PODLESNOITE
$BaCa_2(CO_3)_2F_2$

A NEW MINERAL SPECIES FROM THE KIROVSKII MINE KHIBINY, KOLA PENINSULA, RUSSIA

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ABSTRACT

The new mineral podlesnoite, ideally $BaCa_2(CO_3)_2F_2$, was found at the Kirovskii underground apatite mine, Mount Kukisvumchorr, Khibiny alkaline massif, Kola Peninsula, Russia. Podlesnoite occurs in cavities within a hydrothermal lens-shaped body located in urtite rock. Associated minerals include natrolite, biotite, ilmenite, aegirine, lorenzenite, barytocalcite, calcite, fluorite, astrophyllite and burbankite. Two morphological varieties of podlesnoite were found: (variety I) perfect prismatic crystals up to $1 \times 1 \times 4$ mm typically combined in groups, and (variety II) radial fibrous spherulites up to 8 mm in diameter. Crystal forms are: {100}, {110}, {210}, {001}, {101}, {112}, {313}, {111} and {021}. Crystals (variety I) are colorless, transparent and water-clear; radial fibrous spherulites (variety II) are snow-white and translucent. The streak is white; the luster is vitreous. The mineral is brittle with no observed cleavage. Fracture is conchoidal; Mohs' hardness 3.5–4. $D_{meas} = 3.62(1)$, $D_{calc} = 3.63$ g/cm³. In shortwave ultraviolet light, colorless crystals show strong pinkish orange fluorescence, whereas white spherulites show weak bluish lilac fluorescence. Optically, the mineral is biaxial (−), $\alpha = 1.500(2)$, $\beta = 1.612(2)$, $\gamma = 1.614(2)$, $2V_{meas} = 10(5)°$, orientation: $X = a$, $Y = b$, $Z = c$. Chemical composition is: Na_2O 0.11, K_2O 0.05, CaO 29.02, SrO 0.13, BaO 40.77, MnO 0.07, FeO 0.25, CO_2 22.9, F 9.95, $−O=F_2$ 4.19, total 99.06 wt.%. The empirical formula based on six oxygens is:

$$Ba_{1.02}(Ca_{1.98}Fe_{0.01}Na_{0.01}Sr_{0.005})_{\Sigma2.005}C_{1.99}O_6F_{2.00}.$$

Symmetry is orthorhombic, space group Cmcm; unit cell dimensions are: $a = 12.511(5)$, $b = 5.857(2)$, $c = 9.446(4)$ Å, $V = 692.2(8)$ Å³, $Z = 4$. The strongest reflections of the X-ray powder diagram (d,Å-I[hkl]) are: 5.303-21[110]; 3.527-100[112]; 3.397-71[310]; 2.609-20[402]; 2.313-43[222], 2.302-22[510], 2.211-20[204], 1.948-39[422], 1.940-40[314]. Podlesnoite represents a new structural type remotely related to the aragonite group. The mineral was named in honor of Aleksandr Semenovich Podlesnyi (b. 1948), Russian amateur mineralogist and mineral collector, in recognition of his significant contributions to the mineralogy of the Khibiny massif. The holotype specimen is deposited in the Fersman Mineralogical Museum, Moscow.

INTRODUCTION

The famous Khibiny massif on the Kola Peninsula is the world's largest alkaline complex, covering an area of 1327 km². Huge deposits of a magmatogene apatite are actively mined there, and the Khibiny massif is the world's most prolific geological unit in terms of mineral diversity, with 470 mineral species, and is the type locality for 95 of those species.

The Kukisvumchorr apatite deposit at the southern edge of Mount

Kukisvumchorr was discovered in August, 1926 by Russian mineralogist Aleksandr N. Labuntsov. In October, 1929, the first mine in the Soviet Union situated north of the Arctic Circle was opened there. This mine, first named the Apatitovyi mine, was renamed as the Kirovskii mine in 1935, in memory of the great Soviet political figure Sergey M. Kirov, who actively supported exploration of the Khibiny area. Today, the Kirovskii mine (Fig. 1) operates intensively and on a large scale. It includes extensive underground workings (Fig. 2) and two open pits.

All apatite deposits in Khibiny are localized within a complex of melteigite-urtite[1] rocks. Phosphate ores largely consist of granular, sugar-like fluorapatite with embedded nepheline crystals. The ore rock can contain up to 98% fluorapatite. Nepheline-apatite rocks form numerous lenticular bodies up to several kilometers long and up to 200 meters thick. The Kukisvumchorr deposit is in the northwest portion of a huge (12 km long) lode of nepheline-apatite rock which is prospected and mapped by using boreholes to a depth of 2.5 km. The main orebody of the Kukisvumchorr deposit is a lens roughly 1800 meters long and varying in thickness from 45 to 200 meters (typically 80 to 100 meters). Rocks underlying the orebody are urtites and ijolites[2]; the overlying rocks are rischorrites.[3]

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[1] **Melteigite** is a dark colored plutonic rock that is part of the ijolite series and contains nepheline and 60–90% mafic minerals, especially green pyroxene. **Urtite** is a pale-colored member of the ijolite series that is composed chiefly of nepheline and 0–30% mafic minerals, especially aegirine and apatite (Jackson, 1997).

[2] **Ijolite** refers to a series of plutonic rocks containing nepheline and 30–60% mafic minerals, generally clinopyroxene, and including titanite, apatite and sometimes andradite (Jackson, 1997).

[3] **Rischorrite** is a variety of nepheline syenite in which nepheline is poikilitically enclosed in microcline perthite (Jackson, 1997).

Data on the geology, tectonics and petrology of the Kukisvumchorr deposit were published by Ivanova (1963) and Zak *et al.* (1972), and the mineralogy of apatite ores and host rocks was described by Dudkin *et al.* (1964). The mineralogy of Kukisvumchorr pegmatites and hydrothermal bodies and the history of research and mining at the Kirovskii mine were reported by Pekov and Podlesnyi (2004).

Many hundreds of alkaline pegmatite and hydrothermal bodies with diverse mineralogy were uncovered in the workings of the Kirovskii mine. The pegmatitic-hydrothermal complex of the Kukisvumchorr deposit stands out by its singularity even against a background of the Khibiny massif, an object unique in its mineralogy. The Kirovskii mine is one of the most remarkable mineral localities in Russia, and 220 different minerals are currently known to occur there. It is the type or cotype locality for 23 species, of which nine are found nowhere else: armbrusterite, bussenite, isolueshite, kukharenkoite-(La), kukisvumite, middendorfite, podlesnoite, shirokshinite and tuliokite. The most interesting finds, including 20 new species, were made in the last quarter century at deep levels of the deposit. The presence of an active tectonic zone connected with the large Kukisvumchorr fault facilitated strong hydrothermal activity. As a consequence, an abundance of large cavities were created in which good crystals of numerous minerals have been found—an unusual occurrence for Khibiny. One of the remarkable mineralogical features of the Kukisvumchorr deposit is the diversity of carbonates: 34 carbonate species are known to occur there, most of them containing essential Na, Ca, Sr, Ba or *REE* cations.

A new fluorocarbonate of calcium and barium found at the

Figure 2. Underground galleries and mine trains in the Kirovskii mine. March, 2003; N. A. Pekova photo.

Figure 3. Aleksandr Podlesnyi with underground mine telephone. March, 2003; N. A. Pekova photo.

Kukisvumchorr deposit (Kirovskii mine) is described in this paper. It has been named *podlesnoite* (Cyrillic: подлесноит) (pronounced "pod-**lez'**-no-ite") in honor of Aleksandr Semenovich Podlesnyi (born 1948), Russian amateur mineralogist and prominent mineral collector, in recognition of his significant contributions to the mineralogy of the Khibiny massif. A. S. Podlesnyi (Fig. 3) has worked in the Kirovskii underground mine since 1977, initially as an operator of a loader, and from 1979 to the present day as a blasting operator. Beginning in 1980, he developed a strong interest in mineralogy, collected minerals and forged close contacts with Russian professional mineralogists. He has assembled the best systematic collection of Kirovskii mine minerals in existence, and has also built one of the most representative collections of Khibiny minerals in general. A book describing the mineralogy of pegmatitic and hydrothermal formations at this outstanding mineral locality (Pekov and Podlesnyi, 2004) was prepared based primarily on his collection. Perhaps the most remarkable aspect of his keen eye is reflected in the fact that A. S. Podlesnyi collected and provided for study the specimens which became the holotype specimens of eleven new species (tuliokite, kukisvumite, sitinakite, belovite-(La), labuntsovite-Fe, lemmleinite-Ba, kukharenkoite-(La), shirokshinite, middendorfite, armbrusterite and podlesnoite) and the cotype specimens of four other new species (kukharenkoite-(Ce), tsepinite-K, neskevaaraite-Fe and potassicarfvedsonite)! This is probably a modern record for the number of new mineral species described based on specimens self-collected by a single amateur.

Both the new mineral and its name have been approved by the IMA Commission on New Minerals, Nomenclature and Classification (IMA 2006-033). The holotype specimen of podlesnoite is deposited in the Fersman Mineralogical Museum of the Russian Academy of Sciences, Moscow, with registration no. 3460/1.

OCCURRENCE AND ASSOCIATED MINERALS

The specimens described in the present paper were collected by A. S. Podlesnyi in early February of 2006, in a stope excavated in the last days of January 2006. Podlesnoite was found in a small hydrothermal body (Fig. 4) composed primarily of natrolite. It is located in urtite rock enriched by pyroxene (aegirine-diopside), titanite and fluorapatite. Urtite there contains numerous xenoliths of fine-grained titanite-rich ijolite rock. The lenticular hydrothermal body dips gently toward the east (about 10°), and measures 3.2

meters in length, with a midpoint thickness of 90 cm. The host urtite gradually transitions to a natrolite body, with a natrolitized urtite transition zone 5 to 10 cm thick. This transition zone is enriched by grayish white fibrous lorenzenite and contains pods of brown cancrinite.

The main mineral of the hydrothermal body is white to gray, coarsely columnar natrolite. Individual natrolite crystals and groups up to 5 cm long form chaotic, sheaf-like or radial aggregates. Sporadically, but especially in the eastern part of the lens and near the lower margin, dark brown biotitic mica is abundant. It occurs as coarse, equant crystals up to 2 cm, isolated or forming aggregates up to 7 × 20 cm. Some areas, typically biotite-bearing, are enriched by green acicular aegirine, aggregates of well-shaped equant crystals (up to 3 mm) of ilmenite with strong metallic luster, and small (up to 0.5 mm), colorless, short-prismatic fluorapatite crystals. Nests (up to 2 cm) of softly fibrous grayish white lorenzenite, strongly
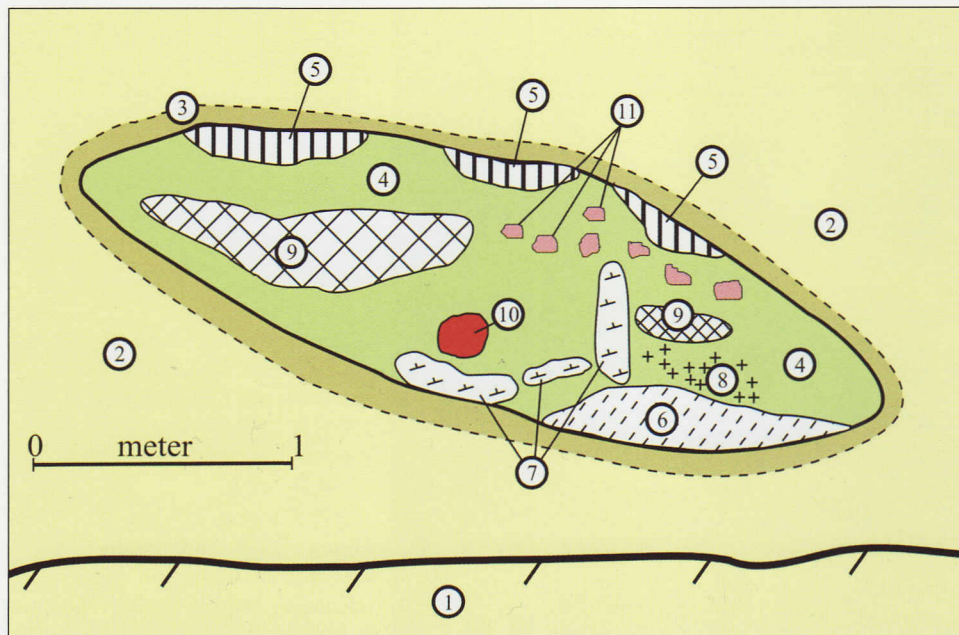
fluorescent greenish yellow in shortwave ultraviolet light, occur in the interstices between the natrolite crystals. Lorenzenite is especially abundant in the upper part of the body.

Natrolite aggregates contain numerous narrow, slit-like, elongated cavities which are especially large (up to 10 cm) and abundant in the axial zone in the western part of the body. Walls of the cavities are covered by natrolite crystals, and some cavities are filled by a clay-like material. Natrolite in the cavities is overgrown by calcite, fluorite, barytocalcite, podlesnoite, astrophyllite and, in minor amounts, burbankite, lemmleinite-K and fluorapophyllite. Calcite forms colorless rhombohedral crystals and shell-like pseudomorphs after pirssonite(?) crystals. Fluorite occurs as small, pale violet cuboctahedral crystals as well as colorless botryoidal crusts. Astrophyllite forms soft, cottony brown aggregates; burbankite forms greenish gray aggregates of tiny acicular crystals; lemmleinite-K forms isolated, pale yellow, rhomboidal lamellar crystals; and fluorapophyllite occurs as isolated colorless, water-clear tabular crystals. Brown films and spherical black droplets of hard bituminous matter typically occur in these cavities as well.

Barytocalcite was observed mainly in large cavities in the lower part of the body. Three different morphologies and colors were found: (1) transparent, lamellar to tabular, lemon-yellow crystals up to $1 \times 3 \times 3.2$ cm combined in clusters up to 5 cm; (2) gray prismatic crystals up to $0.3 \times 1 \times 3.5$ cm forming a cavernous nest of 10 cm across; and (3) snow-white, fine-grained spherical aggregations up to 1.5 cm in diameter covered by a podlesnoite crust.

Biotite, aegirine, ilmenite and fluorapatite are early minerals of the hydrothermal body, whereas natrolite and lorenzenite were formed later. Calcite, barytocalcite, podlesnoite, fluorite, astrophyllite, burbankite, lemmleinite-K and fluorapophyllite are the latest minerals found only in cavities. No feldspars, nepheline, sodalite, aegirine-diopside, amphiboles or eudialyte were found in this body, nor were there any zirconium minerals. An absence of these minerals, which are very typical for alkaline pegmatites of the Khibiny massif, combined with the presence of the transition zone between a natrolite body and urtite, demonstrates that we are observing a "pure hydrothermal" body but not a pegmatite. Note that several typical pegmatite veins occur a few meters from the lens containing the new mineral. The hydrothermally altered areas inside these pegmatites consist of natrolite and aegirine, and they contain biotite and fibrous lorenzenite visually very similar to the material described above. Calcite, fluorite and barytocalcite were found in the cavities, but podlesnoite was not.

MORPHOLOGY OF CRYSTALS AND AGGREGATES

Podlesnoite occurs as overgrowths on natrolite, ilmenite, biotite and barytocalcite in cavities. The new mineral occurs in two varieties that show distinctive morphology, color and fluorescence, but are otherwise identical in their chemical composition, X-ray powder diffraction pattern, IR spectrum and optical characteristics.

Variety I is represented by perfectly shaped prismatic crystals up to $1 \times 1 \times 4$ mm. They are typically combined in groups and crusts (Figs. 5 and 6) up to 1.5×2 cm; isolated crystals are rare.

Variety II forms dense radial spherulites up to 5 mm in diameter which consist of thin acicular to fibrous individuals (Fig. 7). The surface of these variety II spherulites is covered (usually completely) by an overgrowth of variety I crystals oriented in "reclining position" (this orientation is discussed below). This arrangement makes such "combined" spherules (up to 8 mm in diameter) unusual in appearance (Fig. 8). Thus, we can conclude that variety I crystallized later than variety II.

Crystals of variety I are prismatic, elongated along [001] (Fig. 9a–c). Several crystals were measured using a GD-1 two-circle goniometer (LOMO, Russia). In accordance with the X-ray data (see below), podlesnoite is orthorhombic, class *mmm*. Goniometric data are given in Table 1. The major forms observed on podlesnoite crystals (Fig. 10) are: {100}, {110}, {210} and {001}. Forms {101}, {112} and {313} are minor, and forms {111} and {021} are rare. On large crystals the {100}, {001}, {110} and {210} forms are dominant, whereas forms {101}, {112} and {313} are subordinate (Fig. 10a). Such crystals are visually similar to thomsonite crystals. Smaller crystals show more complicated combinations of forms, in some cases including well-developed dipyramidal faces (Fig. 10b–d). Forms {110} and {210} are typically striated parallel to [001]; on some crystals, forms {001} are striated parallel to [010] (Fig. 9). Twins were not observed, but parallel intergrowths are common (Fig. 9d).

As determined by optical study, acicular to fibrous individuals of variety II are elongated along [010], unlike crystals of variety I. The termination of a needle (fiber) of variety II on the surface

Figure 5. Group of podlesnoite crystals (variety I; the largest is 4 mm long). I. V. Pekov collection. N. A. Pekova photo.

of a spherulite becomes the nucleation point for a crystal of variety I which overgrows it in parallel orientation. Thus, crystals of variety I, elongated along [001], always have their axis of elongation perpendicular to that of the underlying acicular fibers of variety II, *i.e.* they are oriented tangential to the surface of spherulites (Fig. 11). This auto-epitaxy clearly explains a phenomenon which initially seems quite amazing, that the surface of spherulites of variety II is covered by crusts of variety I consisting of only "reclining" crystals (Fig. 8). Note that the auto-epitactic intergrowths of varieties II and I of podlesnoite are analogous in their structure to well-known oriented intergrowths of quartz and chalcedony (see Lemmlein, 1946): common rhombohedral-prismatic quartz crystals auto-epitactically, in reclining position, overgrow the surface of radial spherules of chalcedony formed by quartz fibers elongated along [$11\bar{2}0$] or [$10\bar{1}0$].

Optical, infrared, chemical, X-ray diffraction and structural data on podlesnoite presented in this paper were obtained for well-shaped crystals of variety I.

PHYSICAL AND OPTICAL PROPERTIES

Crystals of podlesnoite (variety I) are colorless and water-clear, while fibrous spherulites (variety II) are snow-white and translucent. The streak is white, and the luster is vitreous. The mineral is brittle, cleavage was not observed, and the fracture is conchoidal. Mohs' hardness is 3.5 to 4. The density, measured using heavy liquids, is 3.62(1), whereas calculated density using the empirical formula is 3.63; calculated density using the idealized formula is 3.60 g/cm^3.

Both varieties of podlesnoite fluoresce in ultraviolet light, but each quite differently (Figs. 6, 8). Colorless crystals of variety I show strong pinkish orange fluorescence in shortwave ultraviolet

light (245 nm) and no fluorescence in longwave ultraviolet light (330 nm). Snow-white spherulites of variety II show weak bluish lilac fluorescence in shortwave ultraviolet light and very weak lilac-blue fluorescence under longwave ultraviolet light.

Podlesnoite is optically biaxial negative, $\alpha = 1.500(2)$, $\beta = 1.612(2)$, $\gamma = 1.614(2)$, $2V_{meas} = 10(5)°$, $2V_{calc} = 14°$. Under the microscope, the mineral is colorless and non-pleochroic. Orientation: $X = a$, $Y = b$, $Z = c$.

Accuracy of the determination of the chemical composition, refractive indices and density of podlesnoite is confirmed by the superior values of the Gladstone–Dale compatibility index (Mandarino, 1981): $1 - (K_p/K_c) = 0.005$ for measured density, 0.011 for density calculated using the empirical formula, and 0.002 for density calculated using the idealized formula.

IR SPECTROSCOPY

The infrared spectrum of podlesnoite (Fig. 12a) clearly shows that the mineral is an anhydrous carbonate. No bands are observed in the range 3000–4000 cm^{-1} corresponding to O-H stretching vibrations. The assignment of the strongest bands is as follows: In the range 1300–1600 cm^{-1} there are components of the degenerate band of asymmetric C-O stretching vibrations. At 1067.5 cm^{-1} there are non-degenerate fully-symmetric C-O stretching vibrations. In the range 840–860 cm^{-1} one sees a non-degenerate band of out-of-plane bending vibrations of $(CO_3)^{2-}$ anions. The doublet at 705 + 710 cm^{-1} equals components of the degenerate band of in-plane bending vibrations of $(CO_3)^{2-}$ anions.

The band of out-of-plane bending vibrations is split into two components (at 842 and 855 cm^{-1}), presumably as a result of Fermi resonance. The corresponding overtone doublet has absorption maxima at 1776 and 1782 cm^{-1}.
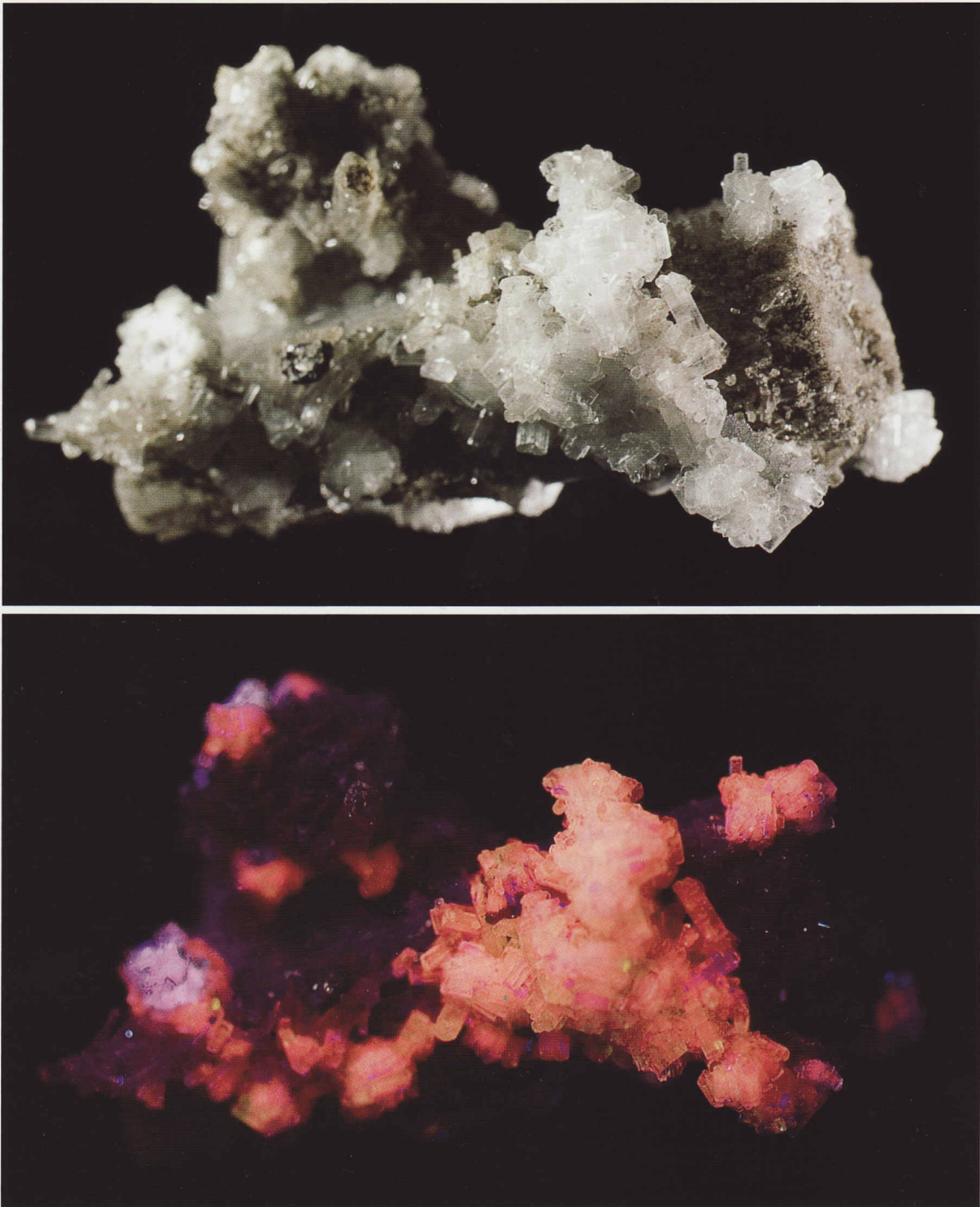
Figure 6. **Groups of podlesnoite crystals (variety I) and spherulites forming a crust on a natrolite crystal: (*a*) in ordinary light, (*b*) in shortwave ultraviolet light. Specimen size: 3 cm. I. V. Pekov collection; N. A. Pekova photo. The difference in the fluorescence color of podlesnoite varieties I and II is well-shown on a broken spherule.**

The absorption activity of non-degenerate, fully-symmetric C-O stretching vibrations is an indication of a distortion of (CO_3) groups. Obviously, this distortion results in the splitting of the band of in-plane bending vibrations. However, band splitting for this reason is impossible for the bands of non-degenerate vibrations. For this reason, the presence of a distinct, very narrow band at 901.5 cm^{-1} (*i.e.* close to the range of out-of-plane bending vibrations of $(CO_3)^{2-}$ anions) is intriguing. It could be explained by a resonance splitting, but this explanation is doubtful because the value of splitting (46.5 cm^{-1}) is too high and essentially exceeds the widths of corresponding individual bands. Such bands are unknown in infrared spectra of other anhydrous carbonate and fluorocarbonate minerals. A possible (though exotic) explanation for the band at 901.5 cm^{-1} could be the hypothetical substitution of a minor part (no more than a few percent?) of carbonate groups by the anions $(CO_2F)^-$. As it was demonstrated for matrix-isolated ion pairs $(CO_2F)^- \cdot Tl^+$ and $(CO_2F)^- \cdot Cs^+$, in particular using the ^{13}C- and ^{18}O-substituted species (Ault, 1982; Shelle and Ault, 1985), the ion $(CO_2F)^-$ is relatively stable and frequencies of its bending vibrations in the IR spectra lie in the range 883–885 cm^{-1}. In the presence of the higher force-strength cation Ca^{2+}, enhancement of this frequency should be expected.

Figure 7. **Two morphological varieties of podle-snoite on grayish natrolite crystals: a broken white spherulite (3 mm in diameter) of variety II and colorless transparent crystals of variety I. I. V. Pekov collection; N. A. Pekova photo.**

In other aspects (except for the unusual band at 901.5 cm^{-1}), the IR spectrum of podlesnoite is close to the spectra of aragonite-group minerals. The greatest similarity is with the spectrum of strontianite (Fig. 12b), and that is probably related to the fact that, by the mean atomic mass and the mean ionic radius, the combination ($BaCa_2$) is close to (Sr_3). The observed splitting of the bands in the IR spectrum of podlesnoite is one of its diagnostic characteristics.

CHEMICAL COMPOSITION
AND CHEMICAL PROPERTIES

The contents of cations and fluorine in podlesnoite were determined using electron microprobe in WDS mode via a Camebax SX 100 instrument, at an accelerating voltage of 15 kV and beam current of 15 nA; the electron beam was rastered over an area of 5×5 µm². The standards used were: albite (Na), microcline (K), andradite (Ca, Fe), $SrSO_4$ (Sr), $BaSO_4$ (Ba), $MnTiO_3$ (Mn), fluorapatite (F). CO_2 content was determined using the selective absorption method: heating to 1000°C under oxygen stream with CO_2 absorption in pipes filled with "ascarite," an asbestiform material saturated with NaOH.

The chemical composition of podlesnoite (wt.%, averaged values for cations and F from 8 point analyses; ranges are in parentheses) is: Na_2O 0.11 (0.0–0.2), K_2O 0.05 (0.0–0.1), CaO 29.02 (28.3–30.1), SrO 0.13 (0.0–0.2), BaO 40.77 (40.0–41.6), MnO 0.07 (0.0–0.15), FeO 0.25 (0.1–0.4), CO_2 22.9, F 9.95 (9.8–10.2), $-O = F_2$ 4.19, total 99.06. Contents of Mg, Pb, Y, lanthanides, Al, Si and Cl are below detection limits. Absence of H_2O in the mineral is confirmed by the IR spectrum and structural data.

Figure 8. **Podlesnoite spherules (the largest is 5 mm in diameter) consisting of a variety II radial core and a crust of variety I crystals, on natrolite: (*a*) in ordinary light, (*b*) in shortwave ultraviolet light. A. S. Podlesnyi collection; N. A. Pekova photo. The difference in the fluorescence color of podlesnoite varieties I and II is well-demonstrated on a broken combined spherule.**
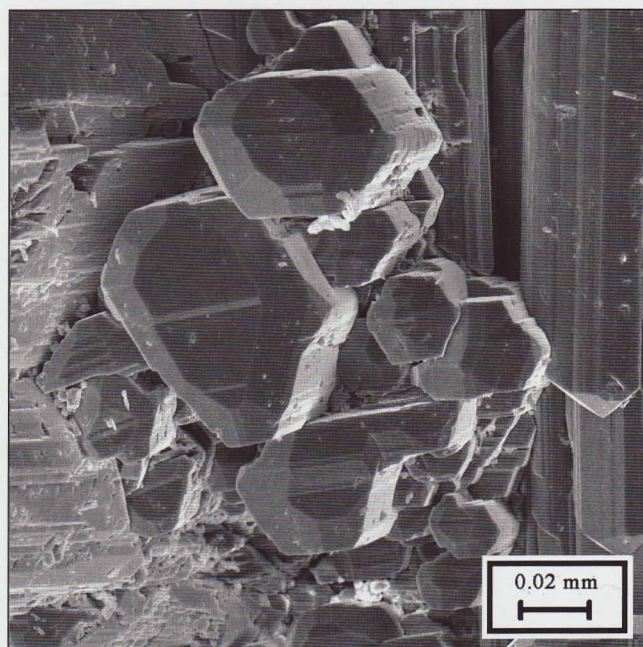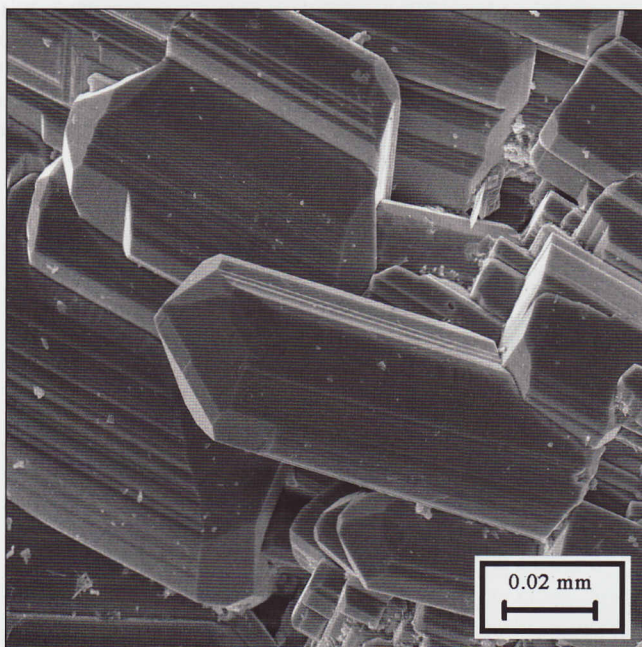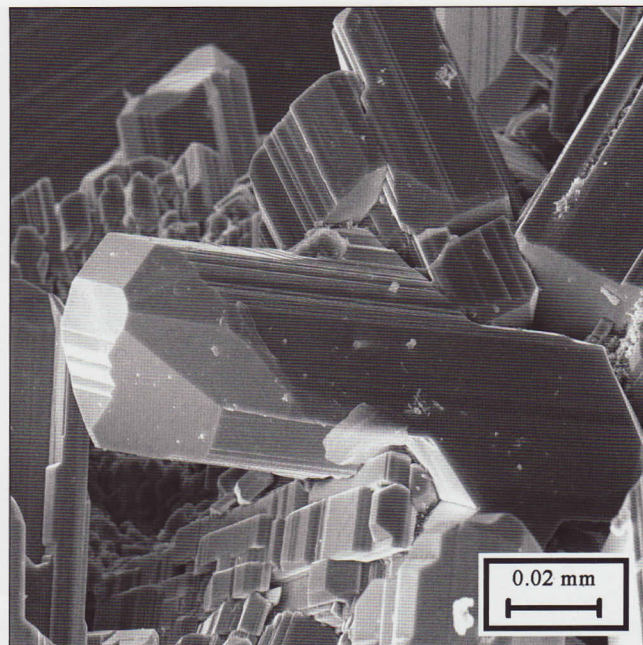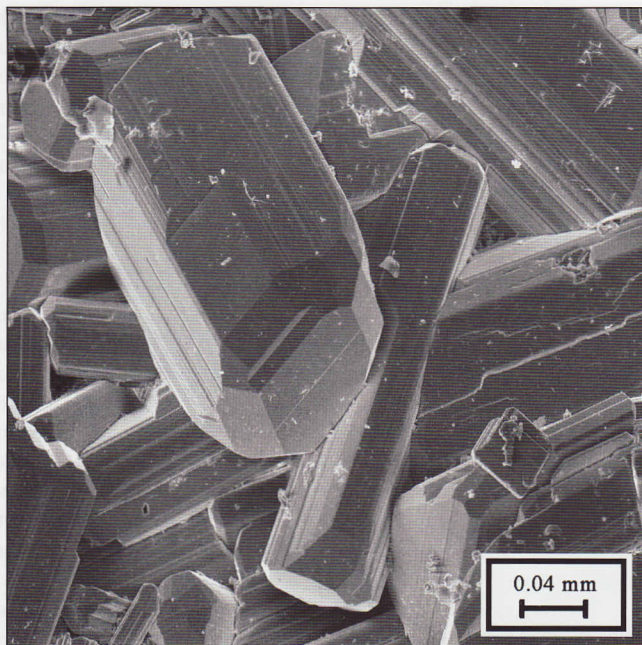
Figure 9. Podlesnoite crystals (*a–c*) and parallel intergrowth (*d*). I. V. Pekov collection and SEM photo.

The empirical formula of podlesnoite calculated on the basis of six oxygens is:

$$Ba_{1.02}(Ca_{1.98}Fe_{0.01}Na_{0.01}Sr_{0.005})_{\Sigma 2.005}C_{1.99}O_6F_{2.00}.$$

The idealized formula is:

$$BaCa_2(CO_3)_2F_2$$

. . . which requires CaO 29.87, BaO 40.83, CO_2 23.44, F 10.12, –O = F_2 4.26, total 100.00 wt.%. Thus the chemical composition of the new mineral as determined by analysis is very close to the ideal composition. No chemical zoning in the crystals was observed.

Crystals of podlesnoite dissolve slowly in both concentrated and dilute HCl at room temperature with very weak effervescence, whereas a fine powder of the mineral under the same conditions easily dissolves in both concentrated and dilute HCl with strong effervescence.

X-RAY CRYSTALLOGRAPHY AND CRYSTAL STRUCTURE FEATURES

The X-ray single-crystal diffraction data of podlesnoite were obtained using an Xcalibur S diffractometer equipped with a CCD detector and Mo$K\alpha$-radiation. The new mineral is orthorhombic, with space group *Cmcm*. Unit cell dimensions are: $a = 12.501(8)$, $b = 5.846(3)$, $c = 9.443(5)$ Å, $V = 690.1(7)$ Å^3, $Z = 4$.

The X-ray powder diffraction data (Table 2) were obtained using a STOE STADI MP diffractometer equipped with a PSD detector and Ge-monochromatized Cu$K\alpha_1$-radiation. Unit cell dimensions refined from powder data are: $a = 12.511(5)$, $b = 5.857(2)$, $c = 9.446(4)$ Å, $V = 692.2(8)$ Å^3, $Z = 4$.

The axial ratios calculated from unit cell data are: $a : b : c = 2.1361 : 1 : 1.6128$. These values are close to the ones calculated from goniometric data (Table 1): $a : b : c = 2.1290 : 1 : 1.5854$.
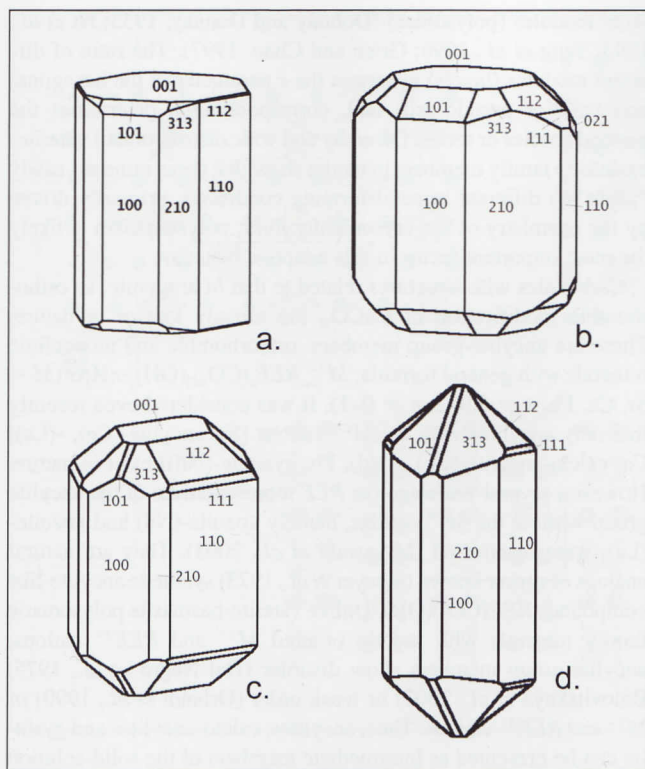
Figure 10. Podlesnoite crystal drawings: (*a*) typical crystal, (*b–d*) rarely observed crystals.

Table 1. Crystal forms of podlesnoite (class *mmm*).

Forms	Spherical coordinates			
	measured		calculated	
	φ	ρ	φ	ρ
{001}	—	0.0°	—	0°
{100}	90.0°	90.0°	90°	90°
{110}	25.2°	90.0°	25.09	90°
{210}	43.2°	90.0°	43.12°	90°
{101}	90.0°	36.7°	90°	37.05°
{021}	0.0°	72.6°	0°	72.78°
{111}	25.2°	60.0°	25.09°	60.68°
{112}	25.2°	41.1°	25.09°	41.68°
{313}	54.5°	42.7°	54.55°	42.83°

NOTE: data averaged for 3 crystals. Standard deviations are ±0.1° for faces {001}, {100}, {110}, {210}, {021}, and {313} and ±0.2° for faces {101}, {111}, and {112}.

From goniometric data, $a : b : c = 2.1290 : 1 : 1.5854$.

The X-ray powder diffraction pattern of podlesnoite is unique and constitutes an unambiguous diagnostic characteristic.

The crystal structure of podlesnoite was studied on a single crystal, $R_F = 2.78\%$. It has been described in a separate publication (Zubkova *et al.*, 2007). Podlesnoite is a representative of a new structural type; there are no known closely related minerals or synthetic compounds.

The base of the crystal structure of podlesnoite (Fig. 13) is a condensed framework consisting of columns of Ca-centered 8-fold polyhedra (CaO_6F_2) stretched along [001]. (CO_3) groups, coplanar to the *ac* plane, and large Ba atoms are located in cavities of the framework. Ba atoms center the 10-fold polyhedra (BaO_6F_4); F atoms center the tetrahedra (FCa_2Ba_2).
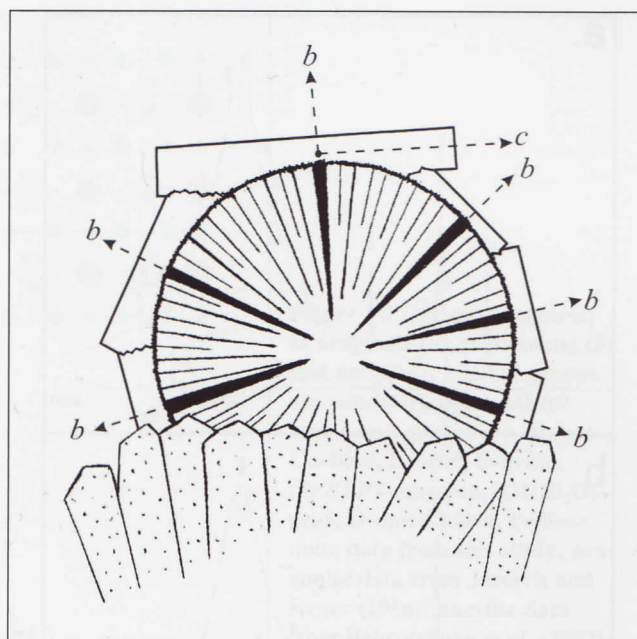

Figure 11. Schematic drawing of an auto-epitactic intergrowth of two morphological varieties of podlesnoite: prismatic crystals of variety I overgrowing a radial spherulite of variety II with the same crystallographic orientation as the fibers of variety II. Underlying natrolite crystals are speckled.

The podlesnoite structure is remotely related to that of minerals of the aragonite group, and can be regarded as a derivative of the aragonite-type structure. Transition from aragonite to podlesnoite can be described as an ordered substitution of ⅓ Ca cations by larger Ba cations and ⅓ (CO_3) groups by pairs of F atoms: $[3Ca] + [3(CO_3)] \rightarrow [2Ca + Ba] + [2(CO_3) + 2F]$. This transformation means a change of the cation-to-anion ratio (from 1 : 1 in aragonite to 3 : 4 in podlesnoite) and leads to very significant structural changes (Fig. 14). As a result, aragonite-group minerals and podlesnoite strongly differ in symmetry, unit cell dimensions and X-ray powder diffraction patterns. However, short-range order interactions between (CO_3) groups and cations in podlesnoite and aragonite-group minerals are not so different, resulting in the close similarity of their IR spectra.

DISCUSSION

Previous to this description of podlesnoite, 27 fluorocarbonate minerals were known. Nineteen of them contain essential rare-earth elements (*REE*), *i.e.* lanthanides or yttrium. Among them, members of the vaterite $CaCO_3$—bastnäsite *REE*(CO_3)F polysomatic family and topologically related Ba,*REE* and Na,*REE* carbonates prevail (17 species); there are minerals without the M^{2+} cations: bastnäsite-(Ce), bastnäsite-(La), bastnäsite-(Y); Ca,*REE* minerals: synchysite-(Ce), synchysite-(La), synchysite-(Y), parisite-(Ce), parisite-(Nd), röntgenite-(Ce); Ba,*REE* minerals: cordylite-(Ce), huanghoite-(Ce), cebaite-(Ce), zhonghuacerite-(Ce), kukharenkoite-(Ce), kukharenkoite-(La), qaqarssukite-(Ce); and an Na,*REE* mineral: lukechangite-(Ce). Horváthite-(Y) and mineevite-(Y) have different structures. The Ca-Th-fluorocarbonate thorbastnäsite is structurally related to the vaterite-bastnäsite family of minerals. Other natural fluorocarbonates include hydrous minerals with uranyl cations (schröckingerite and albrechtschraufite), sodium minerals with Ca (sheldrickite and rouvilleite) or Al (barentsite), a Ca-Bi mineral (kettnerite) and the Ca mineral brenkite. Podlesnoite is
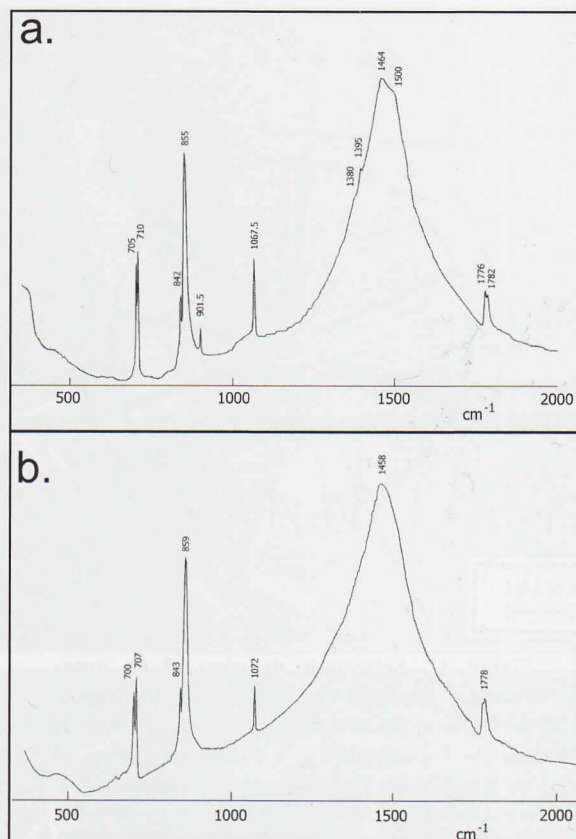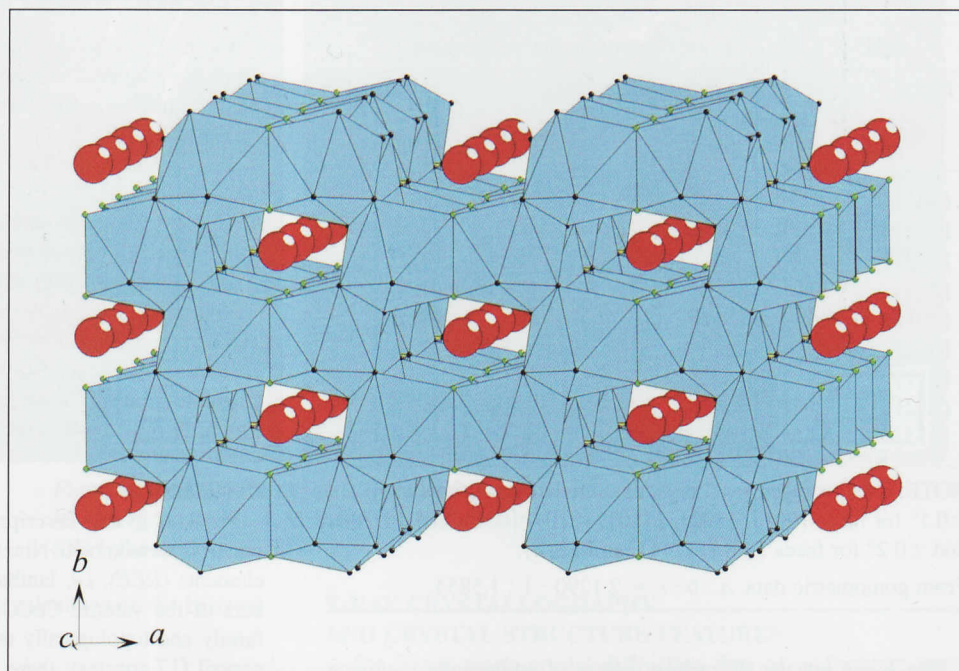
Figure 12. Infrared spectrum of podlesnoite from the Kirovskii mine (*a*) and strontianite from Vishnevye Gory, South Urals, Russia (*b*).

Figure 13. A condensed framework, consisting of (CaO_6F_2) polyhedra, and chains of Ba atoms in the crystal structure of podlesnoite. Ca-centered polyhedra are blue, Ba atoms are large red circles, F atoms are small green circles, and O atoms are small black circles.

layer modules (polysomes) (Donnay and Donnay, 1953; Ni *et al.*, 1993; Yang *et al.*, 1996; Grice and Chao, 1997). The ratio of different modules (layers) generates the *c* parameter of the hexagonal unit cell (or pseudo-cell) and, correspondingly, determines the mineral species or series. Diversity and wide distribution of vaterite-bastnäsite family members in nature show that these minerals easily "adapt" to different mineral-forming conditions, primarily driven by the chemistry of the crystallizing fluid; polysomatism is likely the most important factor in this adaptive behavior.

Carbonates with structures related to that of aragonite, an orthorhombic modification of $CaCO_3$, are already known in nature. These are ancylite-group members: orthorhombic and monoclinic minerals with general formula: $M^{2+}_{2-x}REE_x(CO_3)_2(OH)_x \cdot nH_2O$ (M = Sr, Ca, Pb, x = 0.9–2, n = 0–1). It was considered even recently that only ancylites with the M^{2+} cations [Sr: ancylite-(Ce), -(La); Ca: calcio-ancylite-(Ce), -(Nd); Pb: gysinite-(Nd)] exist in nature. However, several years ago the *REE* representatives of the ancylite group without the M^{2+} cations, namely kozoite-(Nd) and kozoite-(La), were discovered (Miyawaki *et al.*, 2003). They are natural analogs of earlier known (Sawyer *et al.*, 1973) synthetic ancylite-like compounds $REE(CO_3)(OH)$. Unlike vaterite-bastnäsite polysomatic family minerals with strictly ordered M^{2+} and REE^{3+} cations, ancylite-group members show disorder (Dal Negro *et al.*, 1975; Belovitskaya *et al.*, 2002) or weak order (Orlandi *et al.*, 1990) of M^{2+} and REE^{3+} cations. Thus, ancylites, calcio-ancylites and gysinite can be presented as intermediate members of the solid-solution series with the end-members $M^{2+}CO_3$ (aragonite-group minerals with M = Ca, Sr, Pb) and $REE(CO_3)(OH)$ (kozoite).

only the second (after brenkite, $Ca_2(CO_3)F_2$) natural fluorocarbonate containing only alkaline-earth cations.

Thus, the majority of the known natural fluorocarbonates contain essential *REE* and have hexagonal (trigonal) or pseudo-hexagonal layered structures related to the structure of vaterite, a hexagonal modification of $CaCO_3$. Some of these minerals are widespread; in particular, bastnäsite-(Ce) is the main ore mineral of the world's largest rare-earth deposits at Bayan Obo (Inner Mongolia, China) and Mountain Pass (California, U.S.A.). The crystal structures of these minerals are based on regularly interstratified vaterite-like MCO_3 (M = Ca, Ba or Na_2) and bastnäsite-like $REE(CO_3)(F,OH)$

The path of transition from aragonite to podlesnoite is quite different from that of aragonite to ancylite (Fig. 14). Unlike ancylite, the cation/anion ratio in podlesnoite is 3:4, Ca and Ba cations are strictly ordered, and all (CO_3) triangular groups are coplanar with the *ac* plane. The geometric characteristics of both cation and anion sub-lattices in aragonite, podlesnoite and ancylite are different (Fig. 14).

Ca,*REE* members of the vaterite-bastnäsite polysomatic family are represented by parisites, $CaREE_2(CO_3)_3F_2$, röntgenite, $Ca_2REE_3(CO_3)_5F_3$, and synchysites, $CaREE(CO_3)_2F$. Ca/*REE* ratios in them are 0.5, 0.67 and 1.0 respectively, *i.e.* cation compositions
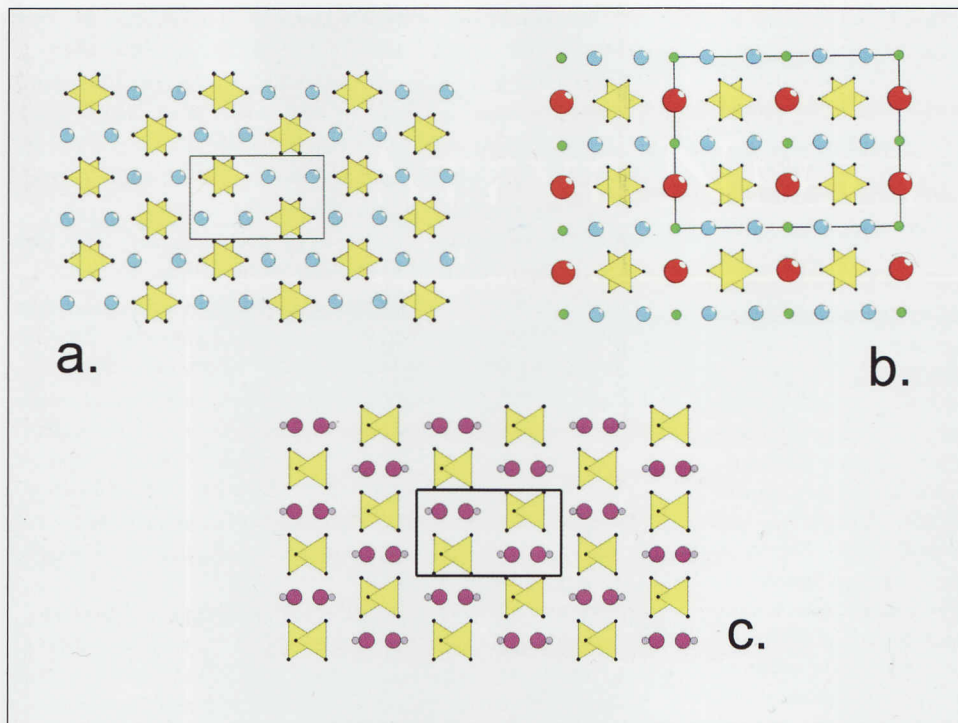
Figure 14. **Crystal structures of aragonite (*a*), podlesnoite (*b*) and ancylite (*c*). (CO₃) groups are yellow triangles, other atoms and groups are circles: Ca–blue, Ba–red, F–green, (Sr,*REE*)–magenta, (OH,H₂O)–gray, O–small black. Podlesnoite data from this study; aragonite data from Jarosch and Heger (1986); ancylite data from Belovitskaya *et al.* (2002).**

Table 2. X-ray powder diffraction data for podlesnoite. NOTE: I_{calc} values were calculated from structural data.

I_{meas}	d_{meas}, Å	I_{calc}	d_{calc}, Å	hkl	I_{meas}	d_{meas}, Å	I_{calc}	d_{calc}, Å	hkl
11	6.250	9	6.255	200	11	1.768	12	1.768	330
21	5.303	20	5.304	110	5	1.698	4	1.699	620
13	4.733	8	4.723	002	3	1.651	1	1.651	315
16	3.771	11	3.769	202	6	1.649	4	1.648	514
100	3.527	100	3.527	112	12	1.607	11	1.607	712
71	3.397	61	3.397	310	7	1.598	3	1.598	622
10	3.125	8	3.128	400	10	1.564	3, 6	1.564, 1.563	800, 604
9	2.928	9	2.928	020	4	1.527	2	1.527	206
10	2.797	9	2.797	021	9	1.510	7	1.509	116
11	2.757	8	2.758	312	7	1.4638	2, 2	1.4642, 1.4635	040, 532
9	2.653	8	2.652	220	3	1.4252	1	1.4284	316
20	2.609	18	2.608	402	5	1.4159	5	1.4154	334
3	2.552	5	2.553	221	3	1.4073	2	1.4062	406
5	2.492	3	2.489	022	6	1.3793	2, 5	1.3795, 1.3789	820, 624
15	2.364	16	2.362	004	2	1.3653	3	1.3649	242
43	2.313	41	2.313	222	7	1.3537	5	1.3538	226
22	2.302	15	2.301	510	5	1.3042	5	1.3039	804
2	2.234	2	2.236	511	4	1.3003	1, 2	1.3003, 1.2993	912, 516
20	2.211	12	2.209	204	6	1.2898	5	1.2895	534
4	2.160	2	2.157	114	5	1.2770	4	1.2768	442
12	2.085	11	2.085	600	10	1.2692	6, 6	1.2698, 1.2677	732, 426
15	2.069	12	2.069	512	4	1.2441	3	1.2444	044
39	1.948	32	1.948	422	6	1.2205	2, 4	1.2205, 1.2197	244, 136
40	1.940	35	1.939	314	7	1.1589	4	1.1581	716
4	1.927	2	1.929	130	7	1.1174	4, 2, 3	1.1178, 1.1165, 1.1153	10.2.2, 11.1.0, 318
10	1.839	9	1.838	024					
18	1.786	15	1.786	132					

of all these minerals lie inside the M^{2+}/*REE* interval typical for ancylite-group members (Pekov *et al.*, 1997). Thus, hypothetical hydroxyl-dominant analogs of these minerals can be considered as cation-ordered dimorphs of calcio-ancylite with different cation compositions. OH-dominant analogs of synchysite, parisite and röntgenite are not known for certain in nature, whereas OH>F in all ancylite-group minerals; fluorine is a minor admixture, but not an essential constituent in them (Pekov *et al.*, 1997). This constraint is likely caused by the fact that (OH) groups form strong hydrogen bonds in ancylites (see Belovitskaya *et al.*, 2002) that hampers their substitution by F atoms. Thus, cation-ordered modifications are more stable for Ca,*REE* fluorocarbonates unlike Ca,*REE* and Sr,*REE*

hydroxycarbonates for which cation-disordered modifications are more stable. This is confirmed by the existence of close paragenetic associations of ancylite-group minerals with synchysite, as demonstrated at Khibiny, Vuoriyarvi (North Karelia, Russia), Narssarssuk (South Greenland) and some other alkaline complexes.

Barium, the largest of the alkaline-earth cations (except Ra), is known in ancylite-group minerals as only a minor admixture, probably the result of the large difference in ionic radii of Ba^{2+} and REE^{3+}. However, seven natural Ba,REE fluorocarbonates with layered bastnäsite-like structures (see above) are known in nature. In these minerals, the Ba and REE cations are ordered, like Ca and REE in parisite, synchysite and röntgenite, whereas Sr,REE carbonates with bastnäsite-like structures are unknown.

Podlesnoite, like Ba,REE and Ca,REE fluorocarbonates, demonstrates strict cation ordering, a strong affinity to fluorine, and insignificant isomorphism of both barium and calcium with strontium.

The chemical formula of podlesnoite, $BaCa_2(CO_3)_2F_2$, can be rendered as $BaCa(CO_3)_2 \cdot CaF_2$. Barytocalcite, $BaCa(CO_3)_2$, and fluorite, CaF_2, are closely associated with podlesnoite. Barytocalcite was formed earlier than the new mineral, whereas fluorite was formed later. The crystallization of podlesnoite probably took place in conjunction with a decrease of Ba concentration in the hydrothermal solution and a corresponding increase in F concentration. Association of barytocalcite and its polymorphous modifications, alstonite and paralstonite, with fluorite is well-known at numerous localities, whereas the first known barium-calcium fluorocarbonate in nature is podlesnoite, and its synthetic analog has yet to be produced. This is probably an indication that the stability field of podlesnoite is quite narrow, and that its formation is possible only under very restricted conditions.

ACKNOWLEDGMENTS

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