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Hydrothermal synthesis, crystal structure, thermal behaviour, IR and Raman spectroscopy of $\text{Na}_3\text{Y}(\text{CO}_3)_3 \cdot 6\text{H}_2\text{O}$

Amor Ben Ali ^{a,b}, Mohamed Osman Awaleh ^a, Marc Leblanc ^{a,*}, Leila Samia Smiri ^b,
Vincent Maisonneuve ^a, Sylvie Houlbert ^c

^a Laboratoire des oxydes et fluorures, UMR 6010 CNRS, faculté des sciences, université du Maine, av. Olivier-Messiaen, 72085 Le Mans cedex 9, France

^b Laboratoire de chimie inorganique et structurale, faculté des sciences de Bizerte, 7021 Jarzouna, Tunisie

^c Laboratoire de physique de l'état condensé, UMR 6087 CNRS, faculté des sciences, université du Maine, av. Olivier-Messiaen, 72085 Le Mans cedex 9, France

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Abstract

A new sodium yttrium carbonate hydrate, $\text{Na}_3\text{Y}(\text{CO}_3)_3 \cdot 6\text{H}_2\text{O}$, is prepared by hydrothermal synthesis and characterized by single crystal X-ray diffraction, thermal analysis, IR and Raman spectroscopy. $\text{Na}_3\text{Y}(\text{CO}_3)_3 \cdot 6\text{H}_2\text{O}$ crystallizes in the hexagonal system, space group $P6_3$; $a = 11.347(5)$ Å, $c = 5.935(5)$ Å; $V = 661.8(5)$ Å³; $Z = 2$. Refinements yield $R(F^2) = 0.058$ and $R_w(F^2) = 0.161$ for 692 unique reflections. The structure is built up from $[\text{YO}_{3+3+3}]$ polyhedra surrounded by $[\text{NaO}_6]$ octahedra. Carbonate groups form infinite layers at $z \approx 0.175$ and $z \approx 0.675$. Dehydration of $\text{Na}_3\text{Y}(\text{CO}_3)_3 \cdot 6\text{H}_2\text{O}$ yields an amorphous carbonate. **To cite this article:** A. Ben Ali et al., C. R. Chimie 7 (2004).

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Résumé

Un nouveau carbonate d'yttrium et de sodium hydraté, $\text{Na}_3\text{Y}(\text{CO}_3)_3 \cdot 6\text{H}_2\text{O}$, est préparé par synthèse hydrothermale et caractérisé par diffraction des rayons X, analyse thermique et spectroscopies d'absorption IR et de diffusion Raman. $\text{Na}_3\text{Y}(\text{CO}_3)_3 \cdot 6\text{H}_2\text{O}$ cristallise dans le système hexagonal, groupe spatial $P6_3$; $a = 11,347(5)$ Å, $c = 5,935(5)$ Å; $V = 661,8(5)$ Å³; $Z = 2$. Les affinements conduisent aux facteurs de confiance $R(F^2) = 0,058$ et $R_w(F^2) = 0,161$ pour 692 réflexions uniques. La structure est bâtie à partir de polyèdres $[\text{YO}_{3+3+3}]$ entourés par six octaèdres $[\text{NaO}_6]$. Les groupements carbonate forment des couches infinies à $z \approx 0,175$ et $z \approx 0,675$. La déshydratation de $\text{Na}_3\text{Y}(\text{CO}_3)_3 \cdot 6\text{H}_2\text{O}$ conduit à un carbonate amorphe. **Pour citer cet article :** A. Ben Ali et al., C. R. Chimie 7 (2004).

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* Corresponding author.

E-mail address: marc.leblanc@univ-lemans.fr (M. Leblanc).

1. Introduction

During the investigation of ternary diagrams $\text{Na}_2\text{CO}_3\text{--YbF}_3\text{--H}_2\text{O}$ [1] and $\text{Na}_2\text{CO}_3\text{--YF}_3\text{--H}_2\text{O}$ [2] at $T = 190^\circ\text{C}$, we have found four new fluoride carbonate families, $\text{Na}_2\text{REE}(\text{CO}_3)_2\text{F}$ (REE = Y, Yb), $\text{Na}_3\text{Y}(\text{CO}_3)_2\text{F}_2$, $\text{Na}_3\text{Yb}(\text{CO}_3)_2\text{F}_2$, $\text{Na}_4\text{Y}(\text{CO}_3)_2\text{F}_3\cdot\text{H}_2\text{O}$, together with one carbonate hydrate $\text{Na}_5\text{Yb}(\text{CO}_3)_4\cdot 2\text{H}_2\text{O}$ [3]. At high carbonate concentration and $T = 220^\circ\text{C}$, two other carbonates appear, $\text{Na}_5\text{Y}(\text{CO}_3)_4$ [3] and $\text{Na}_3\text{Y}(\text{CO}_3)_3\cdot 6\text{H}_2\text{O}$ (this publication). Five sodium yttrium carbonates have been previously reported: four minerals, $\text{NaY}(\text{CO}_3)\text{F}_2$ horvathite [4], $\text{Na}_3(\text{Y,REE})(\text{CO}_3)_3\cdot 3\text{H}_2\text{O}$ shomiokite [5], $\text{Na}(\text{Y,REE})(\text{HCO}_3)(\text{OH})_3\cdot 4\text{H}_2\text{O}$ thomasclarkite [6], $\text{NaY}(\text{CO}_3)_2\cdot 6\text{H}_2\text{O}$ adamsite [7,8], and one synthetic phase, $\text{NaY}(\text{CO}_3)_2$ [9].

In this paper, the synthesis, the crystal structure, the thermal behaviour and the vibrational analysis of $\text{Na}_3\text{Y}(\text{CO}_3)_3\cdot 6\text{H}_2\text{O}$ are reported. A structural relationship is found with $\text{Na}_3(\text{Y,REE})(\text{CO}_3)_3\cdot 3\text{H}_2\text{O}$ shomiokite.

2. Experimental

Crystals of $\text{Na}_3\text{Y}(\text{CO}_3)_3\cdot 6\text{H}_2\text{O}$ grow in a Teflon lined Parr autoclave at 220°C during 48 h from $\text{Na}_2\text{CO}_3/\text{YF}_3/\text{H}_2\text{O}$ in the molar ratio 25:1:55. They are washed with water and acetone and dried in air.

Volume weight was measured with a pycnometer AccuPyc 1330 V3.03. The experimental value $\rho_{\text{exp}} = 2.25(5)\text{ g cm}^{-3}$ is consistent with the calculated value $\rho_{\text{calc}} = 2.24\text{ g cm}^{-3}$.

Thermal analyses were performed with a DTA–TGA TA Instrument 2960 (heating rate $10^\circ\text{C min}^{-1}$, argon atmosphere) in the temperature range 25–1000 $^\circ\text{C}$.

Single crystal diffraction data were obtained on a Siemens AED2 four-circle diffractometer. The conditions of intensity measurement are reported in Table 1.

The infrared spectrum of $\text{Na}_3\text{Y}(\text{CO}_3)_3\cdot 6\text{H}_2\text{O}$ was obtained using a Bomem Michelson MB120 FTIR spectrometer with a diamond-anvil cell as a microsampling device. Infrared data were collected in the range 650–4000 cm^{-1} . Spectral resolution was 4 cm^{-1} .

The Raman scattering study was performed in the backscattering geometry, under microscope ($\times 50$ ob-

Table 1
Crystallographic data of $\text{Na}_3\text{Y}(\text{CO}_3)_3\cdot 6\text{H}_2\text{O}$

Crystal system	Hexagonal
Space group	$P6_3$ (No. 173)
a (\AA)	11.347(5)
c (\AA)	5.935(5)
V (\AA^3), Z	661.8(5), 2
μ (Mo $K\alpha$) (mm^{-1})	4.62
ρ_{calc} (g cm^{-3})	2.24
ρ_{exp} (g cm^{-3})	2.25(5)
Temperature (K)	298
Four-circle diffractometer	Siemens AED2
Monochromator	graphite
2θ range ($^\circ$)	2–55
(hkl) limits (two sets)	$ h \leq 12$; $ k \leq 14$; $ l \leq 7$
Scan mode	ω – 2θ
Absorption correction	Gaussian
Reflections measured/unique/used ($I > 2\sigma(I)$)	1132/983/692
Parameters refined (on F^2)	75
$R(\text{int})/R(\text{sigma})$	0.07/0.11
$^a R/R_w$	0.058/0.161
Goodness of fit	1.05
Weighting scheme ($P = [F_o^2 + 2F_c^2]/3$)	$1/[\sigma^2(F_o^2) + (0.08P)^2]$
Secondary extinction coefficient	$0.5(6) \times 10^{-5}$

$$^a R = \sum \|F_o\| - \|F_c\| / \sum \|F_o\|; R_w = \sum [w(|F_o|^2 - |F_c|^2)^2 / \sum w(F_o^2)^2]^{1/2}.$$

jective), on a powder (without polarisation analysis). The spectrum was collected with a T64000 Jobin–Yvon multichannel spectrometer (in triple subtractive configuration with 1800 lines/mm grating), using the 514.5 nm radiation of an argon–krypton laser as excitation, with 8 mW power on the sample in the range 40–4000 cm^{-1} . The typical spectral resolution was better than 0.7 cm^{-1} .

3. Structure determination

The systematic existing conditions of reflections $000l$ ($l = 2n$) led to the $P6_3$ and $P6_3/m$ space groups. Owing to a positive second harmonic generation test, the non-centrosymmetric $P6_3$ space group was chosen. The positions of yttrium atoms were obtained using the Patterson method (option PATT in SHELXS-86 [10]). Analysis of successive Fourier difference maps allowed the location of the remaining atoms. Na, C, and O were distinguished from distance criteria and from

Table 2

Atomic coordinates, equivalent isotropic displacement parameters and valence bond sums in $\text{Na}_3\text{Y}(\text{CO}_3)_3 \cdot 6 \text{H}_2\text{O}$

Atom	Site	x	y	z	B_{eq} (\AA^2)	Σs^a	$\Sigma s_{\text{expected}}$
Y	2b	1/3	2/3	0.9023(4)	1.31(4)	3.12	3
Na	6c	0.3749(5)	0.3634(5)	0.6788(8)	2.12(8)	1.1	1
C	6c	0.120(1)	0.436(1)	0.676(2)	1.6(2) ^b	3.9	4
O(1)	6c	0.0313(9)	0.3382(7)	0.563(1)	1.8(1)	1.7	2
O(2)	6c	0.2505(9)	0.4869(9)	0.634(2)	1.8(2)	1.8	2
O(3)	6c	0.0914(8)	0.4929(8)	0.841(1)	1.8(1)	1.9	2
Ow(1)	6c	0.158(1)	0.179(1)	0.555(3)	6.6(4)		
Ow(2)	6c	0.493(1)	0.216(1)	0.674(2)	2.3(2)		
H(11)	6c	0.08(1)	0.10(1)	0.47(2)	4.0		
H(12)	6c	0.12(2)	0.25(2)	0.52(2)	4.0		
H(21)	6c	0.47(1)	0.20(1)	0.85(3)	4.0		
H(22)	6c	0.54(2)	0.17(2)	0.68(3)	4.0		

^a The results refer to the equation $s = \exp[(r_0 - r)/0.37]$ with $r_0 = 2.014, 1.80$ and 1.39 for Y–O, Na–O, and C–O, respectively.^b Isotropic displacement.

Table 3

Anisotropic displacement parameters in $\text{Na}_3\text{Y}(\text{CO}_3)_3 \cdot 6 \text{H}_2\text{O}$

Atome	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Y	0.0157(5)	U_{11}	0.0184(7)	0	0	$U_{11}/2$
Na	0.028(3)	0.030(3)	0.025(2)	0.006(2)	0.006(2)	0.016(2)
O(1)	0.023(4)	0.014(4)	0.028(4)	–0.014(3)	–0.003(4)	0.007(3)
O(2)	0.020(4)	0.021(4)	0.030(5)	–0.006(4)	–0.006(4)	0.010(4)
O(3)	0.025(4)	0.025(4)	0.021(4)	–0.005(3)	–0.003(3)	0.013(3)
Ow(1)	0.046(7)	0.044(7)	0.16(1)	–0.018(8)	–0.023(8)	0.025(6)
Ow(2)	0.030(5)	0.033(5)	0.025(4)	–0.006(4)	0.002(4)	0.017(4)

Table 4

Selected inter-atomic distances (\AA) and angles ($^\circ$) in $\text{Na}_3\text{Y}(\text{CO}_3)_3 \cdot 6 \text{H}_2\text{O}$

$3 \times \text{Y–O}_w(2)$	2.37(1)	Na–O(3)	2.329(9)
$3 \times \text{Y–O}(2)$	2.380(9)	Na–O(1)	2.347(9)
$3 \times \text{Y–O}(3)$	2.479(8)	Na–Ow(1)	2.41(1)
		Na–O(2)	2.45(1)
		Na–O(3)	2.508(9)
		Na–Ow(2)	2.61(1)
$\langle \text{Y–O} \rangle$	2.41	$\langle \text{Na–O} \rangle$	2.44
C(1)–O(1)	1.26(1)	O(2)–C–O(3)	116(1)
C(1)–O(2)	1.30(1)	O(1)–C–O(2)	121(1)
C(1)–O(3)	1.31(1)	O(1)–C–O(3)	123(1)
$\langle \text{C–O} \rangle$	1.29	$\langle \text{O–C–O} \rangle$	120
Ow(1)–H(11)	1.0(1)	Ow(2)–H(22)	1.1(2)
Ow(1)–H(12)	1.1(1)	Ow(2)–H(21)	0.9(2)

valence bond analysis. The refinement (SHELXL-97 [11]) of the atomic coordinates and anisotropic displacement parameters after absorption correction (Gauss method in SHELX-76 [12]), decreased the reliability factors to $R = 0.058$ and $R_w = 0.161$.

The final atomic coordinates with isotropic displacement parameters and bond valence analysis, the anisotropic displacement parameters and selected bond distances and angles are given in Tables 2, 3 and 4, respectively.

4. Structure description

In the structure of $\text{Na}_3\text{Y}(\text{CO}_3)_3 \cdot 6 \text{H}_2\text{O}$, yttrium atoms are surrounded by six oxygen atoms and three water molecules to form tricapped triangular prisms $[\text{YO}_{3+3}(\text{H}_2\text{O})_3]$ similar to that found in shomiokite (Fig. 1 left and right). The mean Y–O distance, 2.41 \AA , is very close to that encountered in $\text{Na}_3(\text{Y,REE})(\text{CO}_3)_3 \cdot 3 \text{H}_2\text{O}$ shomiokite (2.42 \AA) and $\text{NaY}(\text{CO}_3)_2 \cdot 6 \text{H}_2\text{O}$ adamsite (2.42 \AA). Sodium cations form distorted $[\text{NaO}_4(\text{H}_2\text{O})_2]$ octahedra. Na–O distances range from 2.33 to 2.61 \AA , with an average of 2.44 \AA ; these values and the coordination number are comparable to that found in $\text{Na}_3\text{Y}(\text{CO}_3)_3 \cdot 3 \text{H}_2\text{O}$ and $\text{NaY}(\text{CO}_3)_2 \cdot 6 \text{H}_2\text{O}$. The Ow(2) atom is bonded to one

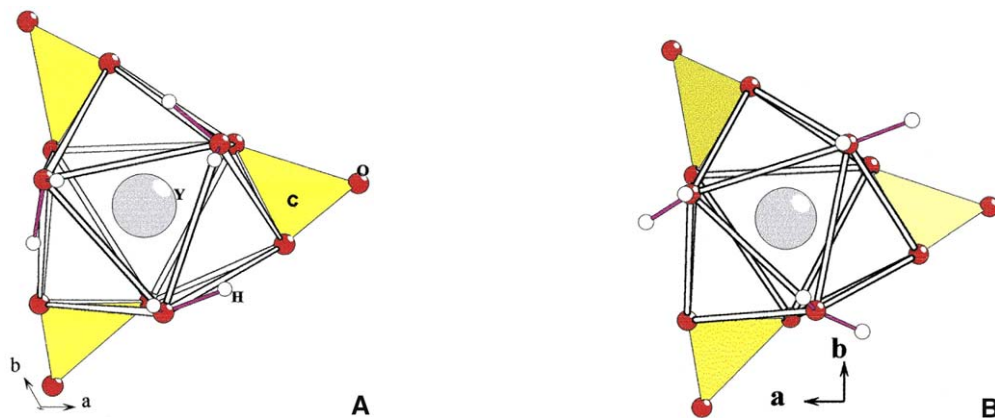


Fig. 1. $[\text{YO}_{3+3+3}]$ and $[(\text{Y}, \text{Ln})\text{O}_{3+3+3}]$ polyhedra in $\text{Na}_3\text{Y}(\text{CO}_3)_3 \cdot 6\text{H}_2\text{O}$ (left) and shomiokite $\text{Na}_3(\text{Y}, \text{Ln})(\text{CO}_3)_3 \cdot 3\text{H}_2\text{O}$ (right).

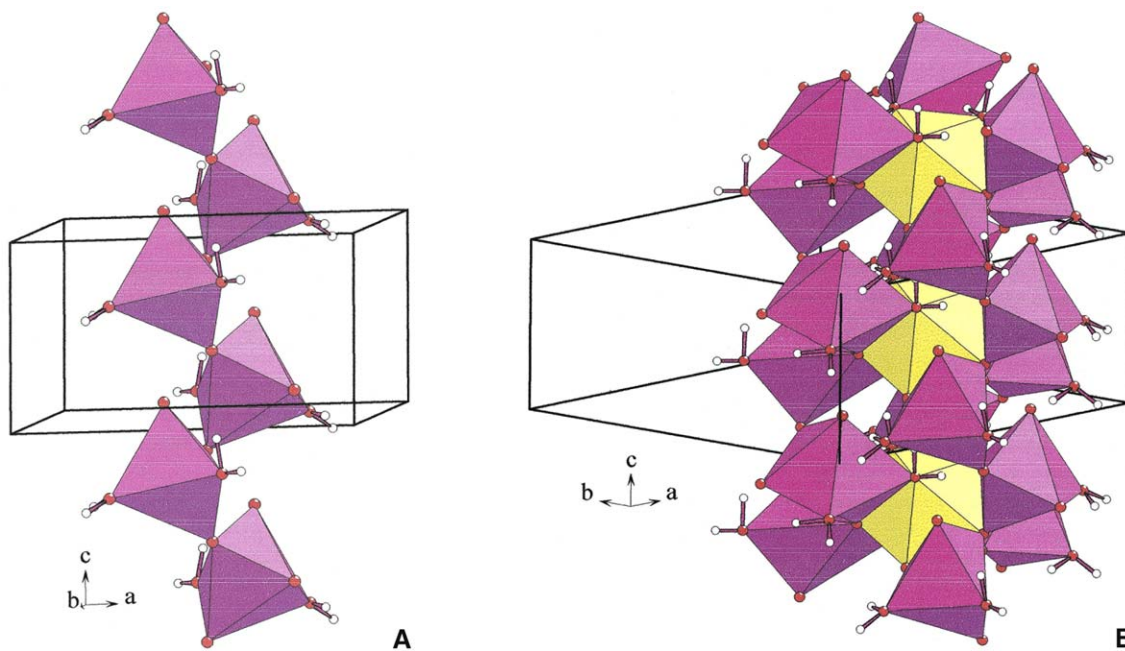


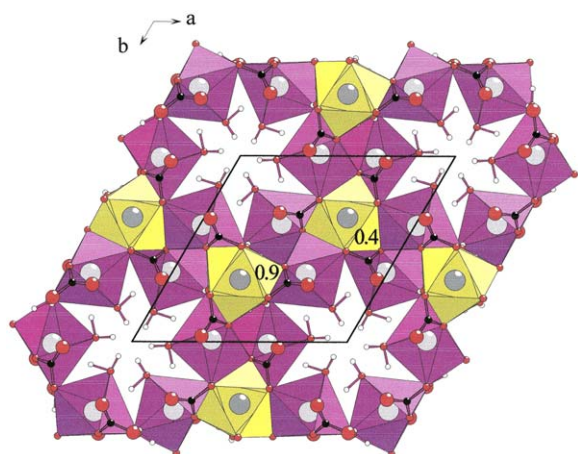
Fig. 2. $[001]$ chains $[\text{NaO}_4\text{O}_{2/2}]_\infty$ (left) and connection of $[\text{YO}_{3+3}(\text{H}_2\text{O})_3]$ polyhedra (yellow) and $[\text{NaO}_4(\text{H}_2\text{O})_2]$ octahedra (violet) in $\text{Na}_3\text{Y}(\text{CO}_3)_3 \cdot 6\text{H}_2\text{O}$ (right).

Y^{3+} (2.37 Å) and 1Na^+ (2.61 Å). $\text{Ow}(1)$ is only bonded to one Na^+ (2.41 Å); consequently, the $\text{Ow}(1)$ atom presents an abnormally high anisotropic displacement parameter ($U_{33} = 0.16(1)$).

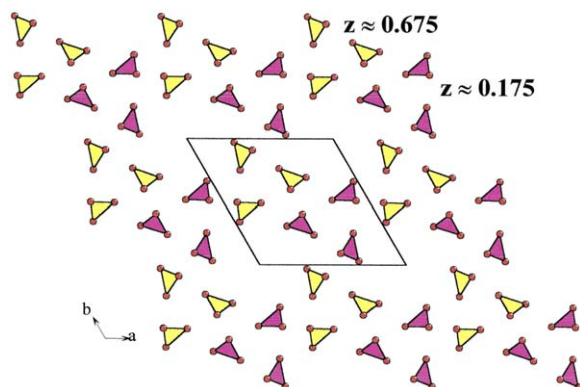
The distorted $[\text{NaO}_4(\text{H}_2\text{O})_2]$ octahedra build infinite $[001]$ corrugated chains $[\text{NaO}_4\text{O}_{2/2}]_\infty$ (Fig. 2, left). Each $[\text{YO}_{3+3}(\text{H}_2\text{O})_3]$ polyhedron is connected by edges to six $[\text{NaO}_4(\text{H}_2\text{O})_2]$ octahedra that belong to three independent $[\text{NaO}_4\text{O}_{2/2}]_\infty$ chains (Fig. 2 right). Two adjacent $[\text{YO}_{3+3}(\text{H}_2\text{O})_3]$ polyhedra located at

$z = 0.4$ and $z = 0.9$ share a unique $[\text{NaO}_4\text{O}_{2/2}]_\infty$ chain. Six chains form cavities in which hydrogen atoms of water molecules point (Fig. 3). Water molecules $\text{H}_2\text{O}_w(1)$ and $\text{H}_2\text{O}_w(2)$ establish hydrogen bonds with $\text{O}(1)$ and $\text{O}(2)$, respectively (Table 5).

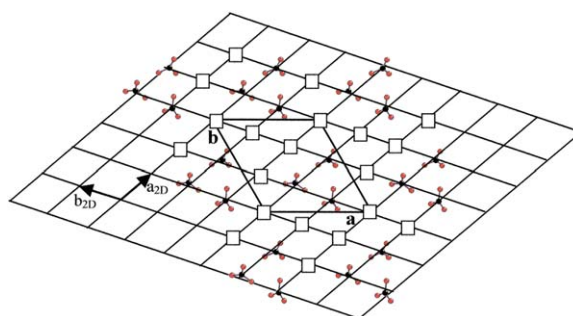
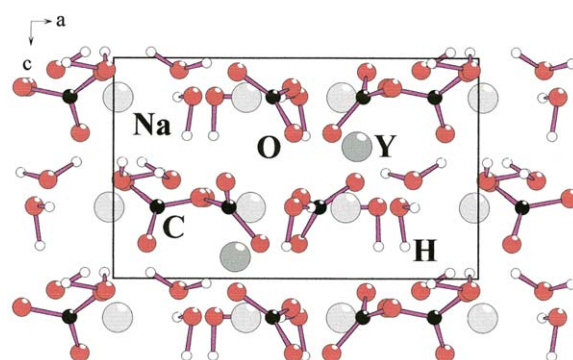
Carbon atoms lie at $z = 0.176$ and $z = 0.676$ (Fig. 4); with $\text{O}(1)$, $\text{O}(2)$ and $\text{O}(3)$ atoms, they form infinite layers of carbonate groups in which the shortest C–C distance is 4.37 Å. In one layer, it is remarkable that carbon atoms are approximately located at the nodes

Fig. 3. [0001] projection of $\text{Na}_3\text{Y}(\text{CO}_3)_3 \cdot 6 \text{H}_2\text{O}$.Table 5
Hydrogen bonds in $\text{Na}_3\text{Y}(\text{CO}_3)_3 \cdot 6 \text{H}_2\text{O}$

O–H...O	H...O (Å)	Ow...O (Å)	OwHO (°)
Ow(1)–H(12)...O(1)	1.8	2.8	172
Ow(1)–H(12)...O(2)	2.5	3.2	160
Ow(2)–H(21)...O(2)	1.9	2.7	174
Ow(2)–H(22)...O(1)	2.3	2.6	155
Ow(2)–H(22)...O(3)	2.1	3.0	164

Fig. 4. Layers of carbonate groups at $z \approx 0.175$ and $z \approx 0.675$ in $\text{Na}_3\text{Y}(\text{CO}_3)_3 \cdot 6 \text{H}_2\text{O}$.

of a two-dimensional hexagonal network with $a_{2D} = 4.01 \text{ \AA}$ ($a = 11.347 = 2a_{2D}\sqrt{2}$) (Fig. 5); three over seven nodes are occupied (Fig. 5). According to Grice et al. [13], this hexagonal network is characteristic of ‘flat-lying’ layers of carbonate groups ($a_{2D} \approx 5.1 \text{ \AA}$) found in numerous carbonates (CaCO_3 calcite, $\text{Na}_5\text{Y}(\text{CO}_3)_4$ [3]). The smaller a_{2D} parameter observed

Fig. 5. Lacunar hexagonal network of carbonate groups in $\text{Na}_3\text{Y}(\text{CO}_3)_3 \cdot 6 \text{H}_2\text{O}$.Fig. 6. $[\text{Na}(\text{CO}_3) \cdot 2 \text{H}_2\text{O}]_\infty$ layers in $\text{Na}_3\text{Y}(\text{CO}_3)_3 \cdot 6 \text{H}_2\text{O}$.

in $\text{Na}_3\text{Y}(\text{CO}_3)_3 \cdot 6 \text{H}_2\text{O}$ is due to the out of plane tilt of the CO_3^{2-} ions.

A relationship between the structures of $\text{Na}_3\text{Y}(\text{CO}_3)_3 \cdot 6 \text{H}_2\text{O}$ and of $\text{Na}_3(\text{Y,REE})(\text{CO}_3)_3 \cdot 3 \text{H}_2\text{O}$ shomiokite can be easily established: the c lattice parameters are similar because of the existence of $[\text{Na}(\text{CO}_3) \cdot 2 \text{H}_2\text{O}]$ and $[\text{Na}(\text{CO}_3) \cdot \text{H}_2\text{O}]$ layers with a comparable thickness (Fig. 6 and Table 6). Moreover, Y^{3+} or Na^+ coordinations are identical in both phases, as was previously indicated.

5. Characterization

5.1. Thermal behaviour

On heating, $\text{Na}_3\text{Y}(\text{CO}_3)_3 \cdot 6 \text{H}_2\text{O}$ exhibits a weight loss in three steps. The first step, which occurs around $125 \text{ }^\circ\text{C}$, is attributed to the departure of six water molecules per mole $\text{Na}_3\text{Y}(\text{CO}_3)_3 \cdot 6 \text{H}_2\text{O}$ (exp./th. = 24.7/24.2%). The anhydrous phase is amorphous and results from the reaction:

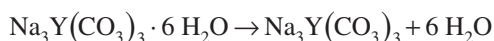


Table 6

Structural relationship between $\text{Na}_3\text{Y}(\text{CO}_3)_3 \cdot 6 \text{H}_2\text{O}$, $\text{Na}_3(\text{Y,REE})(\text{CO}_3)_3 \cdot 3 \text{H}_2\text{O}$ shomiokite, and $\text{NaY}(\text{CO}_3)_2 \cdot 6 \text{H}_2\text{O}$ adamsite

	Y and Na polyhedra	cell parameters			space group
$\text{Na}_3\text{Y}(\text{CO}_3)_3 \cdot 6 \text{H}_2\text{O}$	$\text{Na}^{[6]} \text{Y}^{[9]}$	11.347		5.935	$P6_3$
Shomiokite	$\text{Na}^{[6]} \text{Y}^{[9]}$	10.042	17.349	5.948	$Pbn2_1$
Adamsite	$\text{Na}^{[6]} \text{Y}^{[9]}$	6.2592	13.0838	13.2271	$P\bar{1}$
		91.130	103.554	90.188	

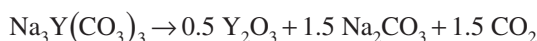
Table 7

Vibrational analysis of $\text{Na}_3\text{Y}(\text{CO}_3)_3 \cdot 6 \text{H}_2\text{O}$

Factor group C_6	External modes								Internal modes				Activity				
	N	A	T_{CO_3}	R_{CO_3}	T_{Y}	T_{Na}	$T_{\text{H}_2\text{O}}$	$R_{\text{H}_2\text{O}}$	CO_3				H_2O				
									ν_1	ν_2	ν_3	ν_4	ν	δ	γ	IR	Raman
A	34	-1	3	3	1	3	6	6	1	1	2	2	2	2	2	z	$\alpha_{xx} + \alpha_{yy}; \alpha_{zz}$
B	34	0	3	3	1	3	6	6	1	1	2	2	2	2	2	-	-
E_1	34	-1	3	3	1	3	6	6	1	1	2	2	2	2	2	(x, y)	$(\alpha_{xx}, \alpha_{yz})$
E_2	34	0	3	3	1	3	6	6	1	1	2	2	2	2	2	-	$(\alpha_{xx} - \alpha_{yy}, \alpha_{xy})$

Note. N , number of degrees of freedom; A number of acoustic modes; T , number of translational modes; R , number of rotational modes.

The second step corresponds to the departure of 1.5 mol of CO_2 gas per mole of $\text{Na}_3\text{Y}(\text{CO}_3)_3$ (exp./th. = 14.1/14.8%); the decomposition reaction is:



The third step is due to the decomposition of Na_2CO_3 and occurs above 850 °C.

5.2. Vibration analysis

In $\text{Na}_3\text{Y}(\text{CO}_3)_3 \cdot 6 \text{H}_2\text{O}$, the Y atom is on the three-fold axis (2 *b*) and all the other atoms lie in general positions (6 *c*). Using the standard correlation method [14] in C_6^6 ($P6_3$), the normal modes of vibration can be classified according to the irreducible representations of C_6 (Table 7):

$$\Gamma^{\text{M}} = 34\text{A} \oplus 34\text{B} \oplus 34\text{E}_1 \oplus 34\text{E}_2$$

The acoustic modes are: $\Gamma^{\text{acous}} = \text{A} \oplus \text{E}_1$. The A and E_1 modes are Raman and IR actives, while E_2 modes are only Raman actives. B modes are inactive.

Free CO_3^{2-} anion has the D_{3h} symmetry and exhibits four normal vibrations $\nu_1(\text{A}'_1)$, $\nu_2(\text{A}''_2)$, $\nu_3(\text{E}')$ and $\nu_4(\text{E}')$. E' modes are IR and Raman actives, while A'_1 is only Raman active and A''_2 is only IR active. ν_1 (1000–1100 cm^{-1}) and ν_3 (1400–1500 cm^{-1}) represent the symmetric and asymmetric stretching vibrations, respectively. ν_2 (650–800 cm^{-1}) and ν_4 (800–1000 cm^{-1}) correspond to out of plane and in plane

deformation vibrations, respectively. The crystal modes (and the macroscopic geometry of observation) can be related to the previous modes by the so-called site method. In $\text{Na}_3\text{Y}(\text{CO}_3)_3 \cdot 6 \text{H}_2\text{O}$, the carbon site symmetry is C_1 ; the correlation analysis is schematised in Table 8.

Fig. 7 shows the Raman spectrum. One line at 1065 cm^{-1} and two lines at 715 and 680 cm^{-1} are attributed to the ν_1 and to the ν_4 modes, respectively. Theoretically, three lines are expected for the ν_1 mode and six lines for the ν_4 mode (Table 7). Though no polarisation analysis was possible, these lines can be unambiguously assigned to the A mode as a reason of the diagonal form of the polarisability tensor. The ν_2 and ν_3 modes around 820 cm^{-1} and 1500 cm^{-1} are very weak. For the ν_2 mode, this feature can be explained by the fact that ν_2 derives from (A''_2), Raman inactive in D_{3h} symmetry.

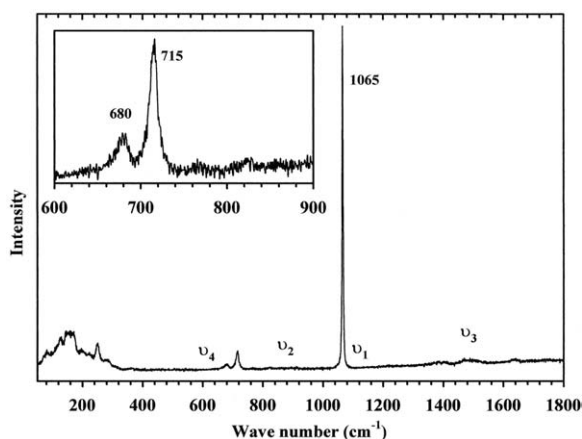
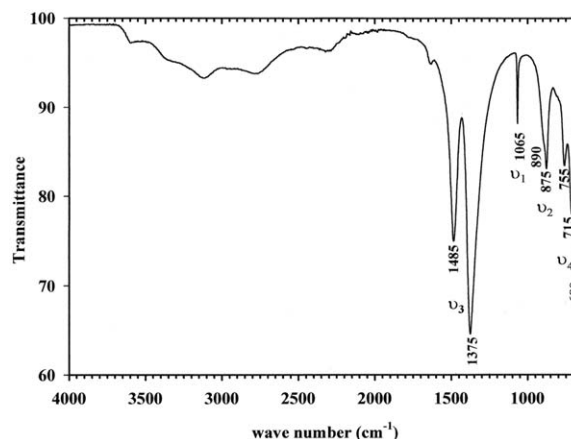
The observed bands at low frequencies are very large. They are attributed to external modes of Na^+ and Y^{3+} translations and H_2O or CO_3^{2-} translations and librations.

The IR spectrum is given in Fig. 8. The band around 1065 cm^{-1} and the shoulder observed at 1045 cm^{-1} are assigned to the symmetric stretching modes ν_1 of CO_3^{2-} . The two bands located at 890 and 875 cm^{-1} are attributed to the out-of-plane deformation modes ν_2 . In the region 1200–1550 cm^{-1} , two large bands, around 1375 and 1485 cm^{-1} , correspond to the asymmetric ν_3 stretching. For the out-of-plane ν_4 deformation, four bands predicted in the region 800–650 cm^{-1} are ob-

Table 8

Correlation scheme for the internal vibration modes of CO₃ groups in Na₃Y(CO₃)₃·6 H₂O

		D_{3h}	C_1	C_6		
		Free CO ₃	Site	Crystal		
R	ν_1	A ₁ '	A	A B E ₁ E ₂	IR, R IR, R R	
IR	ν_2	A ₂ ''	A	A B E ₁ E ₂	IR, R IR, R R	
IR, R	ν_3	E'	2A	2A 2B 2E ₁ 2E ₂	IR, R IR, R R	
IR, R	ν_4	E'	2A	2A 2B 2E ₁ 2E ₂	IR, R IR, R R	

Fig. 7. Raman spectrum of Na₃Y(CO₃)₃·6 H₂O.Fig. 8. IR spectrum of Na₃Y(CO₃)₃·6 H₂O.

served at frequencies 680, 715, 755 cm⁻¹ and 760 cm⁻¹ (shoulder). Then, it is noted that the number of theoretical and observed bands is identical for ν_2 and ν_4 .

H₂O vibration modes, attributed to antisymmetric stretching, symmetric stretching, in plane β -OH deformation and out of plane γ -OH deformation, are expected in the intervals 3600–2000, 1700–1550, 1300–1200 and 800–700 cm⁻¹, respectively. Experimentally, only five very large bands in the region 3600–2000 cm⁻¹, together with one small band at 1635 cm⁻¹, are observed.

6. Conclusion

The crystal structure of a new hydrated carbonate, Na₃Y(CO₃)₃·6 H₂O, is determined and can be described from lacunar layers of carbonate groups. A structural relationship is found with Na₃(Y,REE)(CO₃)₃·3 H₂O shoniokite and both hydrates are acentric. IR and Raman spectroscopy studies of Na₃Y(CO₃)₃·6 H₂O confirm the structural determination. It is observed that O–H vibration lines are very large and also weak, in spite of the presence of six water molecules for three carbonate groups.

It must be noted that shomiokite-(Y) mineral was found in association with an alteration yttrium carbonate. This silky white carbonate was too fine grained and the material quantity was too small; consequently, the structure is still unknown (J.D. Grice, personal communication). It should be interesting to collect X-ray diffraction and/or spectroscopic data of this carbonate, which could be compared with $\text{Na}_3\text{Y}(\text{CO}_3)_3 \cdot 6 \text{H}_2\text{O}$.

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