Microwave-assisted synthesis, crystal structures and thermal behaviour of $Na_5Y(CO_3)_4$ and $Na_5Yb(CO_3)_4 \cdot 2H_2O$

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Abstract

Two new carbonates, $Na_5Y(CO_3)_4$ and $Na_5Yb(CO_3)_4 \cdot 2H_2O$, are synthesized by microwave-assisted hydrothermal method and their crystal structures are established by single crystal X-ray diffraction. $Na_5Y(CO_3)_4$ is monoclinic: $P2_1/c$; $a = 12.209(3)$ Å, $b = 10.085(4)$ Å, $c = 8.783(4)$ Å and $\beta = 90.39(3)°$; $V = 1081.4(5)$ Å^3; $Z = 4$. $Na_5Yb(CO_3)_4 \cdot 2H_2O$, isostructural with $Na_5Sc(CO_3)_4 \cdot 2H_2O$, is tetragonal: $P\text{-}42_1c$; $a = 7.593(2)$ Å, $c = 11.528(8)$ Å; $V = 664.6(3)$ Å^3; $Z = 2$. Dehydration of $Na_5Yb(CO_3)_4 \cdot 2H_2O$ under argon leads to $Na_5Yb(CO_3)_4$, which is isostructural with $Na_5Y(CO_3)_4$. In the structure of $Na_5Y(CO_3)_4$, YO_9 and $Na(1)O_8$ polyhedra share vertices and form, with carbonate $C(2)O_3^{2-}$ and $C(3)O_3^{2-}$ groups, infinite (100) layers $[NaY(CO_3)_2O_6]_\infty$ at $x \approx \frac{1}{4}$; and $x \approx \frac{3}{4}$. In $Na_5Yb(CO_3)_4 \cdot 2H_2O$, YbO_8 and $Na(1)O_4$ polyhedra share carbonate groups and build $[NaYb(CO_3)_4]_\infty$ layers.
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1. Introduction

Microwave-assisted hydrothermal (MH) synthesis of inorganic compounds is mainly used for the elaboration of ceramic oxides, hydroxides or porous materials. Recent examples are found with the well-known stabilized zirconia [1], akaganeite [2] or SBA-15 molecular sieve [3]. This (MH) method can be chosen when fast supersaturation, homogeneous nucleation and rapid kinetics of crystallization are required. In 1999, a literature review had shown that most of (MH) materials were previously prepared by conventional methods [4]. At variance from this trend, it was demonstrated recently that (MH) synthesis can be efficient to explore unknown rare earth (Ln) fluoride carbonate systems in large concentration domains. In the YF_3–Na_2CO_3–H_2O [5] and YbF_3–Na_2CO_3–H_2O [6] systems, four new fluoride carbonate families were evidenced: $Na_2Ln(CO_3)_2F$ (Ln = Y, Yb), $Na_3Y(CO_3)_2F_2$, $Na_3Yb(CO_3)_2F_2$ and $Na_4Y(CO_3)_2F_3 \cdot H_2O$ together with two carbonates $Na_5Yb(CO_3)_4 \cdot 2H_2O$ and $Na_5Y(CO_3)_4$. No

sodium ytterbium carbonate was known before and only five sodium yttrium carbonates were reported: three minerals, $NaY(CO_3)F_2$ horvathite [7], $Na_3(Y,Ln)(CO_3)_3 \cdot 3H_2O$ shomiokite [8], $Na(Y,Ln)(HCO_3)(OH)_3 \cdot 4H_2O$ thomasclarkite [9] and two synthetic phases, $NaY(CO_3)_2$ [10] and $NaY(CO_3)_2 \cdot 6H_2O$ [11].

In this paper, the synthesis, the crystal structures and the thermal behaviour of $Na_5Y(CO_3)_4$ and $Na_5Yb(CO_3)_4 \cdot 2H_2O$ are reported.

2. Experimental

Both compounds, $Na_5Y(CO_3)_4$ and $Na_5Yb(CO_3)_4 \cdot 2H_2O$, were obtained by hydrothermal synthesis in a microwave heater. Crystals of $Na_5Yb(CO_3)_4 \cdot 2H_2O$ grow at $T = 190$ °C, $P = 11 \times 10^5$ Pa, $t = 1$ h for $[Yb^{3+}] > 0.3$ M and $[Na^+]/[Yb^{3+}] > 12$ while $Na_5Y(CO_3)_4$, contaminated with horvathite, is polycrystalline for $T = 200$ °C, $P = 13 \times 10^5$ Pa, $t = 2$ h, $[Y^{3+}] = 1.5$ M and $[Na^+]/[Y^{3+}] = 12$. A pure powder of $Na_5Y(CO_3)_4$ was obtained at higher Na_2CO_3 concentration in a Teflon lined Parr autoclave ($T = 220$ °C, $t = 48$ h, $[Y^{3+}] = 0.5$ M, $[Na^+]/[Y^{3+}] = 20$). The crystallization was further improved in a platinum

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tube at $T = 350\,°C$, $t = 36$ h, $[Y^{3+}] = 1$ M and $[Na^+]/[Y^{3+}] = 25$.

Thermal analyses were performed with a DTA-TGA TA instrument 2960 (heating rate $10\,°C/min$, argon atmosphere) in the temperature range 25–1000 °C. The volume weights were measured with a pycnometer AccuPyc 1330 V3.03.

Single crystal diffraction data were obtained on a Siemens AED2 four-circle diffractometer. The scattering factors and anomalous dispersion corrections for all atoms were taken from *International Tables for X-ray Crystallography*. The X-ray powder pattern of $Na_5Y(CO_3)_4$ was collected on a D8 Bruker diffractometer (2θ step, 0.02°; time/step, 14 s; 2θ range, 8–70°).

3. Structure determination

Conditions of intensity measurement are reported in Table 1. The final atomic coordinates with isotropic displacement parameters and bond valence analysis and selected bond distances and angles are given in Tables 2

and 3 for $Na_5Y(CO_3)_4$ and Tables 4 and 5 for $Na_5Yb(CO_3)_4 \cdot 2H_2O$.

3.1. Na5Y(CO3)4

Most often, the crystals of $Na_5Y(CO_3)_4$ are twinned by merohedry, as a reason of pseudo orthorhombic symmetry of the unit cell; the twin planes are (100) or (001). However, one single crystal was selected. The starting set of atomic coordinates was obtained in $P2_1/c$ from the analysis of the Patterson map (option PATT of SHELXS-86 [12]). Yttrium atoms were located in $4e$ general positions. Analysis of successive Fourier difference maps allowed to locate the remaining atoms. Na, C, and O were distinguished from distance criteria and from valence bond analysis. The refinement (SHELXL-97 [13]) of the atomic coordinates and anisotropic (Y, Na, O) or isotropic (C) displacement parameters, after absorption correction (Gauss method in SHELX-76 [14]), led to the reliability factors $R = 0.065$ and $R_w = 0.118$. Valence bond calculations (Table 2) [15] confirm the advanced formula. Moreover, the Rietveld analysis of the X-ray powder pattern, using the preceding unit cell parameters and atomic

Table 1
Crystallographic data of $Na_5Y(CO_3)_4$ and $Na_5Yb(CO_3)_4 \cdot 2H_2O$

	$Na_5Y(CO_3)_4$		$Na_5Yb(CO_3)_4 \cdot 2H_2O$
Formula weight (g mol^{-1})	443.89		564.06
Crystal system	Monoclinic		Tetragonal
Space group	$P2_1/c$		$P\text{-}42_1c$
a (Å)	12.209(3)		7.593(2)
b (Å)	10.085(4)		
c (Å)	8.783(4)		11.528(8)
β (°)	90.39(3)		
V (Å^3), Z	1081.4(5), 4		664.6(3), 2
μ (Mo Kα) (mm^{-1})	5.67		5.42
$\rho_{calc.}$ (g cm^{-3})	2.73		2.82
$\rho_{exp.}$ (g cm^{-3})	2.74(2)		2.83(2)
Temperature (K)		298	
Four-circle diffractometer		Siemens AED2	
Monochromator		graphite	
2θ range (°)	2–60		2–70
(hkl) limits	$|h| \leq 17$; $0 \leq k \leq 14$;		$|h| \leq 8$; $|k| \leq 12$; $|l| \leq 18$
	$0 \leq l \leq 12$		(two independent sets)
Scan mode		$\omega - 2\theta$	
Absorption correction		Gaussian	
T_{min}, T_{max}	0.71, 0.79		0.271, 0.550
Reflections measured/unique/used ($I > 2\sigma(I)$)	2645/2532/1678		2923/1464/1352
Parameters refined (on F^2)	180		60
R(int)/R(sigma)	0/0.11		0.05/0.04
R^a/R_w^b	0.065/0.118		0.023/0.075
Goodness of fit	1.13		1.22
Weighting scheme ($P = [F_0^2 + 2F_c^2]/3$)	$1/[\sigma^2(F_0^2) + (0.0191P)^2]$		$1/[\sigma^2(F_0^2) + (0.037P)^2]$
Difference Fourier residues (e Å^{-3})	1.1, -0.8		1.2, -1.3
Secondary extinction coefficient	$0.28(4) \times 10^{-6}$		$0.24(2) \times 10^{-5}$

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

Table 2
Atomic coordinates, equivalent isotropic displacement parameters and valence bond sums in $Na_5Y(CO_3)_4$

Atom	x	y	z	B (Å^2)	Σs [b]	$\Sigma s_{expected}$
Y	0.27554(6)	0.12411(8)	0.21440(8)	0.80(1)	3.03	3
Na(1)	0.2122(2)	0.8742(4)	0.6964(4)	1.66(6)	1.09	1
Na(2)	0.1033(3)	0.3737(4)	0.0847(4)	1.57(5)	1.10	1
Na(3)	0.0745(3)	0.8750(5)	0.0458(3)	1.96(6)	1.02	1
Na(4)	0.4015(3)	0.4203(4)	0.0771(4)	1.58(6)	1.25	1
Na(5)	0.3664(3)	0.8243(4)	0.0141(4)	1.84(6)	1.04	1
C(1)	0.0128(6)	0.1083(8)	0.2552(8)	0.9(1)[a]	3.97	4
C(2)	0.2182(6)	0.881(1)	0.3590(8)	1.1(1)[a]	3.96	4
C(3)	0.2768(6)	0.3663(9)	0.3874(8)	1.0(1)[a]	4.04	4
C(4)	0.5043(6)	0.134(1)	0.2613(9)	1.2(1)[a]	3.98	4
O(1)	0.2684(4)	0.3672(6)	0.2432(5)	1.23(9)	2.22	2
O(2)	0.2297(4)	0.8934(6)	0.2124(6)	1.3(1)	2.07	2
O(3)	0.2713(5)	0.2456(7)	0.9573(7)	1.32(9)	2.04	2
O(4)	0.2228(5)	0.9896(6)	0.4351(6)	1.1(1)	2.03	2
O(5)	0.0952(4)	0.1515(6)	0.1751(6)	1.6(1)	2.06	2
O(6)	0.3998(4)	0.8483(6)	0.6894(7)	2.0(1)	2.08	2
O(7)	0.4401(4)	0.0448(6)	0.3226(7)	1.5(1)	2.14	2
O(8)	0.4618(5)	0.2010(6)	0.1511(7)	1.8(1)	1.85	2
O(9)	0.9573(5)	0.0106(6)	0.2008(7)	1.8(1)	1.98	2
O(10)	0.9875(5)	0.1635(7)	0.3791(7)	2.3(1)	2.01	2
O(11)	0.2054(5)	0.7677(6)	0.4193(7)	1.5(1)	2.08	2
O(12)	0.2920(5)	0.0288(6)	0.9675(7)	1.7(1)	1.93	2

[a] Isotropic displacement parameters.
[b] 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.

Table 3
Selected inter-atomic distances (Å) and angles (°) in $Na_5Y(CO_3)_4$

Y–O(5)	2.243(5)	Na(1)–O(6)	2.306(6)	Na(2)–O(10)	2.317(7)			
Y–O(7)	2.356(6)	Na(1)–O(11)	2.427(7)	Na(2)–O(5)	2.380(7)			
Y–O(12)	2.382(6)	Na(1)–O(9)	2.545(7)	Na(2)–O(4)	2.404(7)			
Y–O(2)	2.394(6)	Na(1)–O(10)	2.551(7)	Na(2)–O(1)	2.443(6)			
Y–O(4)	2.455(6)	Na(1)–O(4)	2.577(7)	Na(2)–O(9)	2.453(7)			
Y–O(1)	2.466(7)	Na(1)–O(11)	2.662(7)	Na(2)–O(3)	2.676(8)			
Y–O(8)	2.469(6)	Na(1)–O(2)	2.710(8)					
Y–O(3)	2.507(6)	Na(1)–O(1)	2.727(8)					
Y–O(3)	2.569(6)							
⟨Y–O⟩	2.43	⟨Na–O⟩	2.56	⟨Na–O⟩	2.45			
Na(3)–O(10)	2.359(8)	Na(4)–O(1)	2.256(6)	Na(5)–O(12)	2.289(7)			
Na(3)–O(2)	2.393(6)	Na(4)–O(7)	2.314(7)	Na(5)–O(11)	2.323(7)			
Na(3)–O(9)	2.408(7)	Na(4)–O(8)	2.418(7)	Na(5)–O(6)	2.357(7)			
Na(3)–O(11)	2.425(7)	Na(4)–O(7)	2.464(7)	Na(5)–O(2)	2.519(7)			
Na(3)–O(9)	2.482(7)	Na(4)–O(6)	2.534(7)	Na(5)–O(8)	2.572(7)			
Na(3)–O(5)	2.841(6)	Na(4)–O(3)	2.592(7)	Na(5)–O(6)	2.894(7)			
		Na(4)–O(4)	2.666(7)					
⟨Na–O⟩	2.48	⟨Na–O⟩	2.46	⟨Na–O⟩	2.49			
C(1)–O(10)	1.263(9)	O(5)–C–O(9)	117.5(7)	C(2)–O(11)	1.27(1)	O(2)–C–O(4)	115.1(8)	
C(1)–O(9)	1.29(1)	O(10)–C–O(5)	120.8(8)	C(2)–O(4)	1.29(1)	O(2)–C–O(11)	121.1(9)	
C(1)–O(5)	1.306(9)	O(10)–C–O(9)	121.7(7)	C(2)–O(2)	1.303(8)	O(4)–C–O(11)	123.8(7)	
⟨C–O⟩	1.29	⟨O–C–O⟩	120	⟨C–O⟩	1.29	⟨O–C–O⟩	120	
C(3)–O(1)	1.270(8)	O(3)–C–O(12)	118.0(6)	C(4)–O(6)	1.259(9)	O(7)–C–O(8)	115.5(7)	
C(3)–O(12)	1.28(1)	O(3)–C–O(1)	118.6(8)	C(4)–O(8)	1.29(1)	O(6)–C–O(7)	121.0(8)	
C(3)–O(3)	1.29(1)	O(1)–C–O(12)	123.5(8)	C(4)–O(7)	1.31(1)	O(6)–C–O(8)	123.5(9)	
⟨C–O⟩	1.28	⟨O–C–O⟩	120	⟨C–O⟩	1.29	⟨O–C–O⟩	120	

Table 4
Atomic coordinates, equivalent isotropic displacement parameters and valence bond sums in $Na_5Yb(CO_3)_4 \cdot 2H_2O$

Atom	Site	x	y	z	$B_{eq.}$ (Å^2)	Σs [a]	$\Sigma s_{expected}$
Yb	2a	0	0	0	1.060(7)	3.25	3
Na(1)	2b	1/2	1/2	0	2.18(5)	1.02	1
Na(2)	8e	0.3230(2)	0.1815(2)	0.2075(1)	1.92(2)	1.07	1
C	8e	0.1824(4)	0.2861(3)	−0.0795(2)	1.39(3)	3.94	4
O(1)	8e	0.0954(3)	0.1796(3)	−0.1475(2)	1.46(3)	2.06	2
O(2)	8e	0.1702(3)	0.2527(3)	0.0315(2)	1.61(3)	1.85	2
O(3)	8e	0.2745(3)	0.4092(3)	−0.1197(2)	2.29(4)	2.09	2
O_w	4d	0	1/2	0.1673(3)	2.03(4)	–	2
H	8e	0.056(8)	0.438(8)	0.115(4)	2.03(4)	–	1

[a] The results refer to the equation $s = \exp[(r_0 - r)/0.37]$ with $r_0 = 1.985$, 1.80 and 1.39 for Yb–O, Na–O and C–O, respectively.

positions in $P2_1/c$, gives a good agreement between the experimental and theoretical patterns (FULLPROF [16], $R_p = 12.4\%$, $R_{wp} = 17.3\%$, $R_{exp.} = 5.0\%$ and $R_{Bragg} = 7.3\%$).

3.2. $Na_5Yb(CO_3)_4 \cdot 2H_2O$

Crystals of $Na_5Yb(CO_3)_4 \cdot 2H_2O$ were found to be isostructural with $Na_5Sc(CO_3)_4 \cdot 2H_2O$ [17]. The refinement of the atomic coordinates and anisotropic displacement parameters, taking the atomic coordinates of $Na_5Sc(CO_3)_4 \cdot 2H_2O$ as a starting model, led to the reliability factors $R = 0.023$ and $R_w = 0.075$.

4. Structure description

4.1. $Na_5Y(CO_3)_4$

Projections of the structure of $Na_5Y(CO_3)_4$ along the a- and c-axes appear in Figs. 1–3. Yttrium cations are 9-fold coordinated; the Y–O distances range from 2.243 to 2.569 Å with an average distance of 2.43 Å. The YO_{6+2+1} polyhedra are similar to the LnO_6F_{2+1} polyhedra found in $K_4Ln_2(CO_3)_3F_4$ [18] (Fig. 4, left and right). In shomiokite, yttrium cations present the same coordination number; however, the YO_{3+3+3} polyhedron is a tricapped trigonal

prism (Fig. 4, center). In $Na_5Y(CO_3)_4$, YO_9 polyhedra share two vertices and form infinite [001] chains $[YO_8]_\infty$ (Fig. 1). $Na(1)^+$ cations are surrounded by eight oxygen atoms with a mean Na(1)–O distance of 2.56 Å and form also infinite [001] chains (Fig. 2). Both Y^{3+} and $Na(1)^+$ cations are coordinated by three carbonate groups, $C(2)O_3^{2-}$ and $C(3)O_3^{2-}$, in a mean plane. The YO_{6+2+1} and $Na(1)O_{5+2+1}$ polyhedra share vertices and form, with $C(2)O_3^{2-}$ and $C(3)O_3^{2-}$ carbonate groups, infinite $[NaY(CO_3)_2O_6]_\infty$ layers parallel to the (bc) plane and located at $x \approx \frac{1}{4}$ and $x \approx \frac{3}{4}$. Analogous layers are observed in the structure of $Na_3La_2(CO_3)_4F$ [19] (Fig. 2, right). $Na(2)^+$, $Na(3)^+$, and $Na(5)^+$ cations adopt a distorted octahedral coordination while $Na(4)^+$ cations are 7-fold coordinated; the average Na–O distances are 2.45, 2.48, 2.49, and 2.46 Å, respectively.

In $Na_5Y(CO_3)_4$, the carbonate groups form, according to the notation of Grice et al. [20], two family types. The $C(2)O_3^{2-}$ and $C(3)O_3^{2-}$ carbonate groups form infinite 'flat-lying' layers parallel to the (bc) plane (Fig. 5 right). These dense layers can be described with a pseudo-hexagonal cell ($a_H \approx b_H \approx 5.0$ Å). This arrangement is characterized by the carbonate equivalent area $S = 22.14$ Å^2. A similar area is found in $Na_3La_2(CO_3)_4F$ and $CaCO_3$ calcite with $S = 21.65$ Å^2 and $S = 21.30$ Å^2, respectively (Fig. 5 left and center). $C(1)O_3^{2-}$ and $C(4)O_3^{2-}$ carbonate

Table 5
Selected inter-atomic distances (Å) and angles (°) in $Na_5Yb(CO_3)_4 \cdot 2H_2O$

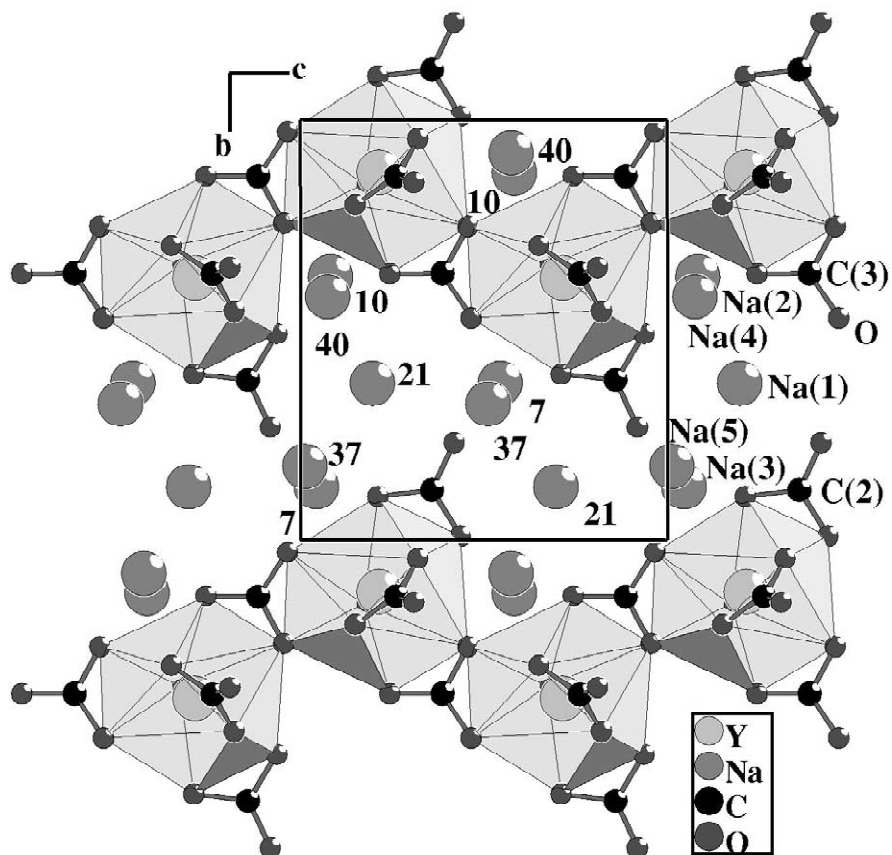|							
4×Yb–O(1)	2.296(2)			4×Na(1)–O(3)	2.304(3)	Na(2)–O(3)	2.379(3)
4×Yb–O(2)	2.342(2)					Na(2)–O(1)	2.381(3)
						Na(2)–O(2)	2.398(3)
						Na(2)–O_w	2.406(2)
						Na(2)–O(1)	2.466(3)
						Na(2)–O(3)	2.682(3)
⟨Yb–O⟩	2.319			⟨Na–O⟩	2.304	⟨Na–O⟩	2.452
C–O(3)	1.256(3)	O(1)–C–O(2)	115.5(2)	O_w–H	0.87(5)		
C–O(1)	1.306(3)	O(1)–C–O(3)	121.5(3)				
C–O(2)	1.308(3)	O(2)–C–O(3)	123.0(3)				
⟨C–O⟩	1.290	⟨O–C–O⟩	120.0				

Fig. 1. [001] chains $[YO_8]_\infty$ at $x \approx \frac{1}{4}$ in $Na_5Y(CO_3)_4$ (sodium atoms are represented by grey spheres; their heights are given in hundreds).
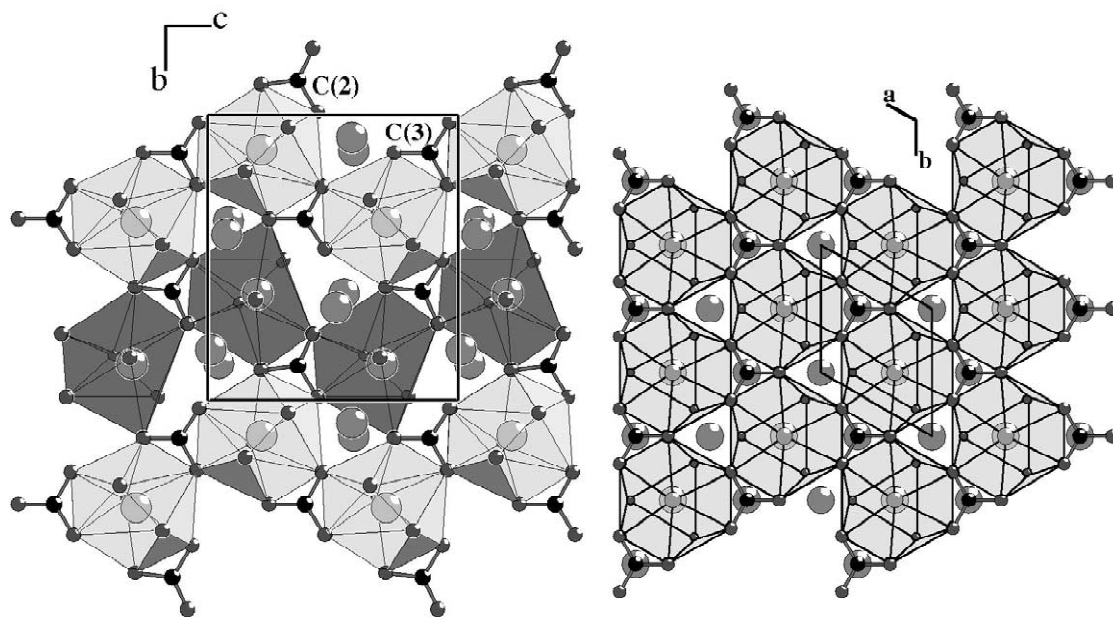

Fig. 2. $[NaY(CO_3)_2O_6]_\infty$ layers in $Na_5Y(CO_3)_4$ ($x \approx \frac{1}{4}$) (left) and $[La(CO_3)O_3F]_\infty$ layers in $Na_3La_2(CO_3)_4F$ (right). Yttrium polyhedra are light shaded, sodium polyhedra are darker.
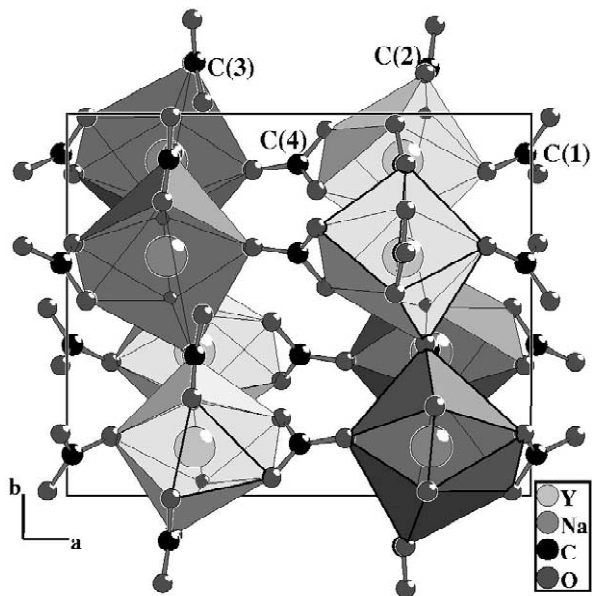
Fig. 3. Connection of the (100) layers $[NaY(CO_3)_2O_6]_\infty$ in $Na_5Y(CO_3)_4$.

groups form infinite [010] rows of 'standing on base' and 'standing on top' triangles.

4.2. $Na_5Yb(CO_3)_4 \cdot 2H_2O$

YbO_8, $Na(1)O_4$ and $Na(2)O_6$ polyhedra (Fig. 6) build the structure of $Na_5Yb(CO_3)_4 \cdot 2H_2O$. The distorted YbO_8 square antiprisms and $Na(1)O_4$ tetrahedra share carbonate groups and form $[NaYb(CO_3)_4]_\infty$ layers located at $z = 0$
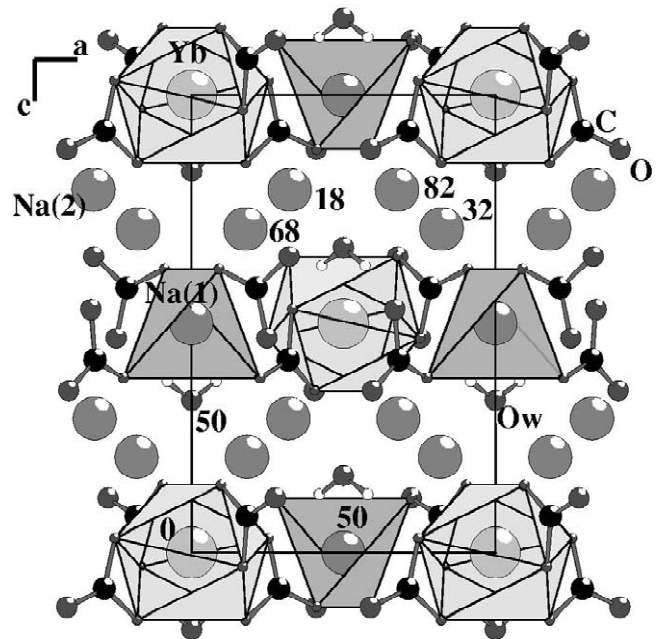

Fig. 6. Projection of the structure of $Na_5Yb(CO_3)_4 \cdot 2H_2O$ along [010].

and $z = \frac{1}{2}$. The $Na(2)^+$ cations and water molecules are inserted between the $[NaYb(CO_3)_4]_\infty$ layers.

5. Characterization

The TGA analysis of $Na_5Y(CO_3)_4$ exhibits a weight loss in two steps. The first step, which occurs in the interval

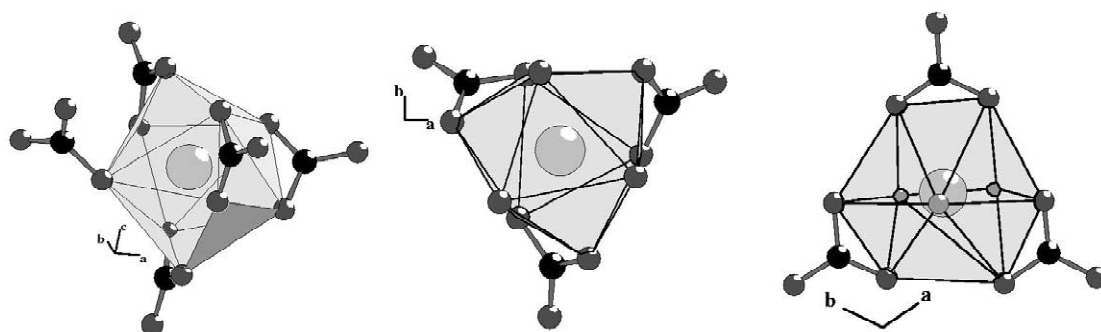Fig. 4. YO_{6+2+1}, $(Y, Ln)O_{3+3+3}$ and LnO_6F_{2+1} polyhedra in $Na_5Y(CO_3)_4$ (left), shomiokite $Na_3(Y,Ln)(CO_3)_3 \cdot 3H_2O$ (center) and $K_4Ln_2(CO_3)_3F_4$ (right), respectively.
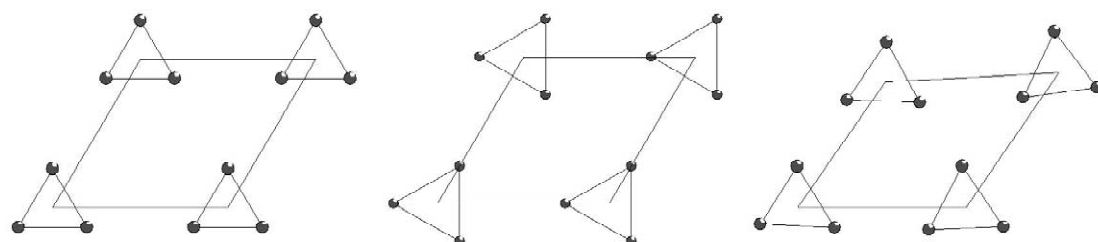
Fig. 5. 'Flat-lying' arrangement of carbonate groups in $Na_3La_2(CO_3)_4F$ (left), $CaCO_3$ calcite (center) and $Na_5Y(CO_3)_4$ (right).

300–650 °C, is attributed to the departure of three moles of CO_2 gas per two moles of $Na_5Y(CO_3)_4$ (exp./th. = 14.9/14.6%); the decomposition reaction can be written:

$$2Na_5Y(CO_3)_4 \rightarrow Y_2O_3 + 5Na_2CO_3 + 3CO_2$$
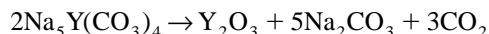
The second step corresponds to the decomposition of Na_2CO_3 and occurs above 850 °C.

The thermal decomposition of $Na_5Yb(CO_3)_4 \cdot 2H_2O$ occurs in the intervals 190–250 °C, 280–650 °C, and above 850 °C. The first weight loss is attributed to the departure of two moles of water per one mole of $Na_5Yb(CO_3)_4 \cdot 2H_2O$ (exp./th. = 6.3/6.4%); X-ray diffraction analysis of the residual shows that the intermediate phase is $Na_5Yb(CO_3)_4$, isostructural with $Na_5Y(CO_3)_4$. However, the crystallinity of this intermediate phase is poor and the diffraction line width is large. Consequently, accurate cell parameters of $Na_5Yb(CO_3)_4$ cannot be given here. The second and third weight loss steps are similar to that of $Na_5Y(CO_3)_4$. The experimental and theoretical second weight loss steps are 11.3 and 11.2%, respectively.

6. Conclusion

The crystal structures of two carbonates, $Na_5Y(CO_3)_4$ and $Na_5Yb(CO_3)_4 \cdot 2H_2O$, are determined. Both compounds are obtained by microwave-assisted hydrothermal method in sub-critical conditions. $Na_5Yb(CO_3)_4 \cdot 2H_2O$, isostructural with $Na_5Sc(CO_3)_4 \cdot 2H_2O$, undergoes dehydration at $190 < T < 250$ °C and leads to $Na_5Yb(CO_3)_4$ which is isostructural with $Na_5Y(CO_3)_4$. In the structure of $Na_5Y(CO_3)_4$, $C(2)O_3^{2-}$ and $C(3)O_3^{2-}$ carbonate groups are stacked in dense 'flat lying' layers between which 'standing on base' and 'standing on top' $C(1)O_3^{2-}$ and $C(4)O_3^{2-}$ carbonate groups are inserted. Dehydration of $Na_5Yb(CO_3)_4 \cdot 2H_2O$ to give $Na_5Yb(CO_3)_4$ implies that ytterbium coordination increases, from 8 to 9, simultaneously with $Na(1)^+$ coordination. In both structures, it is remarkable that $Na(1)^+$ and Yb^{3+} form infinite layers of

polyhedra, separated by four remaining Na^+ cations. The $[NaYb(CO_3)_4]_\infty$ layers in $Na_5Yb(CO_3)_4 \cdot 2H_2O$ transform to $[NaYb(CO_3)_2O_6]_\infty$ layers, connected by the remaining carbonate groups in $Na_5Yb(CO_3)_4$.

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