

LECOQITE-(Y), Na₃Y(CO₃)₃•6H₂O, A NEW MINERAL SPECIES FROM MONT SAINT-HILAIRE, QUEBEC, CANADA

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ABSTRACT

Lecoqite-(Y), ideally Na₃Y(CO₃)₃•6H₂O, a new mineral species, was discovered at the Poudrette quarry, Mont Saint-Hilaire, Quebec, Canada. It is associated with microcline, albite, natrolite, gonnardite, aegirine, siderite, elpidite, gaidonnayite, zircon, franconite, dawsonite, rhodochrosite, cryolite, rutile, and sphalerite. Lecoqite-(Y) forms radiating, spray-like aggregates in compact, tightly packed masses to 2.5 cm across, composed of flexible, extremely thin, capillary crystals up to 2.5 cm long and up to 0.01 mm thick. Individuals are colorless, and aggregates are white. The luster is strikingly silky. $D(\text{calc.}) = 2.358 \text{ g/cm}^3$. Lecoqite-(Y) is optically uniaxial positive, $\omega = 1.521(3)$, $\varepsilon = 1.497(3)$. The IR spectrum is unique. The chemical composition (electron microprobe, H₂O by modified Penfield method, CO₂ by selective absorption, average results) is: Na₂O 19.22, CaO 0.03, Y₂O₃ 17.95, Nd₂O₃ 0.54, Sm₂O₃ 0.41, Gd₂O₃ 0.75, Dy₂O₃ 3.31, Ho₂O₃ 1.12, Er₂O₃ 3.20, Yb₂O₃ 1.48, CO₂ 27.0, H₂O 23.4, total 98.41 wt.%. The empirical formula calculated for 15 O *apfu* is: Na_{2.94}(Y_{0.755}Dy_{0.085}Er_{0.08}Yb_{0.035}Ho_{0.03}Gd_{0.02}Nd_{0.015}Sm_{0.01})Σ_{1.03}(CO₃)_{2.91}(OH)_{0.21}(H₂O)_{6.06}. Lecoqite-(Y) is hexagonal, *P*6₃, *a* 11.316(4), *c* 5.931(2) Å, *V* 657.7(4) Å³, *Z* = 2. The crystal structure was established from X-ray powder data by the Rietveld method, based on the model of the isostructural synthetic Ln-free carbonate Na₃Y(CO₃)₃•6H₂O. Final agreement factors are: $R_p = 0.0468$, $R_{wp} = 0.0657$, $R_{Bragg} = 0.0343$, $R_F = 0.0356$. No mineral is closely related to lecoqite-(Y) in terms of structure. In the structure of lecoqite-(Y), REE atoms (REE = Y + Ln) are surrounded by six O atoms of CO₃ groups and three H₂O molecules to form a tricapped triangular prism. The Na atoms are centered in distorted octahedra [NaO₄(H₂O)₂], which link to form infinite corrugated chains along *c*. The strongest five lines of the X-ray powder pattern [*d* in Å (*I*)(*hkl*)] are: 9.82(57)(100), 5.081(100)(101), 3.779(39)(201), 2.627(39)(112), 2.471(37)(131). Lecoqite-(Y) is named in memory of P.É. Lecoq de Boisbaudran (1838–1912), outstanding French chemist and specialist in the spectroscopic analysis of minerals and synthetic compounds, who made a great contribution to the chemistry of the rare-earth elements. The Levinson suffix modifier -(Y) is in line with the dominance of yttrium over other rare-earth elements in the mineral. The cotype specimens are deposited in the Fersman Mineralogical Museum of Russian Academy of Sciences, Moscow, and the Canadian Museum of Nature, Ottawa.

Keywords: lecoqite-(Y), new mineral species, rare-earth carbonate, crystal structure, Rietveld refinement, infrared spectrum, peralkaline pegmatite, Mont Saint-Hilaire, Quebec.

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SOMMAIRE

La lecoquite-(Y), de composition idéale $\text{Na}_3\text{Y}(\text{CO}_3)_3 \cdot 6\text{H}_2\text{O}$, nouvelle espèce minérale, a été découverte à la carrière Poudrette, mont Saint-Hilaire, Québec, Canada. Lui sont associés microcline, albite, natrolite, gonnardite, aegyryne, sidérite, elpidite, gaidonnayite, zircon, franconite, dawsonite, rhodochrosite, cryolite, rutile, et sphalérite. La lecoquite-(Y) se présente en agrégats de cristaux en gerbes compactes atteignant 2.5 cm de large, faites de cristaux capillaires flexibles, très atténués, jusqu'à 2.5 cm de long et jusqu'à 0.01 mm en épaisseur. Les cristaux individuels sont incolores, et les agrégats sont blancs. L'éclat est soyeux. $D(\text{calc.}) = 2.358 \text{ g/cm}^3$. La lecoquite-(Y) est uniaxe positive, $\omega = 1.521(3)$, $\varepsilon = 1.497(3)$. Le spectre infrarouge est unique. La composition chimique (données prélevées avec une microsonde électronique, avec H_2O déterminé par la méthode de Penfield modifiée, et CO_2 par absorption sélective; résultats moyens) est: Na_2O 19.22, CaO 0.03, Y_2O_3 17.95, Nd_2O_3 0.54, Sm_2O_3 0.41, Gd_2O_3 0.75, Dy_2O_3 3.31, Ho_2O_3 1.12, Er_2O_3 3.20, Yb_2O_3 1.48, CO_2 27.0, H_2O 23.4, pour un total de 98.41 wt.%. La formule empirique, calculée sur une base de 15 atomes d'oxygène par formule unitaire, est: $\text{Na}_{2.94}(\text{Y}_{0.755}\text{Dy}_{0.085}\text{Er}_{0.08}\text{Yb}_{0.035}\text{Ho}_{0.03}\text{Gd}_{0.02}\text{Nd}_{0.015}\text{Sm}_{0.01})_{\Sigma 1.03}(\text{CO}_3)_{2.91}(\text{OH})_{0.21}(\text{H}_2\text{O})_{6.06}$. La lecoquite-(Y) est hexagonale, $P6_3$, a 11.316(4), c 5.931(2) Å, V 657.7(4) Å³, $Z = 2$. La structure cristalline a été établie à partir du spectre de diffraction obtenu sur poudre par la méthode de Rietveld, en utilisant comme point de départ le composé isostructural synthétique dépourvu de terres rares, $\text{Na}_3\text{Y}(\text{CO}_3)_3 \cdot 6\text{H}_2\text{O}$. Les facteurs de concordance finaux sont: $R_p = 0.0468$, $R_{wp} = 0.0657$, $R_{\text{Bragg}} = 0.0343$, $R_F = 0.0356$. Du point de vue structural, la lecoquite-(Y) ne ressemble à aucun autre minéral. Les atomes de terres rares ($= \text{Y} + \text{Ln}$) sont entourés de six atomes d'oxygène faisant partie de groupes CO_3 et de trois molécules de H_2O pour former un prisme trigonal à trois terminaisons. Les atomes de Na sont situés dans des octaèdres $[\text{NaO}_4(\text{H}_2\text{O})_2]$ difformes, agencés en chaînes ondulantes infinies le long de c . Les cinq raies les plus intenses du spectre de diffraction, méthode des poudres [d en Å (I) (hkl)] sont: 9.82(57)(100), 5.081(100)(101), 3.779(39)(201), 2.627(39)(112), 2.471(37)(131). La lecoquite-(Y) honore la mémoire de P.É. Lecoq de Boisbaudran (1838–1912), chimiste français réputé, spécialiste de l'analyse spectroscopique de minéraux et de produits de synthèse, qui a grandement contribué aux connaissances à propos des terres rares. Le suffixe de Levinson -(Y) témoigne de la prédominance de l'yttrium sur les autres terres rares dans ce minéral. Les échantillons cotypes ont été déposés dans le musée minéralogique Fersman de l'Académie des Sciences de la Russie et dans le Musée Canadien de la Nature à Ottawa.

(Traduit par la Rédaction)

Mots-clés: lecoquite-(Y), nouvelle espèce minérale, carbonate de terres rares, structure cristalline, affinement de Rietveld, spectre infrarouge, pegmatite hyperalkaline, mont Saint-Hilaire, Québec.

INTRODUCTION

A new hydrous carbonate of sodium, yttrium and the lanthanides was found in hydrothermal assemblages related to a peralkaline pegmatite, at the mineralogically famous Mont Saint-Hilaire intrusion, Quebec, Canada. The new mineral species is named to honor the memory of an outstanding French chemist and specialist in the spectroscopic analysis of minerals and synthetic compounds, Paul Émile (François) Lecoq de Boisbaudran (1838–1912). He made great contributions to the chemistry of the rare-earth elements: he discovered samarium (1879) and dysprosium (1886), and was the first to isolate gadolinium (1885). In 1875, he also discovered gallium (as a result of the spectroscopic analysis of sphalerite), the existence of which was predicted by Dmitry Mendeleev in 1871, which was a very important confirmation of Mendeleev's theory of periodicity among elements. We use the shortened form, Lecoq, instead of full family name Lecoq de Boisbaudran, as is used in many publications. The Levinson suffix modifier -(Y) is in line with the dominance of yttrium over other rare-earth elements in the mineral. The name in Cyrillic is spelled: лекокит-(Y). Both the new mineral and its name have been approved by the IMA CNMNC (IMA 2008–068). The cotype specimens are deposited in the Fersman Mineralogical Museum of Russian Academy of Sciences, Moscow (registration no.

3761/1), and the Canadian Museum of Nature, Ottawa (catalog no. CNMMC 86065).

BACKGROUND INFORMATION

This mineral was first detected in specimens collected from the hydrothermally altered core of the Poudrette pegmatite, on working level 6 of the Poudrette quarry, in the fall of 1991; however, the date of the first find and the person(s) involved could not be established. Specimens collected by the staff of the Canadian Museum of Nature (CMN) and at least one local collector in November 1991 were analyzed (XRD and EDS) by February 1992. On the basis of the unique XRD pattern and the results of an electron-microprobe analysis (EDS), the phase was designated during 1992 as a potentially new species, UK91, using the established code for unnamed mineral phases at Mont Saint-Hilaire. Since no single crystals suitable for structure analysis were found, any further work on the mineral was suspended in 1993, and apart from routine XRD identifications of material found later, remained suspended for the next fifteen years. Additional specimens of UK91 were found in 1995 and 1997, on working level 7 in the same pegmatite dyke. To our knowledge, however, none were found after 1997, or on the lower working levels (8 and 9) of the quarry. The cotype specimens were collected by one of

the authors (LH) and Elsa Pfenninger-Horváth in June 1995 and were confirmed by XRD as being UK91. As there was no interest in resuming further work on UK91 in Canada, specimens that became the cotype were sent by the Horváths to the senior author (IVP) in 2007, to explore the possibility of reviving work on this phase. From this material, a single crystal suitable for unit-cell determination was separated. In 2008, additional samples collected in 1991 by Gilles Haineault and in 1997 by the Horváths were also provided to IVP, to confirm that these are identical to the cotype.

OCCURRENCE AND GENERAL APPEARANCE

The type locality of lecoqite-(Y) is the Poudrette pegmatite, Poudrette quarry, Mont Saint-Hilaire, Rouville County, Quebec, Canada [45°33'36.9"N, 73°08'31.4"W]. General geological and petrological data for the Mont Saint-Hilaire alkaline pluton are well-known (Currie 1983, Currie *et al.* 1986). Mineralogical information was summarized by Horváth & Gault (1990) and Horváth & Pfenninger-Horváth (2000). To date, nearly 400 species have been confirmed from the pluton, including the 58 mineral species first discovered here [including lecoqite-(Y)].

The Poudrette pegmatite dyke (Fig. 1) is the largest of the bodies of pegmatite exposed to date in the Mont Saint-Hilaire complex, in the extreme south corner of the current Poudrette quarry, which combines the former Demix quarry on the northwest and the original Poudrette quarry on the southeast into a single excavation. Of the many pegmatites exposed at Mont Saint-Hilaire over a period of about 45 years, the Poudrette pegmatite is by far the most diverse mineralogically. Approximately 160 mineral species were confirmed from it, including ten new species: adamsite-(Y), horváthite-(Y), lecoqite-(Y), lukechangite-(Ce), niveolanite, petersenite-(Ce), reederite-(Y), thomasclarkite-(Y), and two other recently IMA-approved species, IMA 2009-020, $\text{Li}_4\text{Na}_{12}(\text{Y}, \text{Na}, \text{Ca}, \text{Ln})_{12}(\text{PO}_4)_{12}(\text{CO}_3)_4(\text{F}, \text{OH})_8$, and IMA 2009-021, $\text{Li}_4(\text{Na}, \text{Ca})_{12}(\text{Y}, \text{Ca}, \text{Ln})_6\text{Zr}_6(\text{PO}_4)_{12}(\text{CO}_3)_4\text{O}_4[(\text{OH}), \text{F}]_4$. A detailed description of this pegmatite and its associated veins and immediate surroundings was recently given by Pekov *et al.* (2008). In total, 30 carbonates, including two insufficiently studied (UK: unnamed phases), and 32 REE minerals have been identified in the Poudrette pegmatite dyke and its satellite veins. Note that all minerals first discovered in the Poudrette pegmatite are carbonates or contain the $(\text{CO}_3)^{2-}$ anion.

Lecoqite-(Y) occurs exclusively in cavities in the microcline lining of the pegmatite dyke as silky, white, radiating spray-like aggregates, compact, tightly packed masses from a few millimeters to 2.5 cm across (aggregates are commonly matted from exposure to water) composed of extremely thin, capillary crystals (Fig. 2). Single crystals are typically 2–10 mm long. The longest observed is 2.5 cm long and up to 0.01 mm thick.

Cross-sections of crystals are hexagonal or irregularly polygonal, with coarse striations along [001]. In visual appearance (color, luster, morphology and habit), lecoqite-(Y) is indistinguishable from the recently described sodium beryllium carbonate *niveolanite* described from a lower zone of the same pegmatite (Pekov *et al.* 2008). Lecoqite-(Y) is a late-stage hydrothermal mineral (one of the latest in this pegmatite) formed under peralkaline (hyperagpaitic) conditions. It is closely associated with microcline, albite, natrolite, gonnardite (pseudomorphs after paranatrolite), aegirine (large corroded and cavernous crystals, most of which are partially replaced by other minerals), siderite, elpidite, gaidonnayite, zircon, franconite, dawsonite (fine and powdery to fibrous), rhodochrosite, cryolite (usually enclosed in microcline), rutile (lamellar aggregates, probably pseudomorph after ilmenite), sphalerite, pyrite, galena and pyrochlore (a pseudomorph after an unknown tabular precursor mineral). Rarely, lecoqite-(Y) is also associated with thomasclarkite-(Y), petersenite-(Ce) and calcioburbankite [epitactic on petersenite-(Ce)]. A brown bituminous substance forms a varnish over most of the cavity minerals except the very late-stage lecoqite-(Y), franconite and gonnardite.

PHYSICAL AND OPTICAL PROPERTIES

Separate individual, capillary crystals are colorless and transparent. The streak is white. The luster is strikingly silky. The mineral is non-fluorescent under ultraviolet radiation. Cleavage and parting were not observed; the fracture is splintery (as observed under the microscope). Individuals are flexible and slightly elastic. It was impossible to measure its hardness and density because of the character of the aggregates, which are soft, fibrous and hair-like. The density is calculated to be 2.358 g/cm³.

Lecoqite-(Y) is optically uniaxial negative, with $\omega = 1.521(3)$, $\epsilon = 1.497(3)$. Under the microscope, its crystals are colorless and non-pleochroic.

INFRARED SPECTROSCOPY

Lecoqite-(Y) was mixed with anhydrous KBr, pelletized, and analyzed using a Specord 75 IR spectrophotometer. The IR spectrum of the KBr disk was subtracted from the overall spectrum. Polystyrene and gaseous NH₃ were used as frequency standards; the precision of the frequency measurement is $\pm 1 \text{ cm}^{-1}$; the mean resolution for the region of 400–1600 cm⁻¹ is 0.8 cm⁻¹.

The infrared-absorption spectrum of lecoqite-(Y) (Fig. 3) is very different from the IR spectra of all other carbonate minerals, and very close to that of synthetic $\text{Na}_3\text{Y}(\text{CO}_3)_3 \cdot 6\text{H}_2\text{O}$ (Ben Ali *et al.* 2004). Bands in the range of 2810–3585 cm⁻¹ correspond to O–H-stretching vibrations of H₂O molecules forming medium (3350 and 3585 cm⁻¹) and very strong (in the



FIG. 1. The Poudrette pegmatite dyke. Summer 1998.



FIG. 2. Typical aggregate of capillary to fibrous lecoquite-(Y) in a cavity, on white natrolite and greyish albite; the brown crust is a solid bituminous substance. Photo: I.V. Pekov & A.V. Kasatkin.

range of 2810–3125 cm^{-1}) hydrogen bonds of at least five locally different types. The band at 2330 cm^{-1} is due to vibrations of extremely polarized O–H bonds. A band at 1638 cm^{-1} corresponds to bending vibrations of H_2O molecules. Strong splitting of the degenerate asymmetric C–O-stretching vibrations (doublet 1495 + 1389 cm^{-1}) and the relatively high intensity of the non-degenerate symmetric C–O-stretching vibration (1067 cm^{-1}) reflect distortion of the trigonal carbonate ion due to hydrogen bonding and polarization by REE^{3+} cations ($\text{REE} = \text{Y} + \text{Ln}$). Bands at 595 and 900 cm^{-1} , in view of their significant width, are assigned to other modes involving vibrations of H_2O molecules. Bands in the range of 685–849 cm^{-1} correspond to bending vibrations of CO_3^{2-} anions.

The IR spectrum of lecoqite-(Y) is considered as an important diagnostic property.

CHEMICAL DATA

Contents of metals were determined with a fully computer-controlled scanning electron microscope, VEGA TS 5130MM, equipped with energy-dispersive X-ray (EDX) microanalyzer, with semi-conductor Si(Li) detector INCA Energy, operating at a voltage of 15.7 kV and a beam current of 0.5 nA. The electron beam was rastered over an area $5 \times 5 \mu\text{m}^2$ to minimize damage of the sample. We used as standards albite (Na), wollastonite (Ca), YPO_4 (Y), NdPO_4 (Nd), SmPO_4 (Sm), GdPO_4 (Gd), DyPO_4 (Dy), HoPO_4 (Ho), ErPO_4 (Er), YbPO_4 (Yb). Other elements with atomic numbers higher than O were below detection limits for the electron microprobe used. Seven point-analyses were obtained for two crystals with thickness 0.008–0.010 mm. The accuracy of data obtained for Y and lanthanides was confirmed using the wavelength-dispersion spectroscopic (WDS) mode (a Camebax SX 50 instrument). It was impossible to use WDS for Na determination in such an unstable mineral because of the high beam-current.

Lecoqite-(Y) loses all CO_2 and H_2O on heating to 1080°C. The CO_2 content was determined by selective absorption of CO_2 on “askarite”, an asbestiform material saturated with NaOH, from gaseous products obtained by heating the mineral at 1080°C in oxygen at 1 atm. The content of H_2O was determined by the Alimarin method [Penfield method modified for small samples and involving selective absorption of H_2O from gaseous products obtained by heating on $\text{Mg}(\text{ClO}_4)_2$].

The absence of Li, Be, B and N was confirmed by the structural data. The IR spectrum demonstrates the absence of organic groups in the mineral.

The averaged chemical composition of lecoqite-(Y) (wt.%, ranges of seven spot electron-microprobe analyses are in parentheses) is: Na_2O 19.22 (18.5–22.0), CaO 0.03 (0.00–0.06), Y_2O_3 17.95 (17.4–18.9), Nd_2O_3 0.54 (0.3–0.7), Sm_2O_3 0.41 (0.3–0.6), Gd_2O_3 0.75 (0.6–0.9), Dy_2O_3 3.31 (2.9–3.5), Ho_2O_3 1.12 (0.9–1.2), Er_2O_3 3.20 (2.7–3.4), Yb_2O_3 1.48 (1.1–1.8), CO_2 27.0, H_2O 23.4, total 98.41 wt.%. The empirical formula calculated for 15 atoms of O per formula unit (*apfu*) is: $\text{Na}_{2.94}(\text{Y}_{0.755}\text{Dy}_{0.085}\text{Er}_{0.08}\text{Yb}_{0.035}\text{Ho}_{0.03}\text{Gd}_{0.02}\text{Nd}_{0.015}\text{Sm}_{0.01})_{\Sigma 1.03}(\text{CO}_3)_{2.91}(\text{OH})_{0.21}(\text{H}_2\text{O})_{6.06}$. The OH: H_2O ratio was formally calculated from charge-balance considerations. The idealized, end-member formula is: $\text{Na}_3\text{Y}(\text{CO}_3)_3 \cdot 6\text{H}_2\text{O}$, which requires Na_2O 20.84, Y_2O_3 25.31, CO_2 29.61, H_2O 24.24, total 100 wt.%.

The Gladstone–Dale compatibility index (Mandarino 1981) is 0.008, superior.

Lecoqite-(Y) dissolves readily in both concentrated and dilute HCl at room temperature, with strong effervescence.

X-RAY CRYSTALLOGRAPHY AND CRYSTAL STRUCTURE

A single-crystal X-ray study of lecoqite-(Y) was carried out using an Xcalibur S diffractometer equipped with a CCD detector, and gave the following dimensions of the hexagonal unit-cell: a 11.339(6), c 5.938(2) Å, V 661.2(6) Å³.

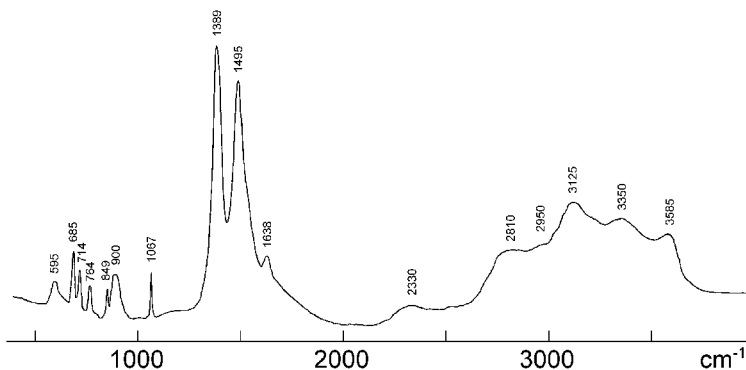


FIG. 3. The IR spectrum of lecoqite-(Y).

Unfortunately, even the “thickest” single crystal of the new mineral used for the single-crystal study is an extremely thin needle. The thinness ($\sim 8 \mu\text{m}$) prevented the collection of a dataset suitable for crystal-structure solution. However, we found that unit-cell dimensions obtained from single-crystal and the X-ray powder diagram of lecoqite-(Y) are very close to ones of the synthetic carbonate $\text{Na}_3\text{Y}(\text{CO}_3)_3 \cdot 6\text{H}_2\text{O}$, reported by Ben Ali *et al.* (2004). The crystal structure of lecoqite-(Y) was refined on a powder sample by the Rietveld method, based on the structure model for this Ln-free synthetic analogue of the mineral.

Powder X-ray-diffraction data were collected using a computer-controlled STOE STADI MP powder diffractometer ($\text{CuK}\alpha_1$ radiation, $\lambda = 1.54056 \text{ \AA}$). A scan range of $7.0 \leq 2\theta \leq 109.28^\circ$ was measured using a STOE linear position-sensitive detector with exposure time of 2400 s per 5° (2θ). The effect of preferential orientation of acicular particles of the mineral on the (001) direction was corrected. Data treatment and the Rietveld structure analysis were carried out using the Wxriet package of computer programs (Schneider 1989). The profiles were

modeled using a pseudo-Voigt function. The structure model of synthetic $\text{Na}_3\text{Y}(\text{CO}_3)_3 \cdot 6\text{H}_2\text{O}$ (Ben Ali *et al.* 2004) with fixed positions of the atoms was used in the initial stage of the refinement. Attempts to refine the occupancy parameters for REE atomic site indicated full occupancy within the standard deviation for $\text{Y}_{0.73}\text{Dy}_{0.27}$, calculated according to electron-microprobe data. Atom coordinates and the isotropic thermal parameters of C and O atoms were refined and fixed at the last stages of the refinement. Final agreement factors are: $R_p = 0.0468$, $R_{wp} = 0.0657$, $R_{Bragg} = 0.0343$, $R_F = 0.0356$. Observed and calculated X-ray powder-diffraction diagrams for lecoqite-(Y) are given in Table 1 and Figure 4.

The mineral is hexagonal, space group $P6_3$. Unit-cell parameters refined from the powder data are close to those obtained from single-crystal study: a 11.316(4), c 5.931(2) \AA , V 657.7(4) \AA^3 , $Z = 2$.

The atom coordinates, displacement parameters and interatomic distances are given in Tables 2 and 3, respectively. The comparison of lecoqite-(Y) with chemically related Na,Y carbonates is given in Table 4.

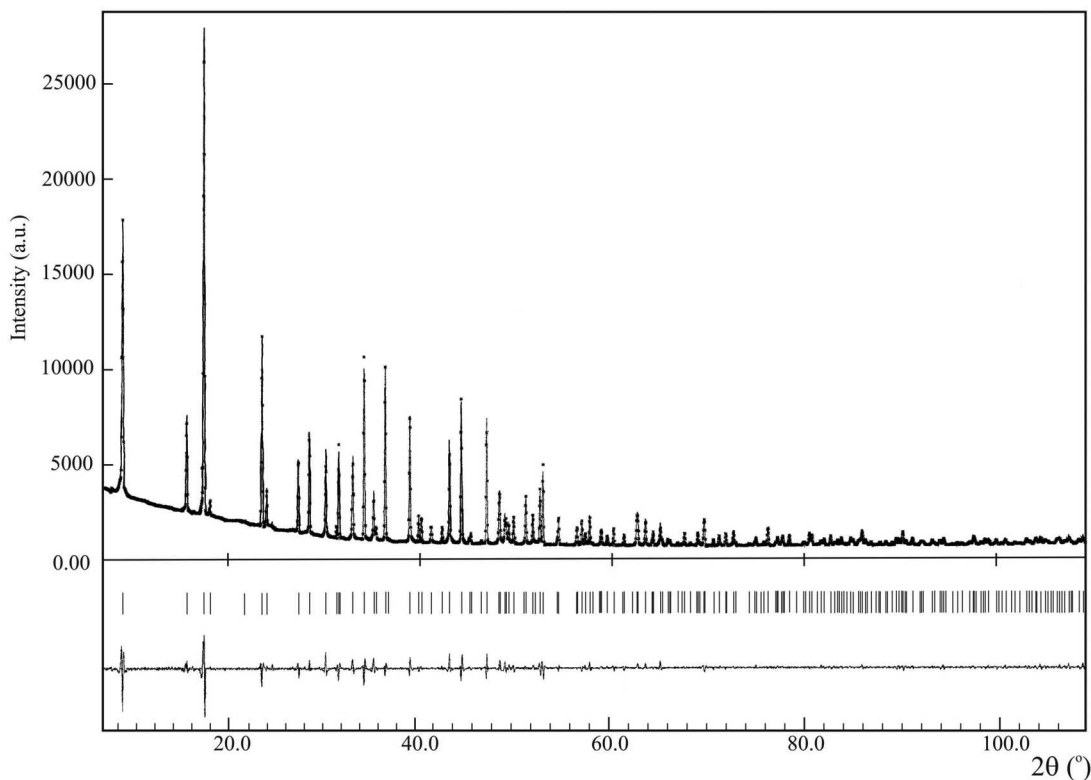


FIG. 4. Observed and calculated X-ray powder-diffraction patterns of lecoqite-(Y). The crosses are the calculated data, the solid line is the observed pattern, and vertical bars mark all possible Bragg reflections. The difference between the observed and calculated patterns is shown at the bottom.

In the structure of lecoqite-(Y) (Fig. 5), the REE atoms are surrounded by six O atoms belonging to CO₃ groups and three H₂O molecules to form a tricapped triangular prism with distances varying from 2.413 to 2.499 Å; this polyhedron is the same as that documented for Y in synthetic Na₃Y(CO₃)₃•6H₂O (Ben Ali *et al.* 2004) and a similar one was noted in shomiokite-(Y) (Grice 1996, Rastsvetaeva *et al.* 1996). In both cases, the Y [or (Y.Ln)] polyhedron has common edges with three CO₃ groups, and the configuration of these complexes is similar. The mean value of <Y.Ln-O>, in lecoqite-(Y), 2.46 Å, is slightly longer than these values in its Ln-free synthetic analogue (<Y-O> = 2.41 Å) and shomiokite-(Y) (2.42 Å) because of the different REE occupancy. The Na atoms occupy distorted octahedra [NaO₄(H₂O)₂], with a mean Na-O distance equal to 2.478 Å; they are linked *via* common vertices to form infinite corrugated chains aligned along the *c* axis. Isolated from each other, the REE polyhedra are connected by edges with Na octahedra. Three infinite

chains of Na octahedra are connected with each REE polyhedron, each of these being connected with six Na octahedra.

DISCUSSION

Besides lecoqite-(Y), four natural carbonates with only Na and Y as species-defining cations exist: horváthite-(Y), thomasclarkite-(Y), adamsite-(Y) and shomiokite-(Y). All five minerals occur in late, hydrothermal assemblages of the Poudrette pegmatite. Comparative data for natural Na,Y carbonates, given in Table 4, show that all these minerals are quite different structurally. Generally, no mineral is closely related to lecoqite-(Y) in terms of structure. Some common features are found in structures of lecoqite-(Y), Na₃Y(CO₃)₃•6H₂O, and shomiokite-(Y), Na₃Y(CO₃)₃•3H₂O; in particular, they have an almost identical *c* unit-cell edge (Table 4). This similarity, already described for synthetic Na₃Y(CO₃)₃•6H₂O and shomiokite-(Y), is caused by the existence of (001)

TABLE 1. X-RAY POWDER-DIFFRACTION DATA FOR LECOQITE-(Y)

<i>l</i> _{meas}	<i>d</i> _{meas}	<i>l</i> _{calc}	<i>d</i> _{calc}	<i>hkl</i>	<i>l</i> _{meas}	<i>d</i> _{meas}	<i>l</i> _{calc}	<i>d</i> _{calc}	<i>hkl</i>
57	9.82	100	9.800	100	5	1.621	5	1.621	223
19	5.669	31	5.658	110	3	1.612	4	1.611	430
100	5.081	69	5.074	101	7	1.599	5	1.599	133
3	4.908	5	4.900	200	5	1.570	2	1.571	250
39	3.779	44	3.778	201	5	1.570	4	1.569	422
8	3.705	12	3.705	120	2	1.555	4	1.555	431
17	3.269	26	3.267	300	3	1.539	4	1.539	403
23	3.142	26	3.142	121	2	1.514	4	1.514	512
17	2.968	5	2.966	002	9	1.484	5	1.485	323
2	2.863	3	2.861	301	2	1.484	2	1.483	004
18	2.840	10	2.838	102	6	1.466	3	1.466	104
17	2.720	24	2.718	310	1	1.452	1	1.452	143
39	2.627	26	2.627	112	2	1.450	6	1.449	161
11	2.556	10	2.553	221	5	1.435	2	1.434	114
3	2.538	2	2.537	202	1	1.420	1	1.420	204
37	2.471	51	2.471	131	1	1.415	½	1.416	432
29	2.316	23	2.315	122	1	1.415	2	1.415	440
4	2.266	8	2.264	401	1	1.401	1	1.400	700
6	2.249	9	2.248	230	2	1.387	5	1.387	522
3	2.196	3	2.196	302	1	1.377	½	1.377	124
3	2.140	6	2.139	140	2	1.363	6	1.363	351
21	2.104	28	2.102	231	6	1.351	5	1.352	423
30	2.047	32	2.047	222	6	1.351	4	1.350	304
1	2.012	2	2.012	411	1	1.335	3	1.335	162
1	2.004	2	2.004	132	3	1.325	5	1.325	621
27	1.938	12	1.938	103	2	1.314	1	1.313	224
15	1.887	6	1.889	402	13	1.886	3	1.302	134
6	1.867	3	1.866	113	4	1.302	1	1.298	710
4	1.862	8	1.861	501	2	1.267	3	1.266	702
5	1.852	7	1.852	420	1	1.255	1	1.255	450
5	1.834	4	1.833	203	4	1.249	6	1.249	343
10	1.792	13	1.792	322	2	1.235	1	1.235	622
7	1.768	10	1.768	241	2	1.235	3	1.235	630
11	1.745	9	1.744	123	3	1.228	4	1.228	451
15	1.735	23	1.735	412	2	1.219	3	1.219	414
5	1.688	1	1.691	511	1	1.200	1½	1.200	801
		10	1.687	303	1	1.200	1	1.197	720
4	1.634	2	1.635	502					
		6	1.633	600					

The *d* values are expressed in Å.

TABLE 2. FRACTIONAL COORDINATES AND ATOMIC DISPLACEMENT PARAMETERS FOR ATOMS IN LECOQITE-(Y)

Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{iso}
REE*	⅓	⅓	0.8878(16)	0.0079(11)
Na	0.3781(13)	0.3543(16)	0.654(2)	0.009(4)
C**	0.122	0.439	0.667	0.006
O(1)**	0.030	0.331	0.561	0.007
O(2)**	0.246	0.482	0.608	0.003
O(3)**	0.088	0.493	0.823	0.011
OW(1)**	0.149	0.156	0.547	0.030
OW(2)**	0.494	0.217	0.673	0.003
H(11)**	0.12	0.13	0.43	0.06***
H(12)**	0.11	0.20	0.57	0.06***
H(21)**	0.47	0.20	0.83	0.06***
H(22)**	0.55	0.19	0.69	0.06***

The numbers in parentheses are e.s.d. values referred to the last digit.
* Refined as Y_{0.73}Dy_{0.27}, according to the electron-microprobe data.

** Atomic coordinates and *U*_{iso} of C and O atoms were refined and fixed at the last stages of the refinement.

*** *U*_{iso} values for the H atoms were not refined.

TABLE 3. INTERATOMIC DISTANCES (Å) IN THE STRUCTURE OF LECOQITE-(Y)

REE	- OW(2)	2.413(3) × 3	Na	- O(3)	2.268(6)
	- O(2)	2.455(3) × 3		- O(1)	2.478(6)
	- O(3)	2.499(2) × 3		- OW(2)	2.485(9)
<REE-O>		2.456		- OW(1)	2.520(5)
				- O(2)	2.556(9)
				- O(3)	2.564(7)
C	- O(3)	1.27	<Na-O>		2.478
C	- O(2)	1.28			
C	- O(1)	1.30			
<C-O>		1.28	OW(2)-H(21)		0.96
OW(1)-H(11)		0.76	OW(2)-H(22)		0.84
OW(1)-H(12)		0.83			

layers with comparable thickness, $[\text{Na}(\text{CO}_3)\cdot 2\text{H}_2\text{O}]_\infty$ in $\text{Na}_3\text{Y}(\text{CO}_3)_3\cdot 6\text{H}_2\text{O}$ [and, consequently, lecoqite-(Y)] and $[\text{Na}(\text{CO}_3)\cdot \text{H}_2\text{O}]_n$ in shomiokite-(Y) (Ben Ali *et al.* 2004). The layering in the structures of REE carbonates was discussed by Grice *et al.* (1994, 2007). Moreover, the values of the long and short diagonals (~ 19.6 and ~ 11.3 Å, respectively) of the hexagonal unit-cell of lecoqite-(Y) are comparable with *a* and *b* parameters of the orthorhombic cell of shomiokite-(Y): *a* 17.36, *b* 10.03 Å. Figure 6 shows the distribution of mixed complexes formed by nine-fold polyhedra YLn and CO_3 groups in the structures of lecoqite-(Y) and shomiokite-(Y).

The nine-fold coordination of Y cation is typical in carbonates. This is caused by the low average valence for O atoms ($-2/3$) participating in the CO_3 groups (Miyawaki & Nakai 1987). This fact leads to the increase of the number of oxygen atoms forming the coordination sphere of Y. Nine-fold polyhedra occupied

by Y and sharing common edges with CO_3 groups were also found in adamsite-(Y), in which the $[\text{YO}_7(\text{H}_2\text{O})_2]$ polyhedra can be described as monocapped, square antiprisms (Grice *et al.* 2000), and in synthetic compounds $\text{Na}_5\text{Y}(\text{CO}_3)_4$ (Awaleh *et al.* 2003) and $\text{Na}_2\text{Y}(\text{CO}_3)\text{F}_3$ (Ben Ali *et al.* 2006). In the bicarbonate thomasclarkite-(Y), the Y cations have an eight-fold coordination, and each Y polyhedron shares an edge with one CO_3 triangle with elongate C–O distances in comparison with the “usual” CO_3 groups (Grice & Gault 1998). Eight-fold polyhedra, $[\text{YO}_6\text{F}_2]$ or $[\text{YO}_4\text{F}_4]$, were also found in $\text{Na}_3\text{Y}(\text{CO}_3)_2\text{F}_2$ (Ben Ali *et al.* 2006) and the fluorocarbonate horváthite-(Y); yttrium atoms share, respectively, two or one edge with CO_3 groups. Among all natural Na,Y carbonates, only shomiokite-(Y) and lecoqite-(Y) are characterized by Y polyhedra isolated from each other. In three other minerals given in Table 4, the Y polyhedra have common edges or vertices (or both).

TABLE 4. COMPARATIVE DATA FOR Na,Y CARBONATE MINERALS AND SYNTHETIC $\text{Na}_3\text{Y}(\text{CO}_3)_3\cdot 6\text{H}_2\text{O}$

	Horváthite-(Y) $\text{NaY}(\text{CO}_3)\text{F}_2$	Thomas-clarkite-(Y) $\text{NaY}(\text{HCO}_3)(\text{OH})_3\cdot 4\text{H}_2\text{O}$	Adamsite-(Y) $\text{NaY}(\text{CO}_3)_2\cdot 6\text{H}_2\text{O}$	Shomiokite-(Y) $\text{Na}_3\text{Y}(\text{CO}_3)_3\cdot 3\text{H}_2\text{O}$	Lecoqite-(Y) $\text{Na}_3\text{Y}(\text{CO}_3)_3\cdot 6\text{H}_2\text{O}$	Synthetic $\text{Na}_3\text{Y}(\text{CO}_3)_3\cdot 6\text{H}_2\text{O}$
System	Orthorhombic	Monoclinic	Triclinic	Orthorhombic	Hexagonal	Hexagonal
Space group	<i>Pmcn</i>	<i>P2</i>	<i>P$\bar{1}$</i>	<i>Pna2₁</i>	<i>P6₃</i>	<i>P6₃</i>
Unit-cell data						
<i>a</i> , Å	6.964	4.556	6.262	17.358	11.316	11.347
<i>b</i> , Å	9.173	13.018	13.047	10.034		
<i>c</i> , Å	6.302	4.556	13.220	5.946	5.931	5.935
α , °			91.17			
β , °		90.15	103.70			
γ , °			89.99			
<i>V</i> , Å ³	402.6	270.2	1049.1	1035.6	657.7	661.8
<i>Z</i>	4	1	4	4	2	2
Strongest reflections of the X-ray powder pattern: <i>d</i> Å (I)						
	5.19 (90)	12.97 (100)	12.81 (100)	8.72 (4)	9.82 (57)	9.827 (100)*
	3.477 (100)	6.52 (30)	6.45 (70)	6.53 (76)	5.081 (100)	5.080 (60)
	2.800 (50)	4.57 (30)	4.456 (60)	5.12 (50)	3.779 (39)	3.785 (38)
	2.087 (50)	4.32 (50)	4.291 (60)	4.91 (66)	2.627 (39)	3.276 (21)
	1.966 (50)	3.223 (30)	2.869 (30)	4.83 (34)	2.471 (37)	2.630 (18)
	1.849 (50)	3.133 (50)	2.571 (60)	4.344 (100)	2.316 (29)	2.477 (22)
	1.763 (50)	2.016 (40)	2.050 (50)	2.857 (55)	2.047 (30)	2.051 (20)
Density, g/cm ³	3.58 (calc.)	2.30 (meas.) 2.32 (calc.)	2.27 (meas.) 2.27 (calc.)	2.52 (meas.) 2.54 (calc.)	2.36 (calc.)	2.25 (meas.) 2.24 (calc.)
Sources	(1)	(2)	(3)	(4)	(5)	(6)

Sources: (1) Grice & Chao (1997), (2) Grice & Gault (1998), (3) Grice *et al.* (2000), (4) Khomyakov *et al.* (1992), Grice (1996), Rastsvetaeva *et al.* (1996), Pekov (1998), (5) this work, (6) Ben Ali *et al.* (2004). * The X-ray powder data were calculated from the structural data reported by Ben Ali *et al.* (2004).

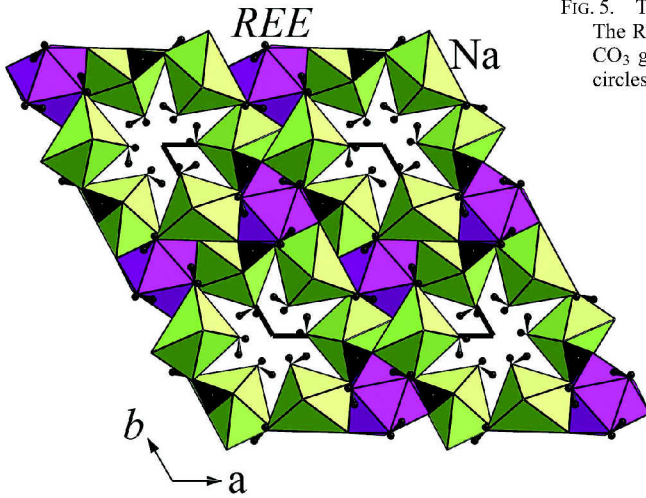
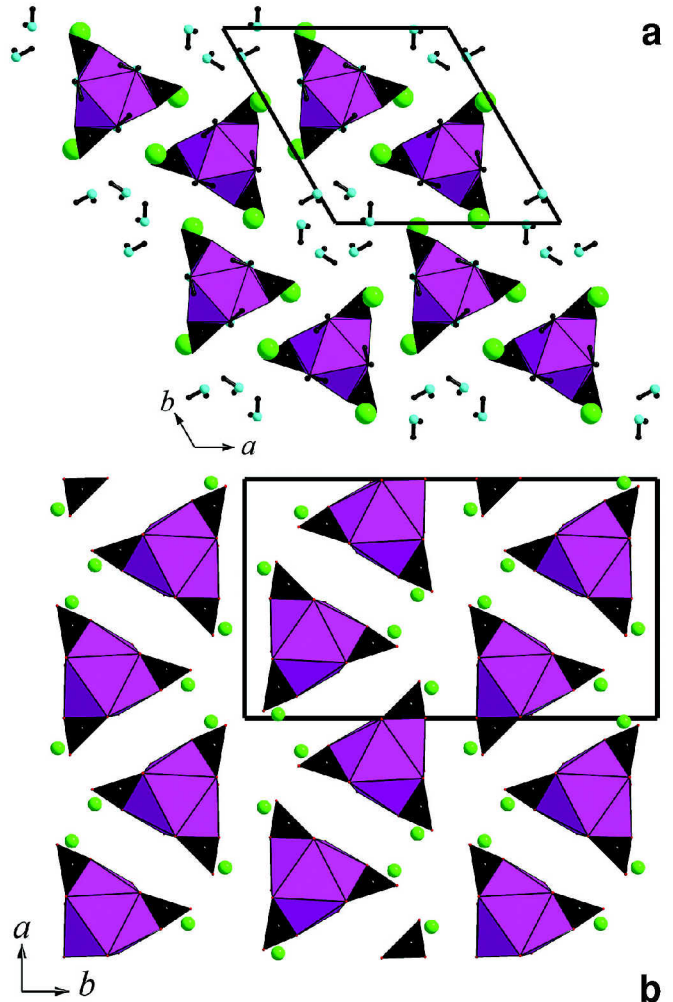


FIG. 5. The crystal structure of lecoqite-(Y), (001) projection. The REE (*i.e.*, Y, Ln) nine-fold polyhedra, Na octahedra, CO₃ groups (black triangles) and H atoms (small black circles) are shown.

FIG. 6. Distribution of mixed complexes formed by the REE (*i.e.*, Y, Ln) nine-fold polyhedra and CO₃ groups (black) in the structures of lecoqite-(Y) (a) and shomiokite-(Y) (b). The Na cations are large circles, the O atoms of H₂O molecules are medium circles, and the H atoms are small black circles.



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