

Figure 1: Top: second voltage-composition continuous galvanostatic data for $\text{Na}_3\text{V}_2(\text{PO}_4)_2\text{F}_3$ and $\text{Na}_3\text{V}_2(\text{PO}_4)_2\text{F}_{2.5}\text{O}_{0.5}$ cycled in Na cells at a rate of C/20 between 2.5 and 4.3 V vs Na^+/Na – Bottom: first two charge steps obtained in intermittent galvanostatic mode, i.e. a 10 minutes galvanostatic charge at a current corresponding to a rate of C/25 and followed by a relaxation until the change in voltage is lower than 1 mV/h.

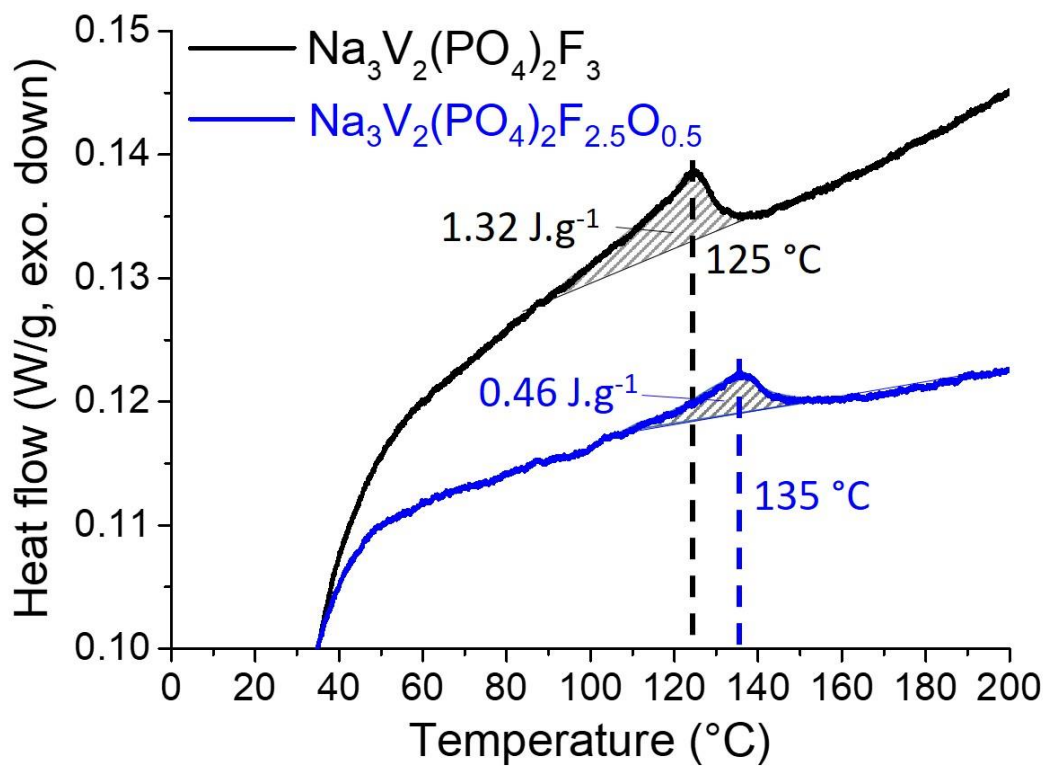


Figure 2: Top: Differential Scanning Calorimetry data obtained by heating $\text{Na}_3\text{V}_2(\text{PO}_4)_2\text{F}_3$ and $\text{Na}_3\text{V}_2(\text{PO}_4)_2\text{F}_{2.5}$ under argon, from RT to 200 °C

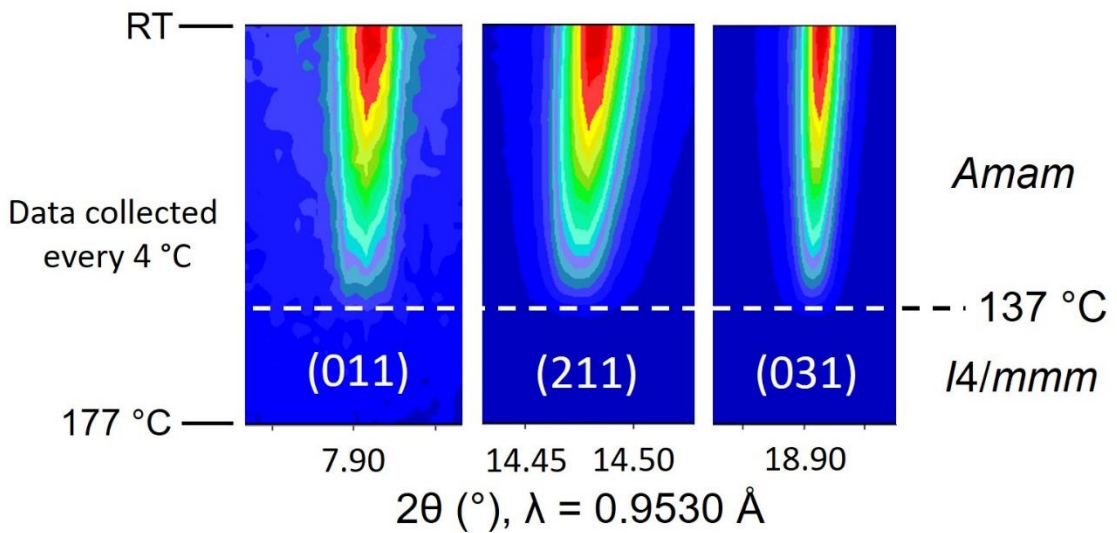
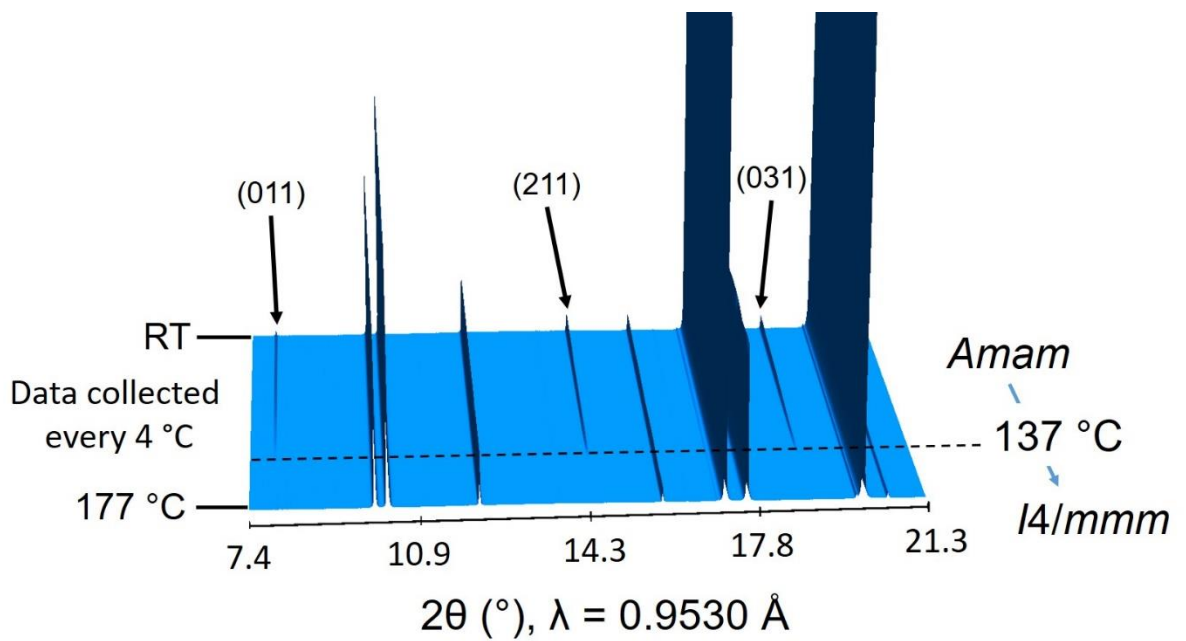


Figure 3: *In situ* SXPD patterns obtained heating $Na_3V_2(PO_{4/2}F_{2.5}O_{0.5})$ from RT to 177 °C, SXPD patterns collected every 4 °C

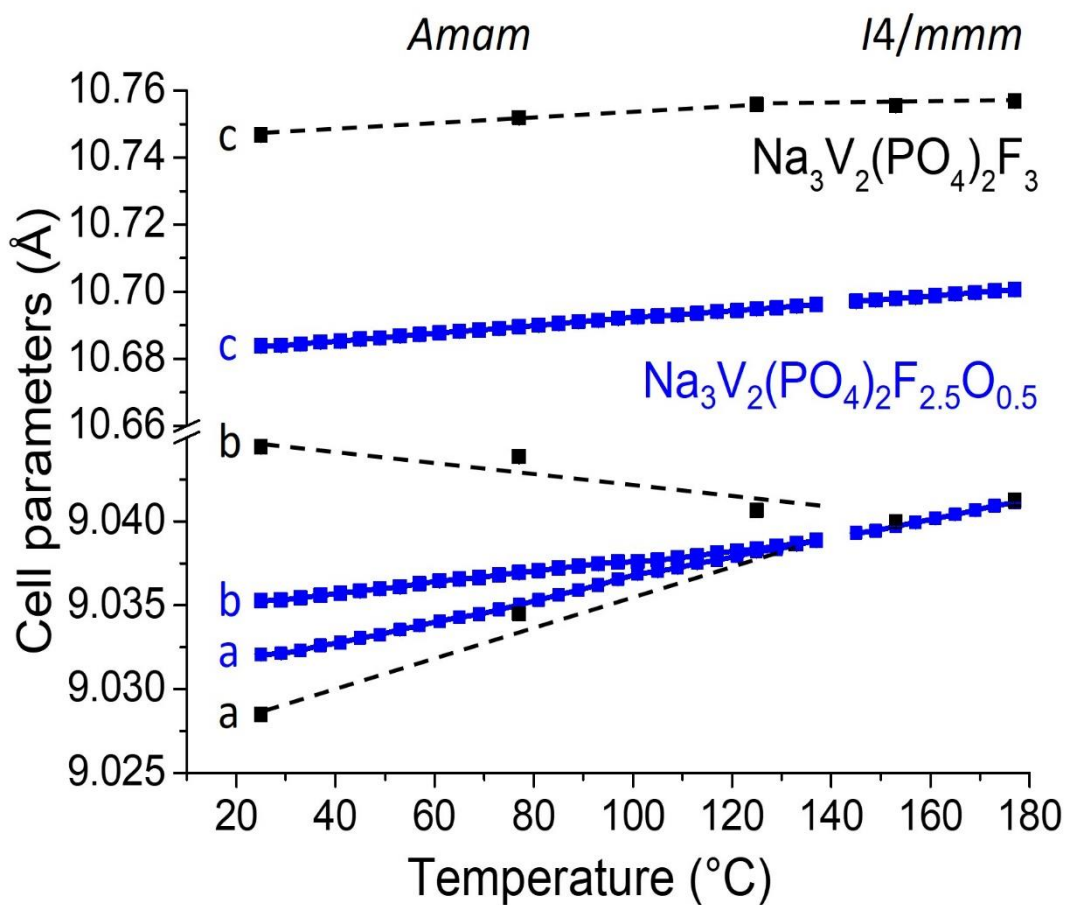


Figure 4: Cell parameters evolution observed upon heating $\text{Na}_3\text{V}_2(\text{PO}_4)_2\text{F}_{2.5}\text{O}_{0.5}$ (blue) and $\text{Na}_3\text{V}_2(\text{PO}_4)_2\text{F}_3$ from RT to 177 °C (black, data from Bianchini *et al.*¹⁵)

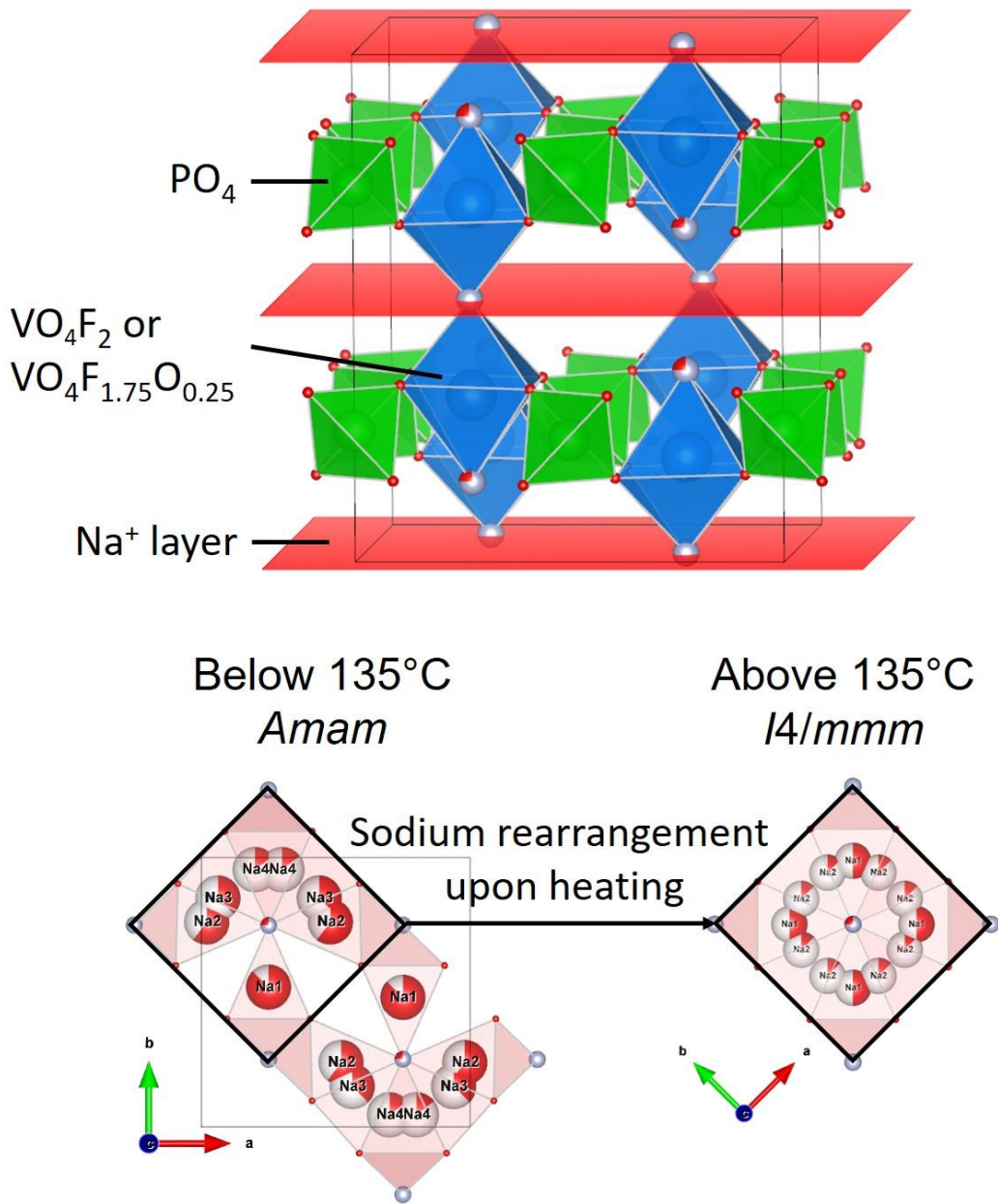


Figure 5: Room and high temperature structures of $\text{Na}_3\text{V}_2(\text{PO}_4)_2\text{F}_{2.5}\text{O}_{0.5}$ highlighting changes in the sodium ions distribution

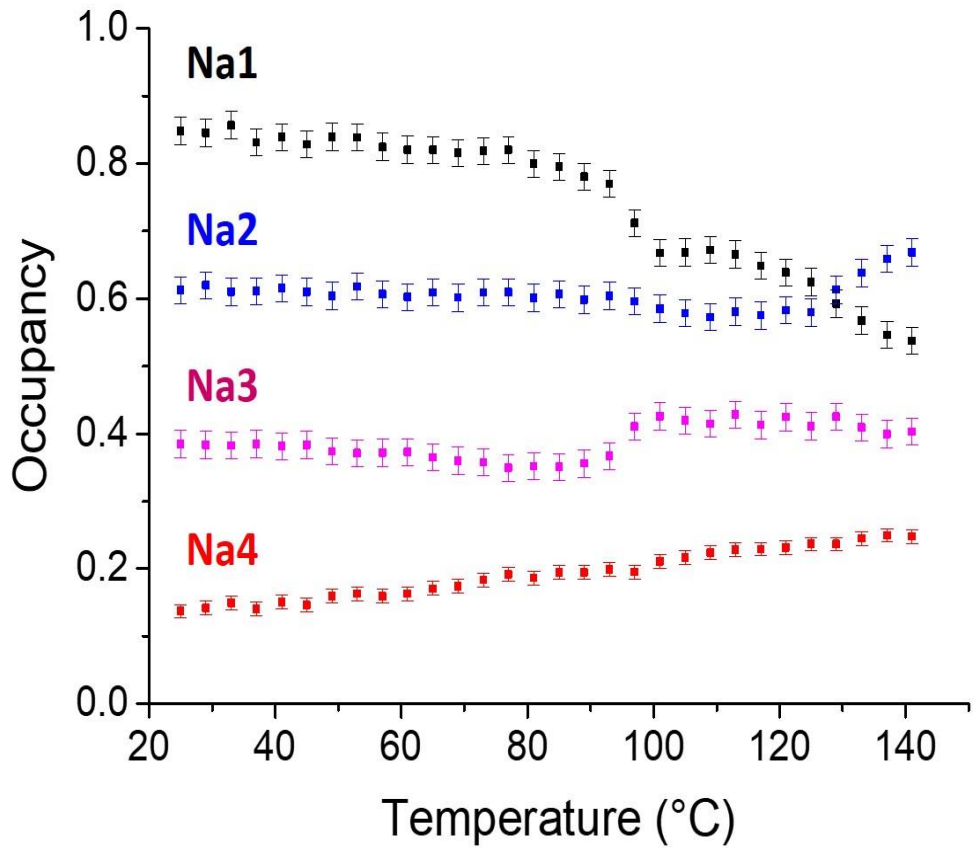


Figure 6: Changes in the sodium ions distribution within the structure of $\text{Na}_3\text{V}_2(\text{PO}_4)_2\text{F}_{2.5}\text{O}_{0.5}$ from RT to 140°C

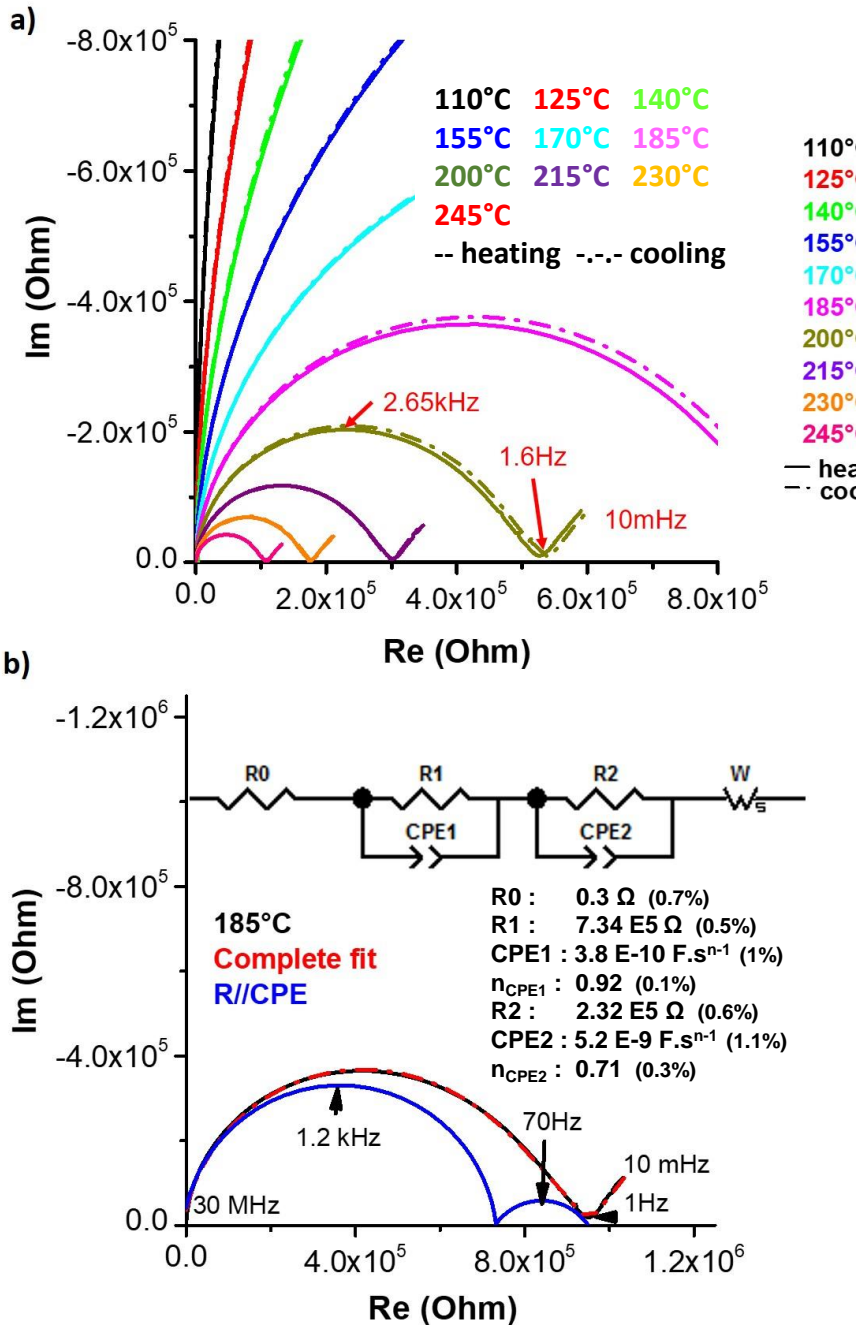


Figure 7: a) Nyquist diagrams of $Na_3V_2(PO_4)_2F_3$ (Au/ $Na_3V_2(PO_4)_2F_3$ /Au) upon heating and cooling as a function of the temperature – b) Identification of grain and grain boundaries in Nyquist diagram at 185 °C with equivalent circuit

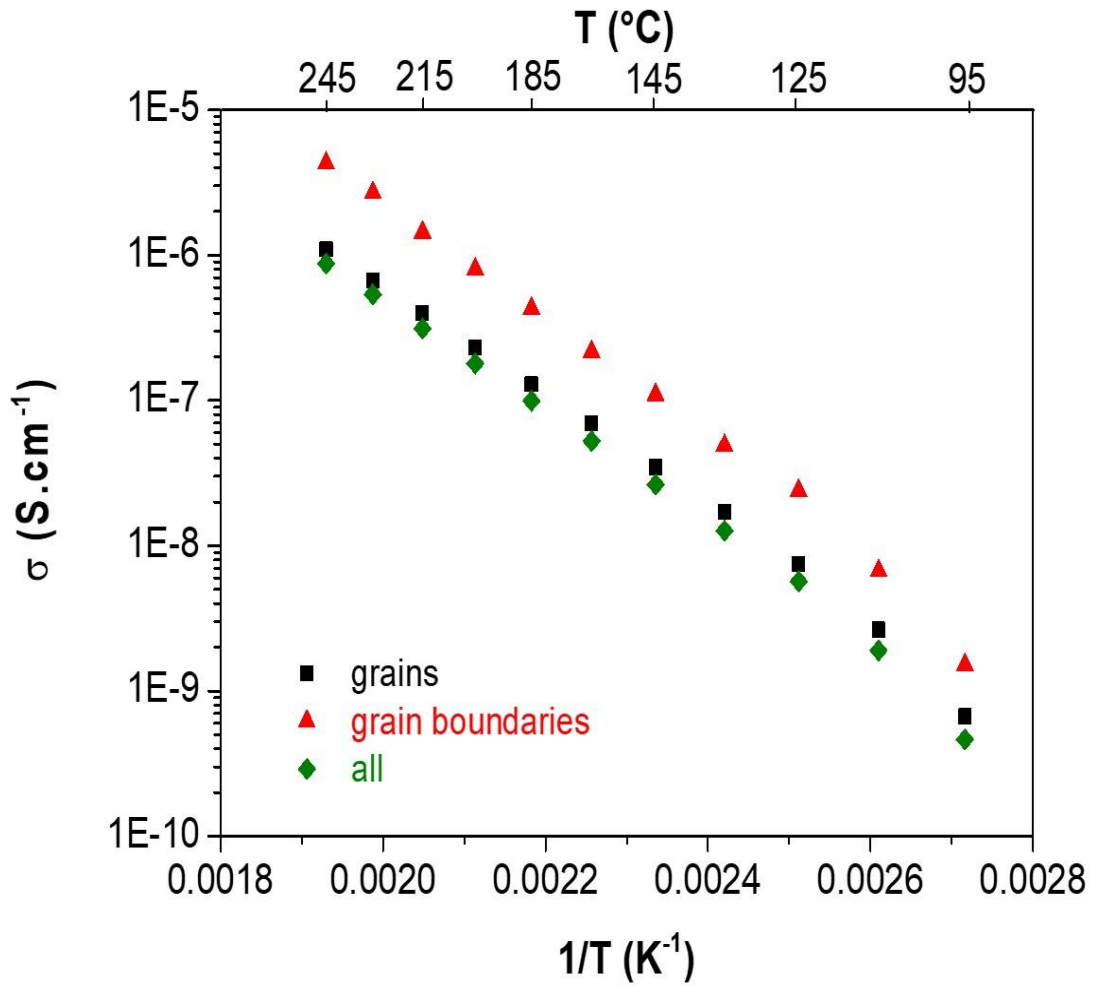


Figure 8: Evolution of the total conductivity with the contribution of grain and grain boundaries signal in function of temperature. Comparable results in heating and cooling.

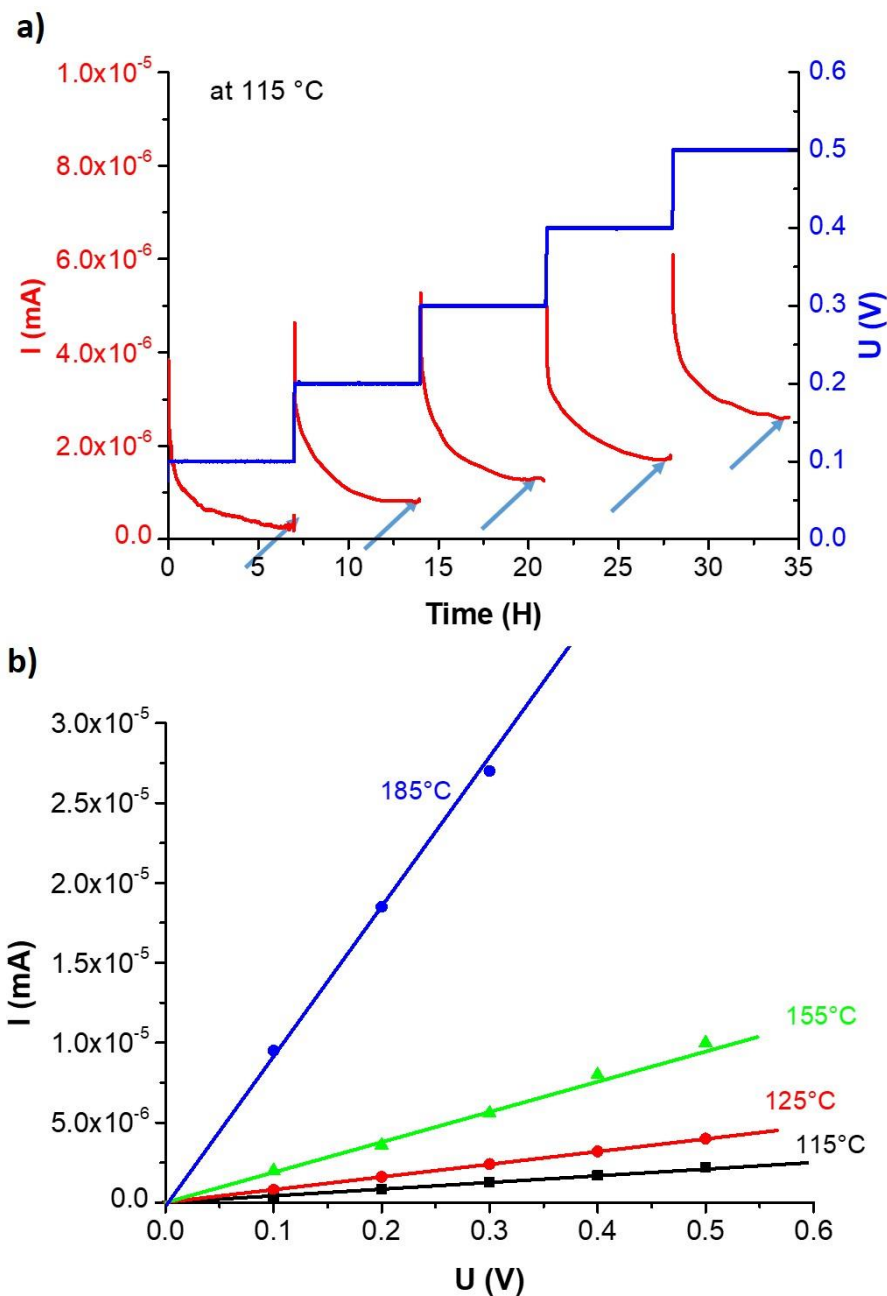


Figure 9 a) DC measurement of $\text{Na}_3\text{V}_2(\text{PO}_4)_2\text{F}_3$ ($\text{Au}/\text{Na}_3\text{V}_2(\text{PO}_4)_2\text{F}_3/\text{Au}$): evolution of current in function of polarization. Arrows: measurement of current after stabilization b) Changes in the relaxation current as a function of the polarization and temperature for $\text{Na}_3\text{V}_2(\text{PO}_4)_2\text{F}_3$

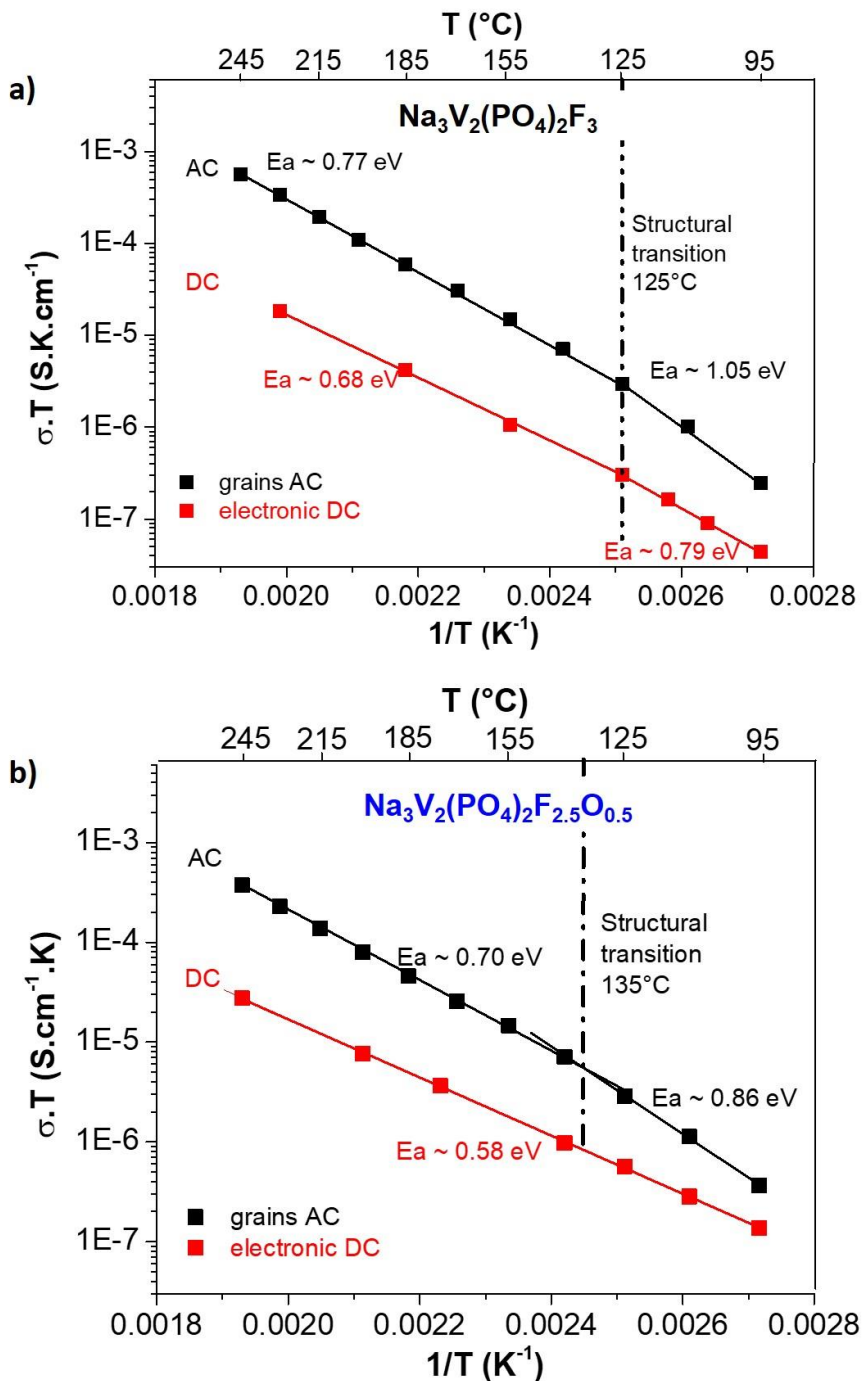


Figure 10: Evolution of the electronic (DC) and total (AC) conductivities of grains obtained from the Arrhenius plots: for $\text{Na}_3\text{V}_2(\text{PO}_4)_2\text{F}_3$ (a) and for $\text{Na}_3\text{V}_2(\text{PO}_4)_2\text{F}_{2.5}\text{O}_{0.5}$ (b). Similar results obtained upon heating and cooling

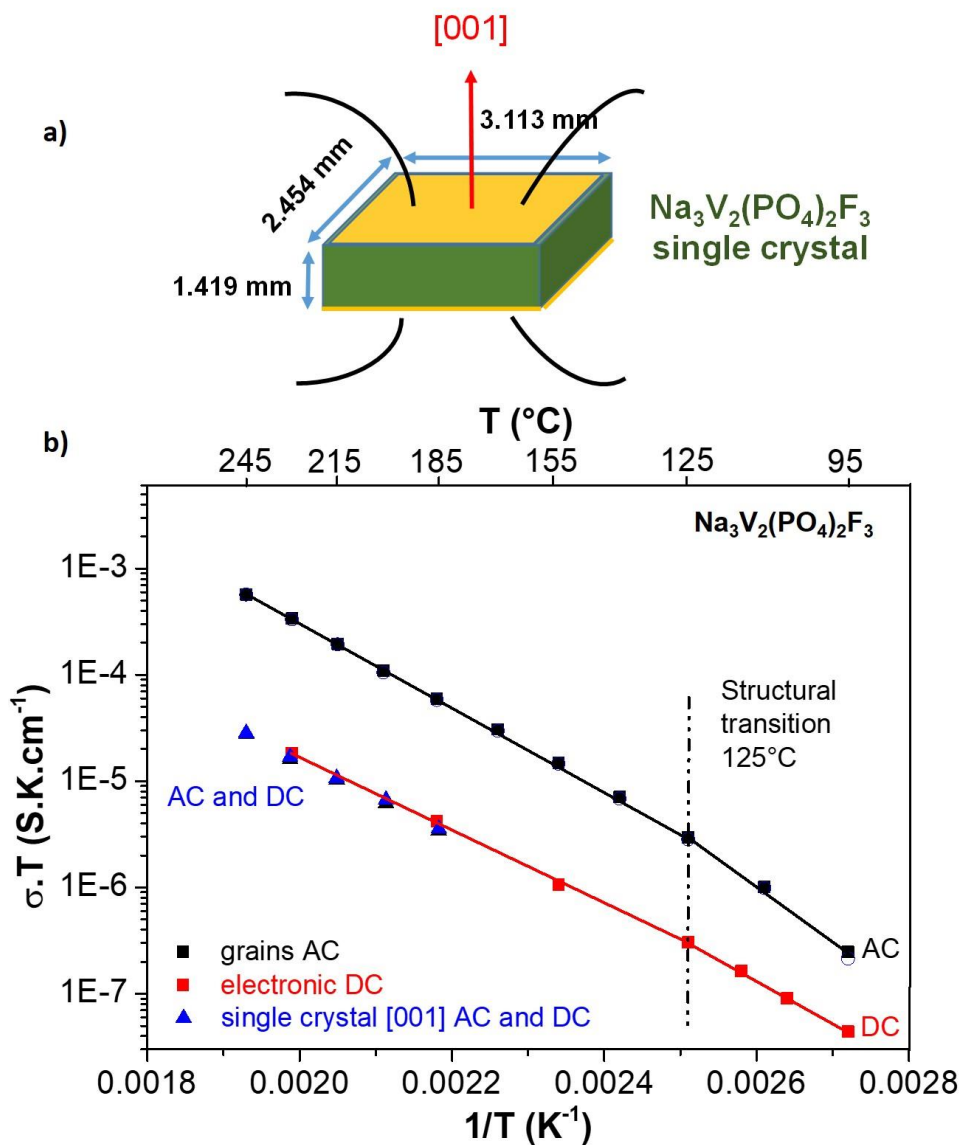
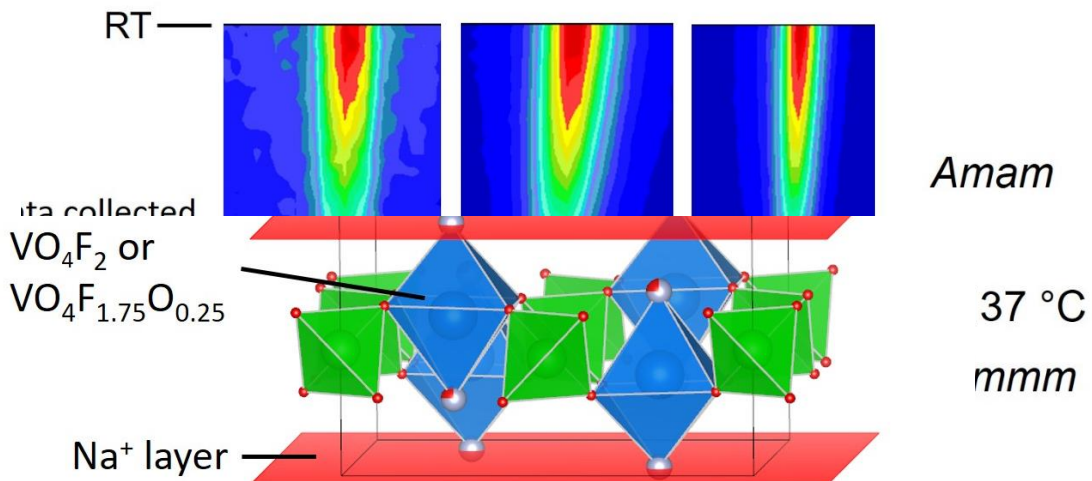
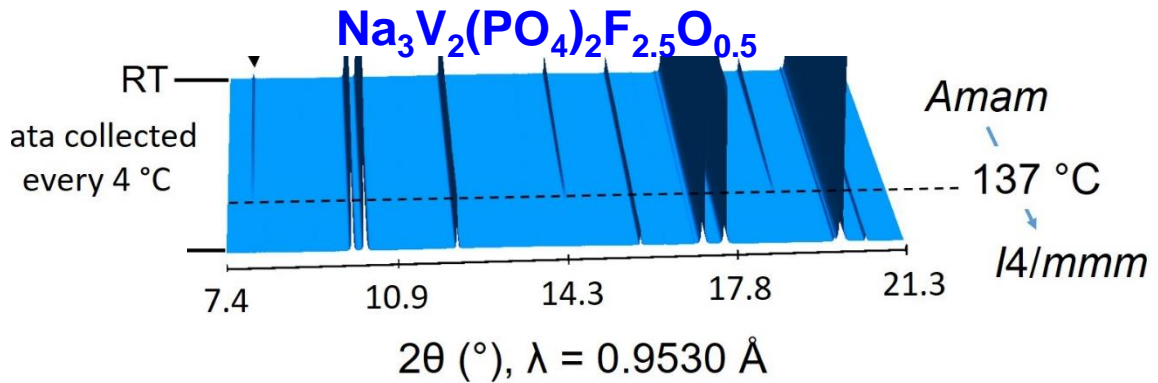


Figure 11: a) Scheme of the rectangular $\text{Na}_3\text{V}_2(\text{PO}_4)_2\text{F}_3$ single crystal giving its dimensions and the orientation considered for impedance analyses. Gold surfaces are those used to make the specific contacts required for the experiment – b) Evolution of the electronic and grains conductivities obtained from the Arrhenius plots for $\text{Na}_3\text{V}_2(\text{PO}_4)_2\text{F}_3$ powders and total conductivity of $\text{Na}_3\text{V}_2(\text{PO}_4)_2\text{F}_3$ single crystal along the $[001]$ axis. Similar results obtained upon heating and cooling.

	Below order-disorder transition 95 °C				Above order-disorder transition 200 °C			
	electronic		ionic		electronic		ionic	
	σ (S.cm ⁻¹)	Ea (eV) (R ²)	σ (S.cm ⁻¹)	Ea (eV) (R ²)	σ (S.cm ⁻¹)	Ea (eV) (R ²)	σ (S.cm ⁻¹)	Ea (eV) (R ²)
Na ₃ V ₂ (PO ₄) ₂ F ₃	1.22 E-10	0.79 (0.998)	4.98 E-10	1.10 (0.999)	1.42 E-8	0.68 (0.997)	2.16 E-7	0.79 (0.998)
Na ₃ V ₂ (PO ₄) ₂ F _{2.5} O _{0.5}	3.76 E-10	0.58 (0.9997)	6.38 E-10	0.97 (0.9993)	1.63 E-8	0.58 (0.9997)	1.61 E-7	0.72 (0.9993)

Table 1: Evolution of electronic and ionic conductivities and activation energy before and after structural transition for Na₃V₂(PO₄)₂F₃ and Na₃V₂(PO₄)₂F_{2.5}O_{0.5}. Due to error on fit and on measurements of surface and thickness, an error around 5% can be estimated for the different conductivities values. The R² on linear fit is indicated in table

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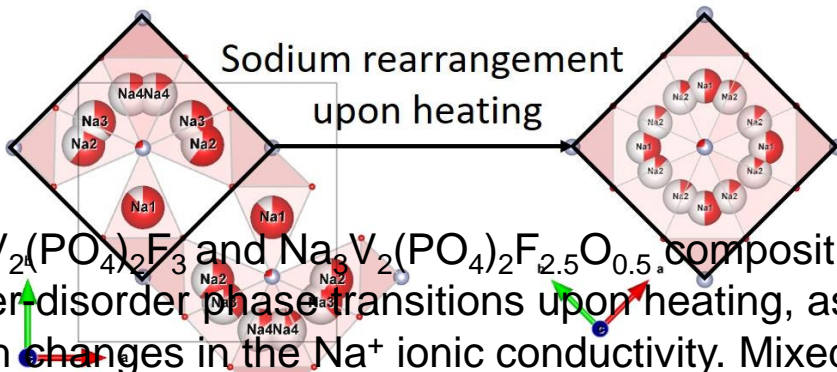


Below 135 °C

Amam

Above 135 °C

I4/mmm



$\text{Na}_3\text{V}_2(\text{PO}_4)_2\text{F}_3$ and $\text{Na}_3\text{V}_2(\text{PO}_4)_2\text{F}_{2.5}\text{O}_{0.5}$ compositions show order-disorder phase transitions upon heating, associated with changes in the Na^+ ionic conductivity. Mixed $\text{V}^{3+}/\text{V}^{4+}$ valence within the bi-octahedral units $\text{V}_2\text{O}_8\text{F}_{3-y}\text{O}_y$ leads to better transport properties.