

Supporting information

Advances in the synthesis and structure of α -canaphite: a multitool and multiscale study

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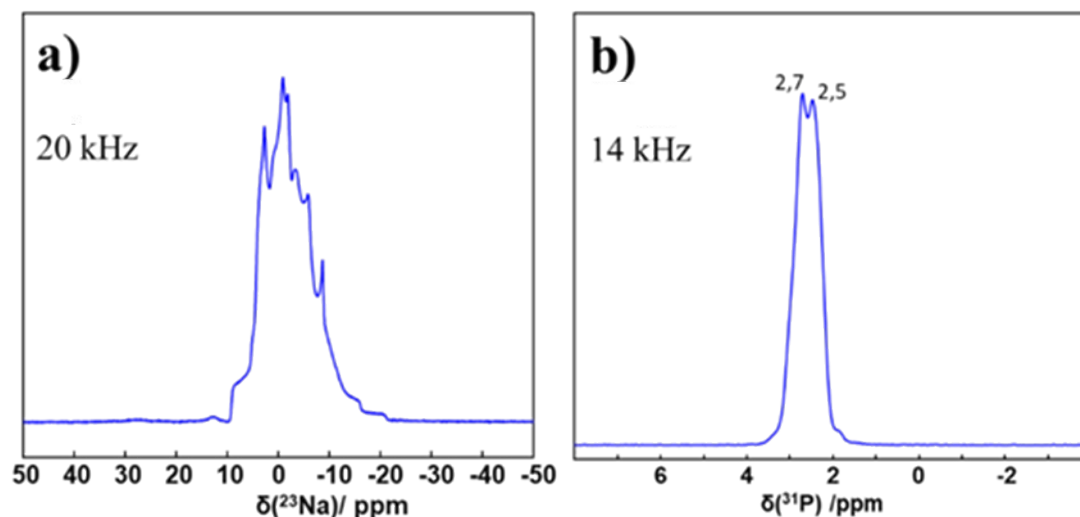


Figure S1: ²³Na (a) and ³¹P (b) MAS NMR spectra at 14.1 T of the as-synthesized sodium pyrophosphate precursor ($\text{Na}_4\text{P}_2\text{O}_7$) used to prepare α -canaphite. Both NMR spectra are in agreement with published data for $\text{Na}_4\text{P}_2\text{O}_7$ (four sites for Na and two sites for P) and confirmed the purity of the sodium and pyrophosphate precursor salt.¹⁻²

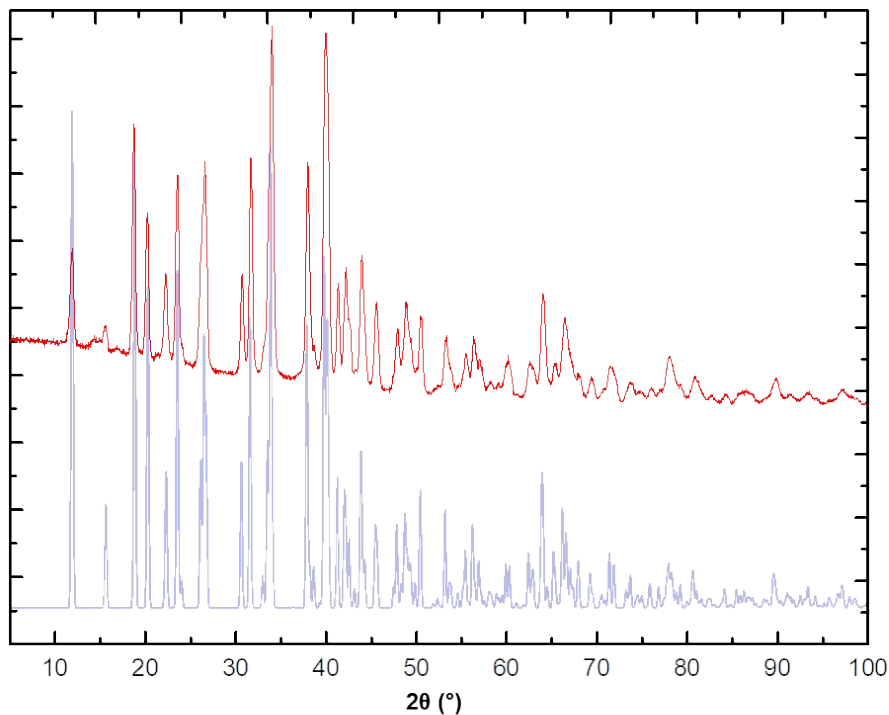


Figure S2: X-ray pattern of the as-synthesized α -canaphite powder obtained with the laboratory X-ray diffractometer ($\lambda_{\text{Co}(K\alpha)} = 1.788970 \text{ \AA}$) (in red) compared to that for a synthetic canaphite monocrystal⁸ (ICSD n°26015) (in blue).

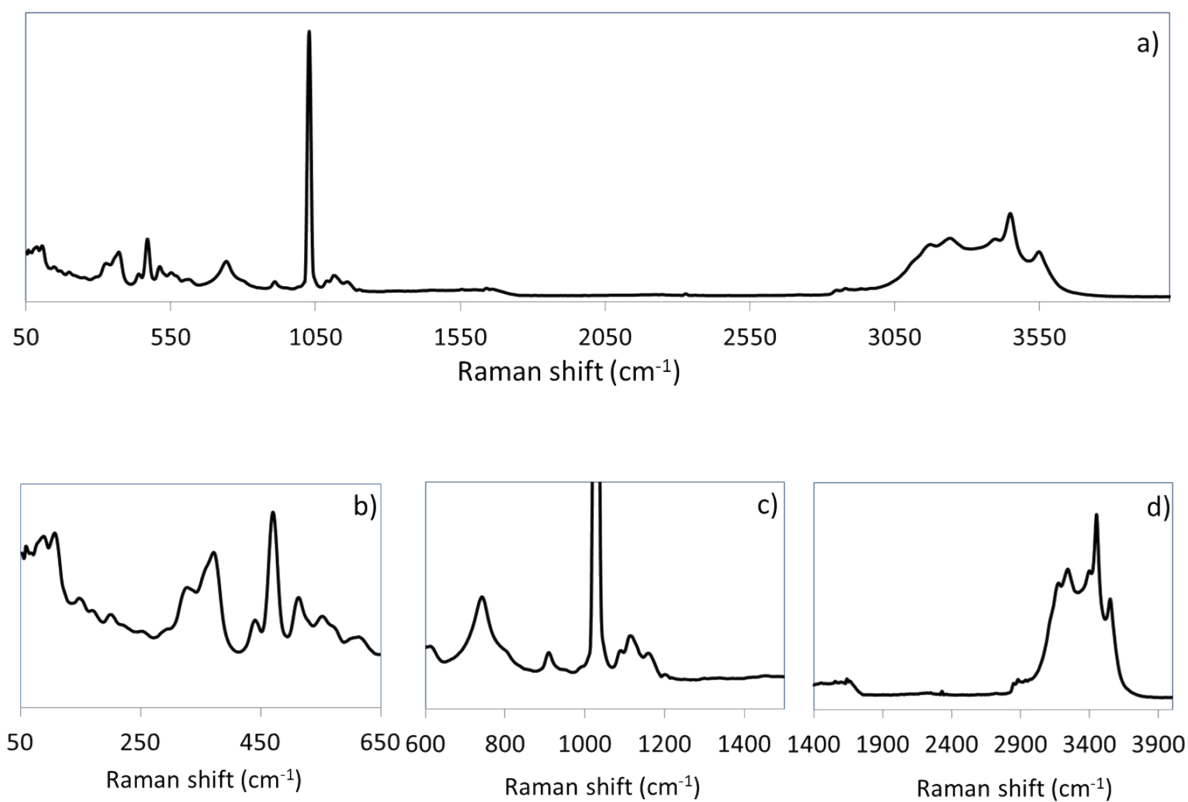


Figure S3: Raman spectrum of the α -canaphite powder synthesized in H₂O: full spectrum (a) and spectrum divided in three separated domains (b, c and d). The positions and assignments of the lines are reported in Table S4.

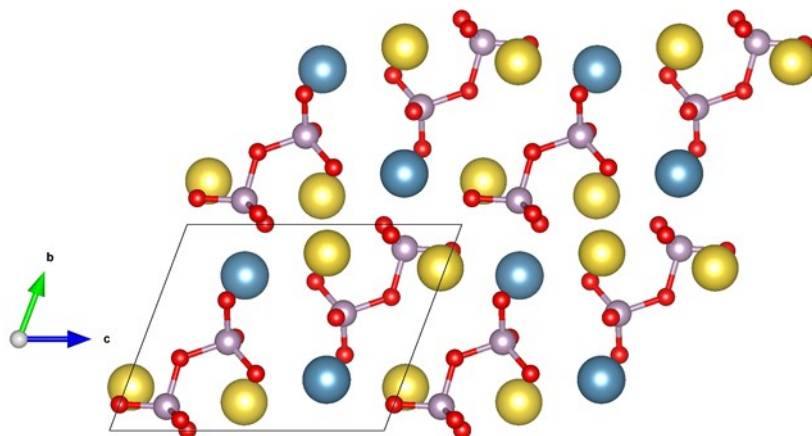


Figure S4: Three-dimensional representation of the triclinic elemental cell of the anhydrous calcium disodium pyrophosphate (α - $\text{CaNa}_2\text{P}_2\text{O}_7$). (yellow: sodium, blue: calcium, grey: phosphorus, red: oxygen)

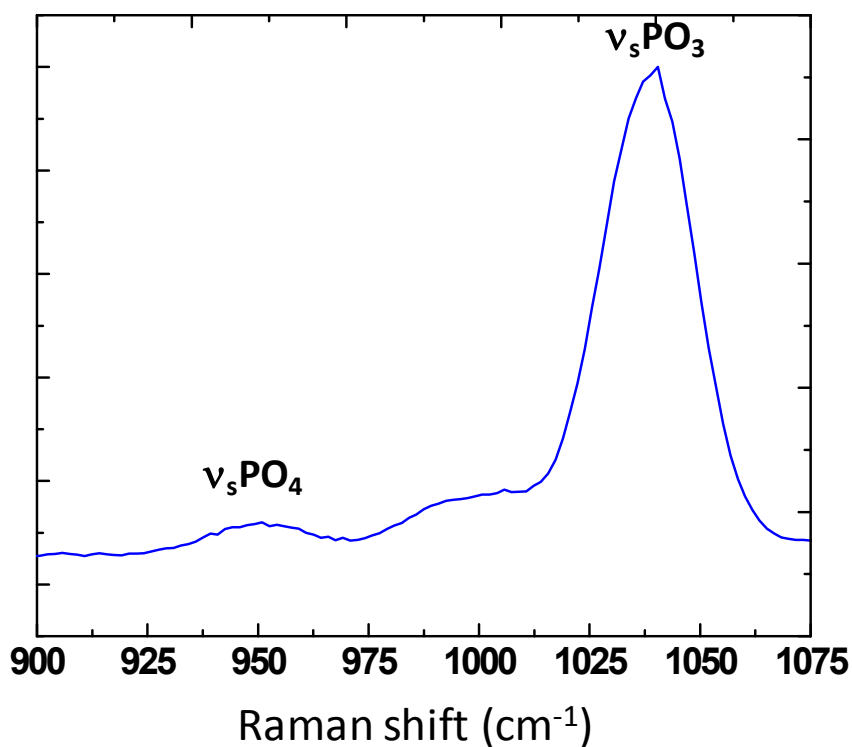


Figure S5: Raman spectrum (900-1075 cm^{-1} domain) of α -canaphite dried at 250°C showing the presence of a weak characteristic vibration band of the orthophosphate group $\nu_s\text{PO}_4$ in addition to the strong $\nu_s\text{PO}_3$ band of pyrophosphate testifying for an internal hydrolysis of part of pyrophosphate ions into orthophosphate ones according to the equation: $\text{P}_2\text{O}_7^{4-} + \text{H}_2\text{O} \rightarrow 2 \text{HPO}_4^{2-}$.

Table S1: Structural parameters and symmetry of α -CaNa₂P₂O₇ determined by XRD analysis on single crystal²⁹ compared to the refinement data (Rietveld refinement on laboratory X-ray diffraction data) of the α -CaNa₂P₂O₇ powder obtained after the heat treatment at 400°C during 15 h of the synthesized α -canaphite.

α -CaNa ₂ P ₂ O ₇ sample	Symmetry	Volume (Å ³)	a (Å)	b (Å)	c (Å)	α (°)	β (°)	γ (°)
Monocrystal (Bennazha 1999)	Triclinic	308.5(3)	5.361(3)	7.029(3)	8.743(4)	69.40(2)	89.02(3)	88.78(4)
As-synthesized powder	Triclinic	316.852 (68)	5.40070 (65)	7.09929 (88)	8.8295(11)	69.4248 (22)	89.0318 (33)	88.7703 (22)

Supporting Information on Vibrational Spectroscopy:

Considering the crystal structure of α -canaphite, the factor group is Cs and the primitive unit cell contains two chemical formula units. The complete treatment results in:

- Acoustic mode (corresponding to crystal vibrations): $2 A' \oplus A''$
- External vibrations: $22 A' \oplus 23 A''$
- Librations $15 A' \oplus 15 A''$ ($3 A' \oplus 3 A''$ for $P_2O_7^{4-}$ and $12 A' \oplus 12 A''$ for H_2O)
- Internal vibrations of $P_2O_7^{4-}$ ($21 A' \oplus 21 A''$) and H_2O ($12 A' \oplus 12 A''$)

Considering the $P_2O_7^{4-}$ molecular unit, the correlation table (Table S2) indicates the distribution of the internal vibrations relative to the original free ion vibratory domains. The 42 total internal vibrations both active in infrared and Raman spectroscopies, are associated to doubling of the vibration levels of the initial free ion. The correlation table for water molecules is reported in Table S3. The 24 total internal vibrations correspond to a multiplication by 8 of the vibration levels of the original molecule. It shall be considered that additional lines corresponding to libration movements of water molecules may possibly occur in the $P_2O_7^{4-}$ vibration range. Lattice vibrations show up at low energies and have not been considered in this MIR analysis.

Table S2: Correlation table for $P_2O_7^{4-}$

Symmetry of free $P_2O_7^{4-}$ ion C_{2v}	Site symmetry (for each $P_2O_7^{4-}$ ion) C_1	Factor group (2 $P_2O_7^{4-}$) C_s
7 A_1 (IR, Raman)	21 A	7 $A' \oplus 7 A''$ (IR, Raman)
4 A_2 (Raman)		4 $A' \oplus 4 A''$ (IR, Raman)
6 B_1 (IR, Raman)		6 $A' \oplus 6 A''$ (IR, Raman)
4 B_2 (IR, Raman)		4 $A' \oplus 4 A''$ (IR, Raman)

Table S3: Correlation table for H_2O (D_2O)

Symmetry of free molecule C_{2v}	Site symmetry (for each water molecule) C_1	Factor group (8 H_2O) C_s
2 A_1 (IR, Raman)	3 A	8 $A' \oplus 8 A''$ (IR, Raman)
B_1 (IR, Raman)		4 $A' \oplus 4 A''$ (IR, Raman)

For libration modes of water molecules the factor group treatment predicts $12 A' \oplus 12 A''$ (IR, Raman).

Table S4: FTIR and Raman spectral lines of α -canaphite and its deuterated analogue (corresponding to the Figure 9): position (cm^{-1}), intensity and assignments.

Assignments	H ₂ O-canaphite		D ₂ O-canaphite		
	FTIR	Raman	FTIR	Raman	
v _s and v _{as} H ₂ O (D ₂ O)	3562 m	3550 m	2633 m	2627 m	
	3501 sh		2563 sh		
	3454 m	3450 m	2549 m	2555 m	
	3392 w	3399 m	2521 w	2522 w	
	3335 vw		2431 m	2438 sh	
				2401 sh	
	3241 m	3241 m	2378 m		
	3169 w	3173 w	2355 sh	2359 m	
	3116 sh		2337 sh		
δ H ₂ O (D ₂ O)	1658 b m	1650 bw	1213 sh	1221 b	
v _s and v _{as} PO ₃	1157 sh	1160 w		1160 w	
	1139 s		1137 s		
	1125 sh	1126 sh	1124 sh	1128 sh	
	1108 m	1114 w	1108 m	1113 w	
	1090 s	1090 w	1089 s	1092 w	
	1032 sh				
	1027 m	1028 vs	1028 m	1029 vs	
	991 w	990 vw	991 w		
	938 m		934 m		
δ P ₂ O ₇ , external modes	v _{as} POP	909 m	908 w	906 w	908 w
	v _L H ₂ O	797 b w	800 b sh	791 sh	
	v _s POP		743 m	740 w	742 m
	v _L H ₂ O	706 b m		705 b w	
		614 w	609 w	617 sh	620 w
				606 sh	
		569 sh	569 sh	570 m	573 w
	v _L H ₂ O	550 m	552 w		
		510 vw	512 w	503 sh	527 w
		468 w	470 m	472 w	470 m
		438 vw	440 w		427 w

b: broad, m: medium intensity, sh: shoulder, v: very, s: strong, w: weak,
v_s and v_{as}: symmetric and antisymmetric stretching, v_L: water libration line, δ : bending

References

- 1 L. Griffiths, A. Root, R. K. Harris, K. J. Packer and F. R. Tromans, *J. Chem. Soc. Dalton Trans*, 1986, **10**, 2247–2251.
- 2 S. Hayashi and K. Hayamizu, *Chemical Physics*, 1991, **157**, 381–389.