fluorophlogopite.

	Untreated	Heat-treated (1450 K)
Symmetry, space group	Monoclinic, <i>C2/m</i>	
λ (Å)	0.71075	
a (Å)	5.3066(4)	5.3040(6)
b (Å)	9.1936(12)	9.1858(9)
c (Å)	10.1663(9)	10.1603(14)
β (°)	100.034(8)	100.025(8)
V (Å ³)	488.39(9)	487.47(10)
Z	2	
Crystal dimensions (mm)	0.28 x 0.2 x 0.02	0.2 x 0.1 x 0.01
μ (mm ⁻¹)	1.398	1.392
# of reflections	10133	8178
$\theta_{\max}$ (°)	30	
R_{int}	0.027	0.043
$h_{\min}, h_{\max}, k_{\min}, k_{\max}, l_{\min}, l_{\max}$	-7, 7, -12, 12, -14, 14	
Obs. Reflections, $N_{\text{obs}}, N_{\text{all}}$	$I > 3\sigma(I)$, 688, 762	$I > 3\sigma(I)$, 595, 762
$R_{\text{obs}}, R_{\text{all}}$	0.026, 0.029	0.052, 0.065
$wR_{\text{obs}}, wR_{\text{all}}$	0.072, 0.076	0.125, 0.132
GoF	1.31	1.87
$\delta_+(\rho), \delta_-(\rho)$ (e Å ⁻³)	0.8, -0.25	1.61, -0.53