

THOMASCLARKITE-(Y), A NEW SODIUM – RARE-EARTH-ELEMENT BICARBONATE MINERAL SPECIES FROM MONT SAINT-HILAIRE, QUEBEC

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ABSTRACT

Thomasclarkite-(Y), ideally $\text{Na}(\text{Y},\text{REE})(\text{HCO}_3)(\text{OH})_3 \cdot 4\text{H}_2\text{O}$, is a newly identified mineral species from Mont Saint-Hilaire, Quebec. It occurs as individual, well-formed, blocky, white-to-yellow crystals up to 2 mm in length. Associated minerals include aegirine, albite, analcime, ancylite-(Ce), astrophyllite, calcite, catapleite, dawsonite, elpidite, epididymite, franconite, gaidonnayite, galena, genthelvite, microcline, molybdenite, natrolite, petersenite-(Ce), polyolithionite, pyrochlore, rhodochrosite, rutile, sérandite, siderite, sphalerite, zircon and an unidentified NaREE carbonate. The transparent to translucent mineral has a vitreous luster and a white streak. It is soft (Mohs hardness 2–3) and brittle, with an uneven fracture, a perfect {010} cleavage and good {101} parting. Merohedral twinning on {101} is ubiquitous. Thomasclarkite-(Y) is pseudo-uniaxial negative, $\omega = 1.540(4)$ and $\epsilon = 1.40(2)$. It is monoclinic, space group $P2_1$, a 4.556(1), b 13.018(6), c 4.556(2) Å, β 90.15(3)°, V 270.2(2) Å³ and $Z = 1$. The strongest X-ray powder-diffraction lines [d in Å(hkl)] are 12.97(10)(010), 6.52(3)(020), 4.57(3)(100, 001), 4.32(5)(110, 011), 3.223(3)($\bar{1}01, 101$), 3.133(5)($\bar{1}11, 111$), 2.593(3)($\bar{1}31, 131$), 2.035(3)(201, 102), 2.016 (4)(230, 032) and 1.844(3)(231, 132). The infrared spectrum is given. Two electron-microprobe analyses and a thermogravimetric analysis gave Na_2O 6.72 (6.20–7.24), CaO 0.33 (0.35–0.32), Y_2O_3 14.52 (14.97–14.07), La_2O_3 8.63 (8.54–8.72), Ce_2O_3 17.11 (18.44–15.79), Pr_2O_3 1.92 (1.94–1.90), Nd_2O_3 5.63 (5.60–5.66), Sm_2O_3 1.22 (1.27–1.17), Gd_2O_3 1.22 (1.13–1.31), Dy_2O_3 2.04 (2.08–2.00), Er_2O_3 2.20 (2.20–2.20), Yb_2O_3 1.32 (1.45–1.19), ThO_2 0.54 (0.48–0.60), F 0.17 (0.35–0.00), CO_2 12.00 and H_2O 26.60, $\text{O} = \text{F} - 0.07$, total 102.10 wt.%. The empirical formula, based on 10 anions and one atom of C, is $(\text{Na}_{0.80}\text{Ce}_{0.18}\text{Ca}_{0.02})_{\Sigma 1.00}(\text{Y}_{0.48}\text{La}_{0.20}\text{Ce}_{0.21}\text{Pr}_{0.04}\text{Nd}_{0.12}\text{Sm}_{0.03}\text{Gd}_{0.03}\text{Dy}_{0.04}\text{Er}_{0.04}\text{Yb}_{0.03})_{\Sigma 1.22}(\text{HCO}_3)[\text{O}_{6.97}\text{F}_{0.03}]\text{H}_{9.93}$. $D_{\text{calc.}} = 2.34 \text{ g/cm}^3$ and $D_{\text{meas.}} = 2.30(2) \text{ g/cm}^3$. The structure has been refined to $R = 0.055$ using a twinned crystal. The structure is layered on {010}. One layer consists of $[\text{HCO}_3]^-$ groups oriented perpendicular to (010) and H-bonded to a H_2O layer. A second layer consists of (YF_8) polyhedra and (NaF_6) polyhedra which are H-bonded to the H_2O layer. In other bicarbonate minerals, the H-bonding is between the CO_3 groups forming chains, whereas in thomasclarkite-(Y), the H-bonding is directed toward the H_2O groups.

Keywords: thomasclarkite-(Y), new mineral species, bicarbonate, crystal structure, twinning, Mont Saint-Hilaire, Quebec.

SOMMAIRE

La thomasclarkite-(Y), dont la formule idéale est $\text{Na}(\text{Y},\text{REE})(\text{HCO}_3)(\text{OH})_3 \cdot 4\text{H}_2\text{O}$, a été découverte récemment au mont Saint-Hilaire, Québec. Elle se présente en cristaux trappus isolés bien formés, blancs à jaunes, atteignant 2 mm en longueur. Lui sont associés aegyrine, albite, analcime, ancylite-(Ce), astrophyllite, calcite, catapléite, dawsonite, elpidite, epididymite, franconite, gaidonnayite, galena, genthelvite, microcline, molybdenite, natrolite, petersenite-(Ce), polyolithionite, pyrochlore, rhodochrosite, rutile, sérandite, siderite, sphalérite, zircon et un carbonate à NaREE non identifié. Le minéral, transparent à translucide, possède un éclat vitreux et une rayure blanche. Sa dureté de Mohs est entre 2 et 3, et elle est cassante, avec une fracture irrégulière, un clivage {010} parfait, et un bon plan de séparation {101}. Un maclage par méroédrie sur {101} est ubiquiste. La thomasclarkite-(Y) est pseudo-uniaxe négative, $\omega = 1.540(4)$ et $\epsilon = 1.40(2)$. Elle est monoclinique, groupe spatial $P2_1$, a 4.556(1), b 13.018(6), c 4.556(2) Å, β 90.15(3)°, V 270.2(2) Å³ et $Z = 1$. Les raies les plus intenses du spectre de diffraction X [d en Å(hkl)] sont 12.97(10)(010), 6.52(3)(020), 4.57(3)(100, 001), 4.32(5)(110, 011), 3.223(3)($\bar{1}01, 101$), 3.133(5)($\bar{1}11, 111$), 2.593(3)($\bar{1}31, 131$), 2.035(3)(201, 102), 2.016 (4)(230, 032) et 1.844(3)(231, 132). Nous en reproduisons le spectre infra-rouge. Deux analyses à la microsonde électronique et une analyse par thermogravimétrie ont donné Na_2O 6.72 (6.20–7.24), CaO 0.33 (0.35–0.32), Y_2O_3 14.52 (14.97–14.07), La_2O_3 8.63 (8.54–8.72), Ce_2O_3 17.11 (18.44–15.79), Pr_2O_3 1.92 (1.94–1.90), Nd_2O_3 5.63 (5.60–5.66), Sm_2O_3 1.22 (1.27–1.17), Gd_2O_3 1.22 (1.13–1.31), Dy_2O_3 2.04 (2.08–2.00), Er_2O_3 2.20 (2.20–2.20), Yb_2O_3 1.32 (1.45–1.19), ThO_2 0.54 (0.48–0.60), F 0.17 (0.35–0.00), CO_2 12.00 et H_2O 26.60, $\text{O} = \text{F} - 0.07$, pour un total de 102.10% (poids). La formule empirique, fondée sur 10 anions et un atome de C, est $(\text{Na}_{0.80}\text{Ce}_{0.18}\text{Ca}_{0.02})_{\Sigma 1.00}(\text{Y}_{0.48}\text{La}_{0.20}\text{Ce}_{0.21}\text{Pr}_{0.04}\text{Nd}_{0.12}\text{Sm}_{0.03}\text{Gd}_{0.03}\text{Dy}_{0.04}\text{Er}_{0.04}\text{Yb}_{0.03})_{\Sigma 1.22}(\text{HCO}_3)[\text{O}_{6.97}\text{F}_{0.03}]\text{H}_{9.93}$. La densité calculée est de 2.34, tandis que la densité mesurée, 2.30(2) g/cm^3 . Nous avons affiné la structure d'un cristal maclé jusqu'à un résidu R de 0.055. Elle montre des couches sur {010}; un niveau est fait de groupes $[\text{HCO}_3]^-$ orientés perpendiculairement à (010) et rattachés par liaisons hydrogène à un niveau de groupes H_2O .

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Un second niveau contient des polyèdres ($Y\phi_8$) et ($Na\phi_6$) aussi rattachés aux groupes H_2O par liaisons hydrogène. Dans les autres minéraux contenant du bicarbonate, les liaisons hydrogène impliquent les groupes CO_3 agencés en chaînes, tandis que dans la thomasclarkite-(Y), elles sont dirigées vers les groupes H_2O .

(Traduit par la Rédaction)

Mots-clés: thomasclarkite-(Y), nouvelle espèce minérale, bicarbonate, structure cristalline, macle, mont Saint-Hilaire, Québec.

INTRODUCTION

The new mineral species described herein, thomasclarkite-(Y), occurs in the Poudrette quarry, Mont Saint-Hilaire, Rouville County, Quebec. Mont Saint-Hilaire is known throughout the world for its diversity in mineral species (Horváth & Gault 1990). To date, 320 species have been identified from this locality, 56 of which are carbonate minerals. As well, several undescribed carbonate species have been reported (Chao *et al.* 1990). Of the carbonate minerals, 20 contain rare-earth elements (*REE*) as essential constituents, 45 contain essential sodium or alkaline earths, and 20 contain essential hydrogen.

Thomasclarkite-(Y), formerly designated as UK93, is named in honor of Professor Thomas Henry Clark (1893–1996). Dr. Clark held a position at McGill University for 69 years, during which time he authored more than 100 scientific publications, particularly concerning the geology of the St. Lawrence Lowlands in which Mont Saint-Hilaire is situated. He was President of the Royal Society of Canada, Sigma Xi (McGill Chapter) and the Geological Association of Canada. He received numerous medals for his scientific contributions. The new mineral and the name were approved by the Commission on New Minerals and Mineral Names, IMA. Cotype material is housed in the collection of the Canadian Museum of Nature, catalogue numbers CMNMI 81553, CMNMI 81554 and CMNMI 81555.

OCCURRENCE

Mont Saint-Hilaire is an alkaline intrusive complex of Cretaceous age and one of the ten Monteregian Hills, a series of plutons aligned along the St. Lawrence Valley for almost 150 km eastward from Oka to Megantic.

Thomasclarkite-(Y) occurs as a late-stage hydrothermal phase in a system of alkaline pegmatite dikes in nepheline syenite in the southern corner of the Poudrette quarry. Associated minerals include aegirine, albite, analcime, ancylite-(Ce), astrophyllite, calcite, cataleite, dawsonite, elpidite, epididymite, franconite, gaidonnayite, galena, genthelvite, microcline, molybdenite, natrolite, petersenite-(Ce), polyolithionite, pyrochlore, rhodochrosite, rutile, sérandite, siderite, sphalerite, zircon and an unidentified Na-*REE* carbonate. Thomasclarkite-(Y) was first collected on level 7 of the quarry in November of 1991 by museum staff and private collector Gilles Haincault. In more recent years, with enlargement of the quarry, the same dike

system was exposed again on the next level, and more specimens were collected by several private collectors. However, at present, thomasclarkite-(Y) must be considered a rare mineral, as there are less than one hundred milligrams known to exist.

PHYSICAL AND OPTICAL PROPERTIES

Thomasclarkite-(Y) occurs as individual crystals and as groups of well-formed, blocky, pseudotetragonal crystals up to 2 mm in length (Fig. 1). Forms observed are the pedions $\{010\}$ and $\{0\bar{1}0\}$, sphenoids $\{111\}$, $\{1\bar{1}1\}$, $\{\bar{1}11\}$ and $\{\bar{1}\bar{1}1\}$ and the pinacoids $\{101\}$ and $\{\bar{1}01\}$ (Fig. 2). The metrically tetragonal unit-cell has ubiquitous merohedral twinning on $\{101\}$. The mineral is white to yellow, with a white streak and vitreous luster. It is brittle, with an uneven fracture, a perfect $\{010\}$ cleavage and good $\{101\}$ parting. Thomasclarkite-(Y) is relatively soft (Mohs hardness 2 to 3) and does not fluoresce in either long- or short-wave ultraviolet light. The density, measured twice by suspension in a solution of bromoform and butyl alcohol, is $2.30 \pm 0.02 \text{ g/cm}^3$, which compares very well to the calculated density of 2.34 g/cm^3 .

Thomasclarkite-(Y) is pseudo-uniaxial negative, ω 1.540(4) and ϵ 1.40(2) (for $\lambda = 589 \text{ nm}$), and non-pleochroic. In some cases, there is a small $2V$ of $\sim 5^\circ$. A Gladstone–Dale calculation gives a compatibility index of -0.027 , which is regarded as excellent (Mandarinov 1981).

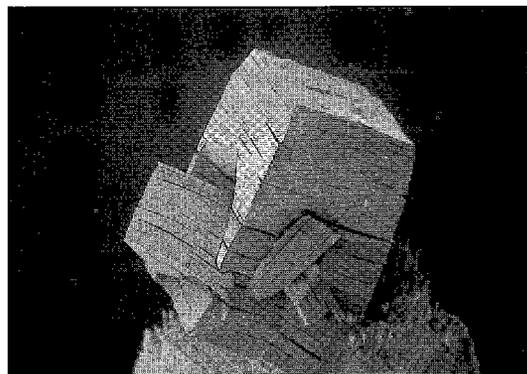


FIG. 1. Scanning electron micrograph of thomasclarkite-(Y) showing exfoliation along cleavage planes due to loss of H_2O under vacuum. Scale bar: 500 μm .

CHEMICAL COMPOSITION

Chemical analyses were done in wavelength-dispersion (WD) mode on a JEOL 733 electron microprobe using Tracor Northern 5500 and 5600 automation. Data reduction was done with a conventional ZAF routine in the Tracor Northern TASK series of programs. Several initial attempts were made to analyze thomasclarkite-(Y), with poor results owing to the decrepitation of the sample and the lifting of the carbon coat under prolonged vacuum. This decrepitation under vacuum results from the weak H-bonding of the H₂O groups to the (OH)⁻ and (HCO₃)⁻ anions. To minimize this effect, calibration of the standards were performed first, and the samples were introduced later into the specimen chamber and analyzed immediately. Using this method, two points were analyzed on a single grain with a beam 40 μm in diameter to limit migration and volatilization of Na and general burn-up of the sample. This method, while reducing the effects of the problem, did not eliminate them, resulting in a high analytical total and nonstoichiometric formula. The operating voltage was 15 kV and the beam current was 0.20 μA. Data for all elements in the samples were collected for 25 s or 0.50% precision, whichever was attained first. A 100 s energy-dispersion scan indicated no elements with *Z* greater than 8 other than those reported here. The presence of CO₂ (as CO₃) and H₂O was confirmed by infrared spectroscopy, and their concentration was established by thermogravimetric analysis. The following standards were used in the electron-microprobe analyses: albite (NaKα), calcite (CaKα), synthetic yttrium iron garnet (YIG) (YKα), a set of synthetic REE phosphates (LaLα, CeLα, PrLβ, NdLα, SmLα, GdLα, DyLβ, ErLα, YbLα), synthetic ThO₂ (ThMα) and synthetic La(CO₃)F (FKα).

Data for standards were collected for 50 s or 0.25% precision, whichever was attained first. The REE data were corrected for overlaps. The chemical composition (with ranges) is Na₂O 6.72 (6.20–7.24), CaO 0.33 (0.35–0.32), Y₂O₃ 14.52 (14.97–14.07), La₂O₃ 8.63 (8.54–8.72), Ce₂O₃ 17.11 (18.44–15.79), Pr₂O₃ 1.92 (1.94–1.90), Nd₂O₃ 5.63 (5.60–5.66), Sm₂O₃ 1.22 (1.27–1.17), Gd₂O₃ 1.22 (1.13–1.31), Dy₂O₃ 2.04 (2.08–2.00), Er₂O₃ 2.20 (2.20–2.20), Yb₂O₃ 1.32 (1.45–1.19), ThO₂ 0.54 (0.48–0.60), F 0.17 (0.35–0.00), CO₂ 12.00 and H₂O 26.60, O = F – 0.07, total 102.10 wt.%. Trace amounts of Eu, Tb, Tm and Lu also were detected. The empirical formula based on 10 anions and one C ion from the crystal-structure analysis is (Na_{0.80}Ce_{0.18}Ca_{0.02})Σ1.00(Y_{0.48}La_{0.20}Ce_{0.21}Pr_{0.04}Nd_{0.12}Sm_{0.03}Gd_{0.03}Dy_{0.04}Er_{0.04}Yb_{0.03})Σ1.22(HCO₃)₃[O_{6.97}F_{0.03}]H_{9.93} or, ideally, Na(Y,REE)(HCO₃)₃•4H₂O, with the H₂O sites usually only partially occupied. The assignment of cations to the Na site is based on the site-occupancy refinement in the crystal-structure analysis.

Thomasclarkite-(Y) dissolves readily with strong effervescence in 10% HCl.

THERMOGRAVIMETRIC
AND DIFFERENTIAL THERMAL ANALYSES

The thermogravimetric analysis (TG) of thomasclarkite-(Y) was done using a Mettler – Toledo TA8000 system (software version 3.0), which uses a Mettler TG50 module linked to a Mettler M3 microbalance. The purge gas is dry nitrogen, with a flow rate of 200 mL/min. A 5.970 mg sample of material was ground to a fine powder and heated from room temperature to 1000°C at a rate of 5°C min⁻¹. The weight loss of 2.302 mg occurred in two steps (TG, Fig. 3): between 20 and 110°C, 1.222 mg (20.5 wt.%) and between 380 and 510°C, 1.080 mg (18.1 wt.%). The first weight-loss step is interpreted as the loss of [H₂O] groups. This loss begins at room temperature because some of the H₂O groups are only weakly H-bonded to the (OH)⁻ and (HCO₃)⁻ anions. It is this instability in thomasclarkite-(Y) that caused so many analytical problems. The second weight-loss step presumably is a result of driving off the (OH)⁻ and (HCO₃)⁻ anions as water and carbon dioxide.

The differential thermal analysis curve (DTG, Fig. 3) reveals one smooth endothermic peak for the initial loss in H₂O, whereas the second loss in weight is bimodal on the DTG curve owing to the difference in energy required to drive off the hydroxyl as opposed to the carbon dioxide at a higher temperature.

INFRARED ANALYSIS

The infrared spectrum of thomasclarkite-(Y) (Fig. 4) was obtained using a Bomem Michelson MB-120 Fourier-transform infrared spectrometer with a diamond-anvil cell as a microsampling device. The

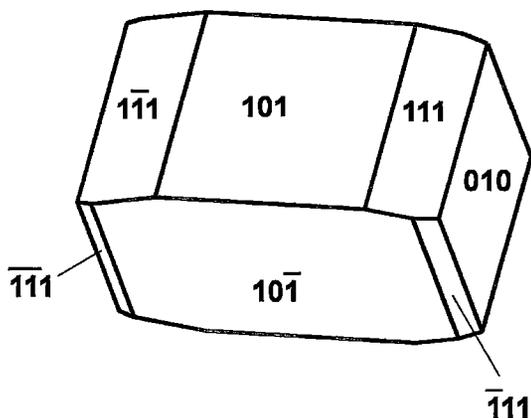


Fig. 2. Idealized drawing of a crystal of thomasclarkite-(Y) showing the most common habit and forms.

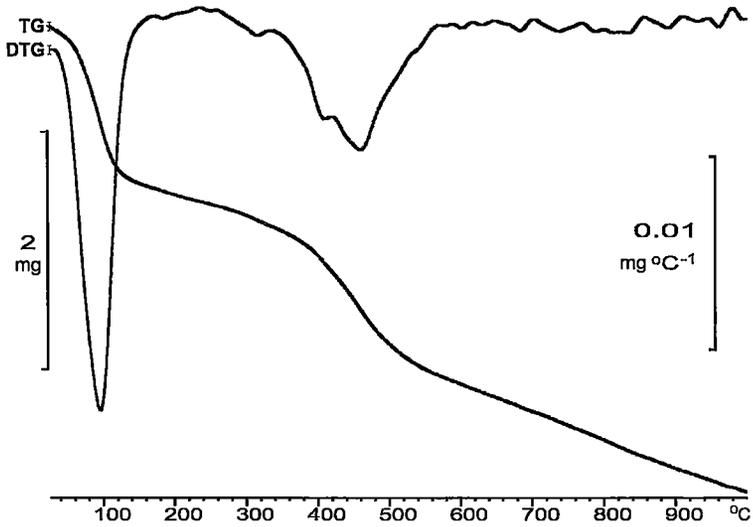


FIG. 3. Results of thermogravimetric (TG) and differential thermal analyses (DTG) of thomasclarkite-(Y).

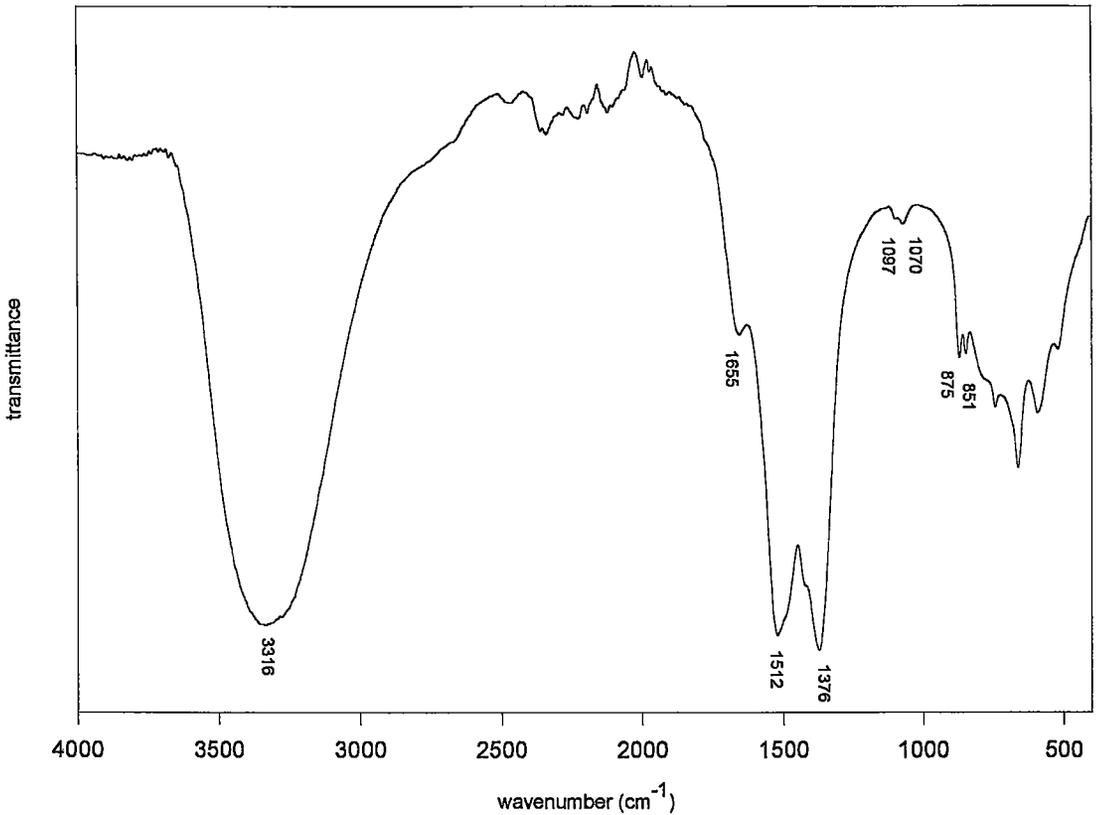


FIG. 4. Infrared spectrum of thomasclarkite-(Y).

dominant absorption band is that of the O-H stretching mode (3316 cm^{-1}). The (H_2O) bending band (1655 cm^{-1}) forms a shoulder on the large, split, asymmetric stretching band for (CO_3). This splitting (1512 and 1376 cm^{-1}) is explained by the fact that the carbonate group is actually (HCO_3) having two distinct C-O bond lengths, as seen in the crystal-structure determination. For this reason, the (CO_3) symmetric band also is split (1097 and 1070 cm^{-1}). The weak intensity of this symmetrical band is due to the limited ability of the (HCO_3) group to undergo this type of stretching mode. The 875 and 851 cm^{-1} are due to out-of-plane bending of (CO_3). The remainder of the spectra could not be unequivocally assigned.

X-RAY CRYSTALLOGRAPHY AND CRYSTAL-STRUCTURE DETERMINATION

Precession photographs initially showed thomasclarkite-(Y) to be tetragonal, diffraction symmetry $4/mmm$. X-ray powder-diffraction data (XRPD), obtained with a Gandolfi camera having a diameter of 114.6 mm and using $\text{CuK}\alpha$ radiation, are given in Table 1. The XRPD data can be indexed on a tetragonal cell, but are indexed on the monoclinic cell discovered in the crystal-structure analysis. The cell determined with the four-circle diffractometer revealed one angle to be non-orthogonal. With the solution of the crystal structure, it became apparent that the true symmetry of thomas-

clarkite-(Y) is monoclinic, space group $P2_1$, and the pseudotetragonal symmetry is due to merohedral twinning.

Four sets of intensity-data measurements were made. It became apparent after the first set that this was not going to be an easy experiment. The initial data-collection was interrupted because of instrument problems. The crystal remained in the University of Manitoba lab from the spring until winter, at which time it was remounted and centered again. It became evident in this second centering process that the crystal had decrepitated severely owing to extremely low levels of humidity in Winnipeg at that time of the year. Reflection intensities were less than one-half of those measured previously, and the peaks had become very broad. New material was found that seemed more stable. In the final data-collection, which we are reporting here, a crystal fragment of cotype thomasclarkite-(Y) was mounted on a Siemens $P3/P4$ fully automated four-circle diffractometer operated at 50 kV and 40 mA . Two asymmetric units of intensity data were collected (*i.e.*, $> h \pm k \pm l$) up to $2\theta = 60^\circ$ using a $\theta:2\theta$ scan-mode, with scan speeds inversely proportional to intensity, varying from 4 to $29.3^\circ/\text{minute}$. Information relevant to the data collection and structure determination are given in Table 2. For the ellipsoidal absorption correction, 10 intense diffraction-maxima in the range 12 to $60^\circ 2\theta$ were chosen for ψ diffraction-vector scans after the method of North *et al.* (1968). The merging R for the ψ -scan data set (360 reflections) decreased from 13.1% before the absorption correction to 3.4% after the absorption correction. Reduction of the intensity data, structure determination and initial refinement of the structure were done with the SHELXTL (Sheldrick 1990) package of computer programs.

Phasing of a set of normalized structure-factors gave a mean value $|E^2 - 1|$ of 0.33 . This low value may be of little significance on a twinned crystal. In a non-centrosymmetric space group, one would expect a low value, but not this low. The phase-normalized structure-factors were used to give an E -map on which were

TABLE 1. THOMASCLARKITE-(Y): X-RAY POWDER-DIFFRACTION DATA

I/I_0	d_{obs}	$d_{calc}(\text{\AA})$	hkl	I/I_0	d_{obs}	$d_{calc}(\text{\AA})$	hkl
10	12.97	13.01	010			1.847	$\bar{2}31, \bar{1}32$
3	6.52	6.50	020	3	1.844	1.845	231, 132
3	4.57	4.56	100, 001	1	1.801	1.800	$\bar{1}61, 161$
		4.34	030			1.728	241, 142
5	4.32	4.30	110, 011	2	1.724	1.721	071, 170
<1	3.725	3.735	120	2	1.606	1.605	$\bar{2}51, \bar{1}52$
3	3.223	3.219	$\bar{1}01, 101$	<1	1.570	1.571	260, 062
		3.142	$\bar{1}30, 031$	<1	1.514	1.513	$\bar{2}32$
5	3.133	3.136	$\bar{1}11, 111$			1.511	310, 130
2	2.889	2.891	$\bar{1}21, 121$	1	1.445	1.444	$\bar{1}42, 242$
2	2.643	2.648	140, 041	<1	1.443	1.443	$\bar{1}03, \bar{1}01$
		2.601	050	<1	1.436	1.435	330, 033
3	2.593	2.589	$\bar{1}31, 131$			1.409	$\bar{3}21, \bar{1}23$
2	2.287	2.290	$\bar{1}41$	<1	1.408	1.408	321, 123
		2.281	002	<1	1.376		
		2.260	150	<1	1.370		
<1	2.253	2.246	210	<1	1.320		
		2.168	060	<1	1.302		
<1	2.155	2.153	220, 022	<1	1.262		
		2.042	$\bar{2}01, \bar{1}02$	<1	1.221		
3	2.035	2.039	201, 102	<1	1.201		
4	2.016	2.018	230, 032	<1	1.180		
1	1.954	1.958	160, 061				
<1	1.865	1.867	240, 042				

114.6 mm Gandolfi camera, $\text{CuK}\alpha$ radiation, visually estimated intensities.
Indexing based on cell: $a = 4.563(2)$, $b = 13.007(9)$, $c = 4.562(3)\text{ \AA}$, $\beta = 90.1(1)^\circ$

TABLE 2. THOMASCLARKITE-(Y): DATA-COLLECTION INFORMATION

Space Group	$P2_1$	Measured reflections	1862
a (\AA)	4.556(1)	Observed reflections $[> 4\sigma(F)]$	1616
b (\AA)	13.018(6)	Merged reflections	843
c (\AA)	4.556(2)	$R(\text{int})$	0.025
β°	90.15(3)	Min/Max transmission	0.158/0.350
V (\AA^3)	270.2(2)	Refined parameters	72
Radiation	$\text{MoK}\alpha$	GoOF	1.115
Monochromator	Graphite	wR^2	0.157
μ (mm^{-1})	4.29	R	0.055
Unit-cell contents 1[Na(Y; REE)(HCO_3)(OH) $\cdot 4\text{H}_2\text{O}$]			

located the *Na* site, a *Y* site and five lighter-element sites. This model refined to $R = 0.16$ but could not be improved. In particular, the (CO_3) groups could not be located, and some O sites had unusual coordinations. The next stage in the structure determination involved incorporating a twin law for the intensity data, using the program SHELXL-93 (G.M. Sheldrick, unpubl. data). Application of a twin law by reflection on (101) immediately improved the model, as it located the (CO_3) group, and reduced the R index to 0.065. In the final least-squares refinement, all atomic positions were refined with anisotropic displacement factors to a final residual of $R = 0.058$. Bond-valence calculations (Bresé & O'Keeffe 1991) helped establish the *OH* and H_2O sites. The addition of an isotropic-extinction factor did not improve the results. Inverting the polarity of the structure did not change the R index appreciably. The fractional contribution of each of the two twin components refined to 0.496(9) (*i.e.*, within one sigma of equal amounts of each component). The structure was checked for higher symmetry with the program MISSYM (Le Page 1987). The *Na*, *Y*, *C* and *OH3* sites have $m4m$ symmetry (cell orientation retained), and this tetragonal model refined to $R = 0.16$ but could be improved. The *Na*, *Y*, *C*, *O1*, *OH2* and *OH3* sites have symmetry close to $m2m$. This orthorhombic model, when reoriented,

refines to $R = 0.16$, but once again the structure refinement cannot be improved. The authors have found by experience that determining the structure of minerals with merohedral twinning is best done in a step-wise fashion, beginning with the higher symmetry, then fitting the parts of the structural model that are reasonable to each of the subgroups until a satisfactory final model is determined. The β angle, slightly off 90° , was a valuable clue to determining the true symmetry of thomascarkite-(Y). Some of the pseudosymmetry can be seen in Figure 5, the (001) planes being almost m planes.

Table 3 contains the final positional and equivalent isotropic-displacement parameters and bond-valence sums, and Table 4 contains selected interatomic distances and angles. Anisotropic-displacement factors and observed and calculated structure-factors have been submitted to the Depository of Unpublished Data, CISTI, National Research Council of Canada, Ottawa, Ontario, Canada K1A 0S2.

DESCRIPTION AND DISCUSSION OF THE STRUCTURE

The structure of thomascarkite-(Y) has two large-cation sites with distinct polyhedra. The *Na*, with 6-fold co-ordination, occupies a polyhedron that may be described as a bifurcated rhombic pyramid, with the *Na* atom slightly above the rhombic base consisting of four *W5* atoms, whereas the bifurcated apex consists of two *OH3* "atoms". The 8-fold coordination around the *Y* site leads to a bisdisphenoid with four *W7* atoms defining the rhombic equatorial plane and two *OH3* and *O1* atoms outlining the disphenoid. In this polyhedron, there is insufficient space for the *W7* atoms to coexist with the *OH4* atoms; thus the *W7* sites are considered to be half occupied, in conjunction with the half-occupied *OH4* sites.

The crystal structure of thomascarkite-(Y) is layered on (010) (Fig. 5). The layering of *REE* carbonates is described in detail by Grice *et al.* (1994). In thomascarkite-(Y), there are three layers of differing composition: (1) edge-sharing ($\text{Y}\phi_8$) and ($\text{Na}\phi_6$) polyhedra,

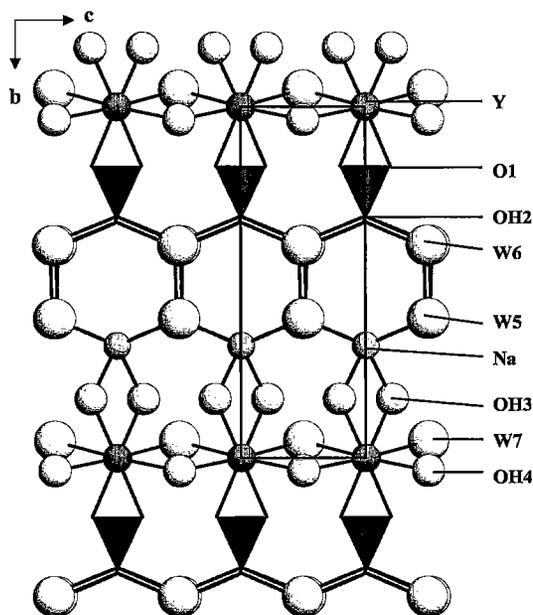


FIG. 5. The structure of thomascarkite-(Y) projected along [100]. Dark triangles represent (CO_3) polyhedra, and the other atoms or groups are labeled. H-bonds are indicated by unfilled rods, whereas other bonds are solid lines. The unit cell is outlined.

TABLE 3. THOMASCLARKITE-(Y): ATOMIC COORDINATES, ISOTROPIC DISPLACEMENT FACTORS ($\text{\AA}^2 \times 10^3$)

Atom	x	y	z	U_{eq}
Na	0	0.3190(6)	0	0.043(2)
Y	0	0	0	0.0209(2)
C	0	0.7819(7)	0	0.031(2)
O1	0.814(4)	0.8320(4)	0.204(3)	0.049(2)
OH2	0	0.6806(6)	½	0.027(3)
OH3	0.169(3)	0.1673(5)	0.210(2)	0.048(3)
OH4	0.199(2)	-0.0380(7)	0.500(3)	0.032(2)
W5	0.205(3)	0.3911(9)	0.499(4)	0.057(3)
W6	0.824(4)	0.608(1)	0.487(6)	0.068(6)
W7	½	0.0477(8)	½	0.042(4)

where ϕ denotes O, OH or H₂O, (2) an H₂O layer (W6) H-bonded to the H₂O group (W5) in the (Na ϕ)₆ polyhedra, and 3) a standing-on-edge (Grice *et al.* 1994) (HCO₃) group that is H-bonded to the H₂O layer and cross-linked to the (Y ϕ)₈ polyhedra. In Figure 5, the pseudo-*m* planes (twin planes) pass through the Y and Na sites and the apex of the (HCO₃) group.

The two most obvious features in the crystal structure of a bicarbonate mineral are the disproportionate bond-lengths within the (CO₃) group and, in some structures, the apparent "unshared" corner of one of the ligands in the (CO₃) triangular polyhedron. Within the [HCO₃] group, the C–O bond lengths are always shorter than the C–OH bond length. In thomasclarkite-(Y), all C–O bond lengths are longer than usual for a [CO₃] group. An interpretation of these data is difficult. We have designated the O2 site as an OH group since it has a lower bond-valence than O1, but we concede that O1 could in fact be an OH group with the hydrogen atom being disordered about the twofold axis.

Eleven minerals have been described as bicarbonates: ashburtonite, barentsite, kalicinite, mineevite-(Y), nahcolite, nesquehonite, teschemacherite, thomasclarkite-(Y), trona, qilianshanite and wegscheiderite. Of the crystal structures that have been solved for this chemical class, only three bear any semblance to the structure of thomasclarkite-(Y). Nahcolite, Na(HCO₃) (Sass & Scheuerman 1962), trona, Na₂(HCO₃)(CO₃)•2H₂O (Pertlik 1986) and wegscheiderite, Na₅(HCO₃)₃(CO₃) (Fernandes *et al.* 1990) all have layered structures, with the (HCO₃) group standing on-end and forming a separate layer between the Na polyhedra and (H₂O) groups. The main difference is that in all three of these structures, the H atom associated with the (HCO₃) group is H-bonded to the adjacent (CO₃) or (HCO₃) group, forming CO₃ chains. In thomasclarkite-(Y), the H-bonding of the (HCO₃) group is directed toward the H₂O layer and does not in any way interact with the other carbonate groups.

GENESIS OF THOMASCLARKITE-(Y)

Thomasclarkite-(Y) occurs in a pegmatite phase in the nepheline syenite intrusion. Bicarbonate minerals typically form in low-temperature, slightly acidic conditions. The [HCO₃] group is a weak Lewis base, typically 0.17 valence units (*vu*) (O'Keeffe & Navrotsky 1981). In keeping with the valence-matching principle, such weak Lewis bases require weak Lewis acids. A weak Lewis acid is a cation with either a low valence-charge and a high coordination-number or with simply a high coordination-number such as the alkalis, Na (0.16 *vu*) and K (0.13 *vu*), alkaline earths, Ca (0.29 *vu*) and Ba (0.20 *vu*), or rare-earth elements such as Y [0.38 *vu* in thomasclarkite-(Y)]. Thus without even solving the crystal structure of thomasclarkite-(Y), one might suspect it to be a bicarbonate mineral simply from its chemical composition, as proposed by Grice (1991).

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TABLE 4. THOMASCLARKITE-(Y): INTERATOMIC DISTANCES (Å) AND ANGLES (°)

Na polyhedron		Y polyhedron		H-bonded O	
Na-OH3	2.32(1) x 2	Y-O1	2.522(8) x 2	OH2-W6	2.65(2)
Na-W5	2.63(2) x 2	Y-OH3	2.499(8) x 2	OH2-W6a	2.55(2)
Na-W5a	2.64(2) x 2	Y-OH4	2.50(1) x 2	W6-W5	2.82(2)
⟨Na-φ⟩	(2.530)	Y-OH4a	2.51(1) x 2		
		(Y-W7)	(3.28(1) x 4)		
		(Y-φ)	(2.508)		
C triangle					
C-O1	1.42(1) x 2	O1-O1	125.1(9)		
C-OH2	1.32(2)	O1-OH2	117.4(5) x 2		
⟨C-φ⟩	(1.387)	⟨O-φ⟩	(120.0)		

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