

SUPPLEMENTARY INFORMATION

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Characterization of mixed Silicon-tin oxides found in the autoclave after crystal growth

I. Experimental

SEM-EDX

After crystal growth, the solid phases crystallize in the autoclave were characterized by using a FEI Quanta FEG 200 scanning electron microscope. The graphic resolution is 2.5nm for a voltage of 30kV leading to an image resolution of 4096x3536 pixels.

X-ray diffraction

Single crystal X-ray diffraction measurements and data collection were performed on a Rigaku Oxford Diffraction Gemini-S diffractometer with sealed-tube Mo-K α radiation using the CrysAlis Pro program [1] at 175 K. The integration of the 984 data frames was done with the same program using default parameters. Lorentz and polarization effects were also corrected, and the empirical absorption correction was done using spherical harmonics employing symmetry-equivalent and redundant data. The crystal structure was solved using the ab-initio iterative charge flipping method with parameters described elsewhere [2] using the Superflip program [3].

Raman and Infrared spectroscopies

The compounds were characterized by Raman and infrared spectroscopies by using a Horiba LabRam Aramis spectrometer. For Raman measurements a laser of 473nm wavelength was used with an Olympus confocal microscope. The sample was placed on a micrometric motorized stage allowing to obtain maps of the sample. The backscattered beam is filtered and detected with a CCD camera cooled with a Peltier device. The infrared measurements were performed by using the infrared module of the Horiba Jobin-Yvon spectrometer and the All Reflecting Objective of the microscope. The infrared beam (from 650cm⁻¹ to 4000cm⁻¹) is produced by a Globar source with a KBr beamsplitter. For the detection, a Mercury Cadmium Telluride detector cooled by liquid nitrogen was used.

II. Results.

a. SEM-EDX.

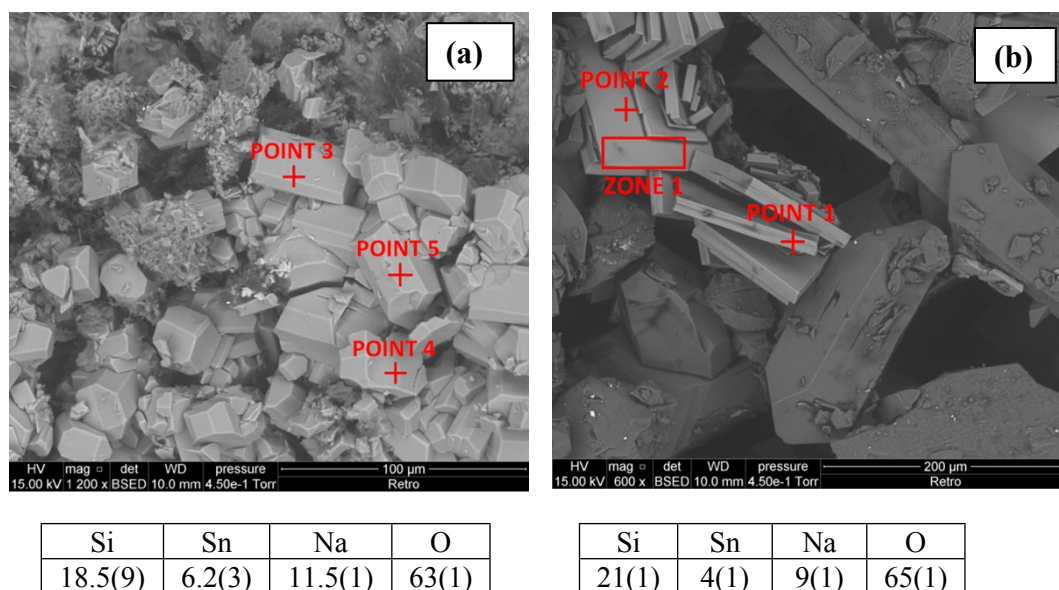


Figure S1: Back-scattering SEM photographs and EDX analyses (at%) of nutrient in the lower part of the autoclave (a) and compound crystallized in the upper part of the autoclave (b)

The unidentified phases recorded by powder XRD have been analyzed by EDX. They correspond to the different points on the SEM-photographs. The chemical compositions of these phases could be proposed. The compound formed in the nutrient is $\text{Na}_2\text{Si}_3\text{SnO}_{11}$ while that crystallized in the upper part of the autoclave is $\text{Na}_2\text{Si}_4\text{SnO}_{13}$.

In order to comply with the electro-neutrality of the compound found in the nutrient, 4 hydrogen atoms have to be added in the formula. The chemical composition could be $\text{Na}_2\text{Si}_3\text{SnO}_{11}\text{H}_4$, for the compound found in the nutrient and $\text{Na}_2\text{Si}_4\text{SnO}_{13}\text{H}_4$ for that found in the crystallization zone in the upper part of the autoclave.

b. Single crystal x-ray diffraction

Only one single crystal from the crystal growth part of the autoclave was isolated (Figure 2) and the structure was determined by single crystal x-ray diffraction. It was technically impossible to isolate one single crystal from the nutrient.

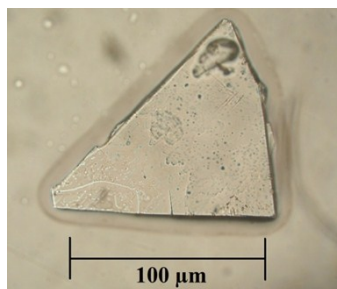


Figure S2: Photo of $\text{Na}_2\text{Si}_4\text{SnO}_{13}\text{H}_4$ single crystal

The symmetry of the crystal structure appeared to be $Pbcn$ and it was refined in this space group using full-matrix least-squares procedures as implemented in CRYSTALS software [4] on all independent reflections with $I > 2\sigma(I)$ (Table 1).

One hydrogen atom could be located in a difference Fourier map, but it was slightly shifted for accomodating the second hydrogen atom of the water molecule. The hydrogen atoms were then treated as riding on their parent oxygen atoms.

formula	$\text{H}_4\text{Na}_2\text{O}_{13}\text{Si}_4\text{Sn}$
moiety	$\text{Na}_2\text{O}_{11}\text{Si}_4\text{Sn}, 2(\text{H}_2\text{O})$
T (K)	175
spacegroup	$Pbcn$
crystal system	Orthorhombic
a (Å)	8.7892(3)
b (Å)	7.4533(2)
c (Å)	16.4801(4)
α (°)	90
β (°)	90
γ (°)	90
V (Å ³)	1079.58(3)
Z	4
ρ (gcm ⁻³)	3.009
M_r (gmol ⁻¹)	489.08
μ (mm ⁻¹)	2.967
R_{int}	0.055
θ_{max} (°)	29.269
resolution (Å)	0.73
N_{tot} (measured)	22341
N_{ref} (unique)	1422
N_{ref} ($I > 2\sigma(I)$)	1362
N_{ref} (least-squares)	1362
N_{par}	93
$\langle \sigma(I)/I \rangle$	0.0563
R_1 ($I > 2\sigma(I)$)	0.0714
wR_2 ($I > 2\sigma(I)$)	0.0653
R_1 (all)	0.0735
wR_2 (all)	0.0667
GOF	0.8506

$\Delta\rho$ ($e\text{\AA}^{-3}$)
crystal size (mm^3)

-3.48/3.75
0.02x0.05x0.08

Table 1. Crystallographic parameters and experimental data of single crystal X-ray diffraction

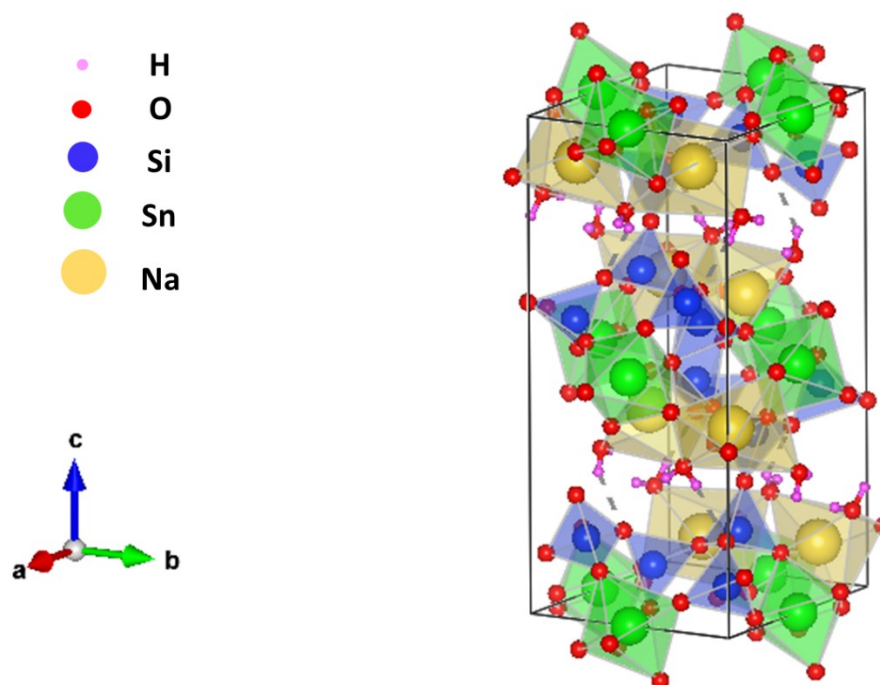
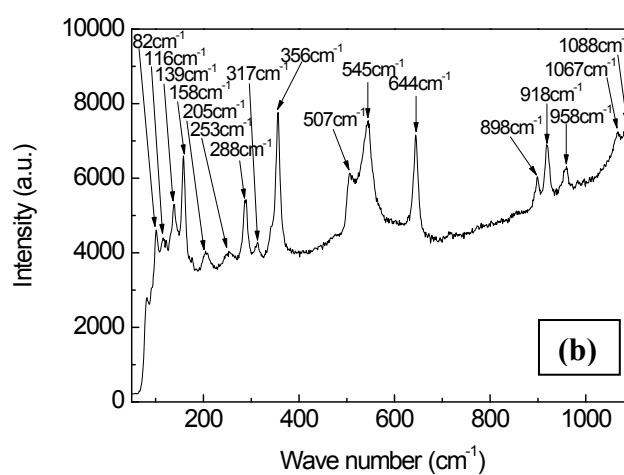
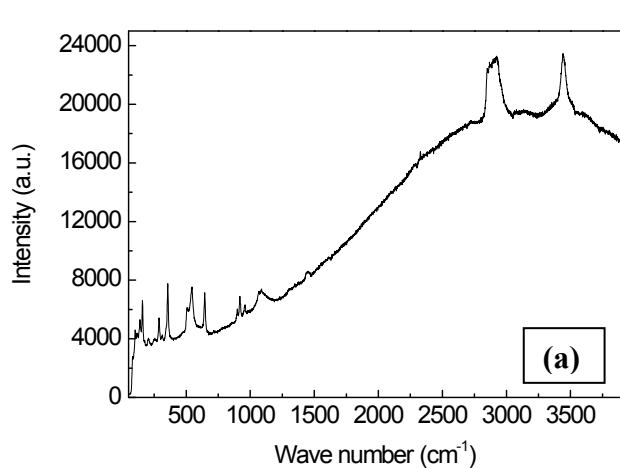


Figure S3: $\text{Na}_2\text{O}_{11}\text{Si}_4\text{Sn}_2(\text{H}_2\text{O})$ crystal structure
(the structure has been draw again with the labels of the atoms)

c. Raman and Infrared spectroscopies.

Raman spectroscopy:



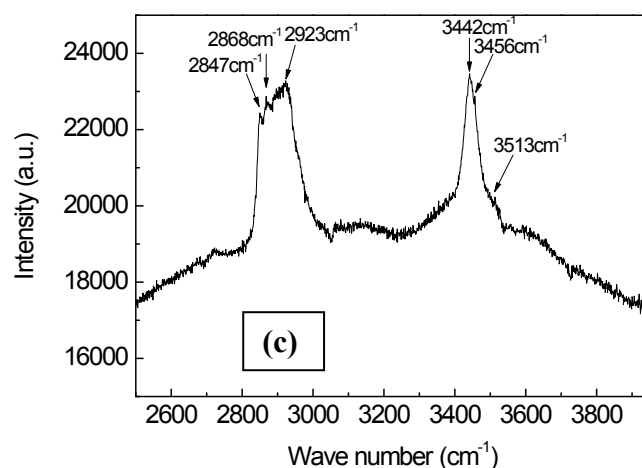


Figure S4: Raman spectra ($\lambda = 473\text{nm}$) of $\text{Na}_2\text{Si}_4\text{SnO}_{13}\text{H}_4$ single crystal

(a) Full Raman shift range (50-4000cm⁻¹)

(b) Low-wavenumber range (50-1500cm⁻¹)

(c) High-wavenumber range (2500-4000cm⁻¹)

The numerous modes present in the low-frequency range from 50cm⁻¹ to 1500cm⁻¹ (Fig S4b) are due to Na-O, Si-O and Sn-O vibrations of the crystal lattice. At high frequencies (Fig S4c), modes from 2847cm⁻¹ to 2923cm⁻¹ are due to C-H vibrations coming from organic oil used to select the crystal. The modes from 3442cm⁻¹ to 3513cm⁻¹ correspond to free -OH groups.

All Reflective Objective Infrared spectroscopy

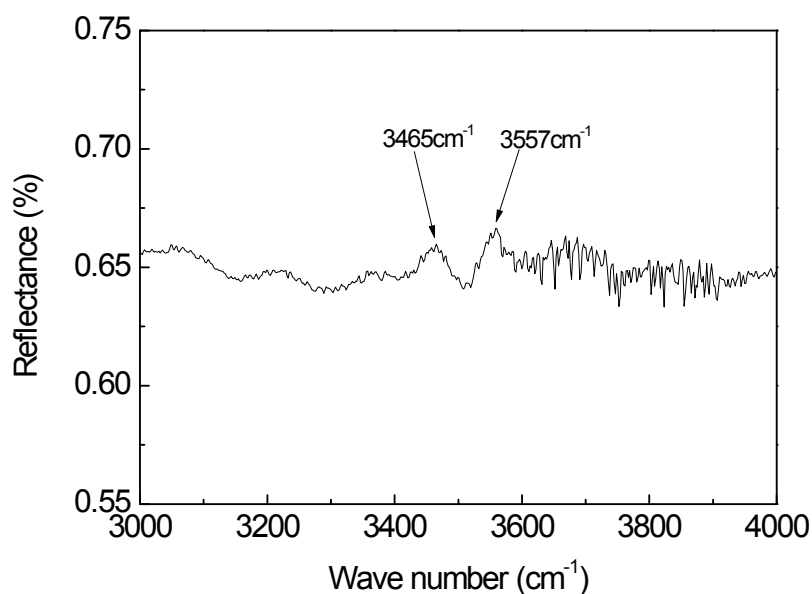


Figure S5: High frequency range of the ARO-IR spectrum of the $\text{Na}_2\text{Si}_4\text{SnO}_{13}\text{H}_4$ single crystal

Both modes at 3465cm^{-1} and 3557cm^{-1} are due to the vibrations of free –OH groups. No broad band corresponding to hydrogen bonded -OH groups (water molecule) is present, thus the $\text{Na}_2\text{Si}_4\text{SnO}_9(\text{OH})_4$ chemical formula is proposed. TGA analysis would have been able to confirm the presence of water molecules in the structure, but the sample is too small to perform such an experiment with reasonable accuracy.

References:

- [1] CrysAlis^{Pro} Rigaku Oxford Diffraction, England 2017.
- [2] A. van der Lee, *J. Appl. Crystallogr.* **2013**, *46*, 1306-1315.
- [3] L. Palatinus, G. Chapuis, *J. Appl. Crystallogr.* **2007**, *40*, 786-790.
- [4] P. W. Betteridge, J. R. Carruthers, R. I. Cooper, K. Prout, D. J. Watkin, *J. Appl. Crystallogr.* **2003**, *36*, 1487-1487.