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# Kukharenkoite-(Ce), $Ba_2Ce(CO_3)_3F$, a new mineral from Kola peninsula, Russia, and Québec, Canada

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**Abstract:** Kukharenkoite-(Ce), ideally $Ba_2Ce(CO_3)_3F$, is a new rare-earth fluorocarbonate mineral, occurring as an accessory mineral in the late REE-carbonatites and REE-rich carbonate-zeolite rocks of the Khibina massif, Kola peninsula, Russia. It has also been found in other associations within the Khibina complex as well as in the Vuorijärvi massif, Kola peninsula and the related alkaline intrusions of the Mont Saint-Hilaire complex and the Saint-Amable sill, Québec, Canada. Kukharenkoite-(Ce) occurs in cavities as small (0.01-1.0 mm), prismatic, bladed crystals which are often in dendritic or stellate groups up to 2-3 mm across. Associated minerals are manganoan ankerite, ferroan rhodochrosite, manganoan siderite, natrolite, synchysite-(Ce), orthoclase, barite, pyrite, cordylite-(Ce), mckelveyite-(Y), ewaldite, galena and sphalerite. The mineral is yellow with a white streak; transparent with a vitreous lustre. Cleavage and parting were not observed. The microhardness $VHN_{25}$ is 280(25), the Mohs hardness is 4.5; density (meas.) is 4.7(1) $g/cm^3$ and density (calc.) is 4.62 $g/cm^3$. The infrared absorption spectrum includes the following bands: $\nu_4$ 685-695-705-715-735; $\nu_2$ 870-885; $\nu_1$ 1090; $\nu_3$ 1380-1430-1480 $cm^{-1}$. It is optically biaxial (-), with $\alpha$ 1.584(1), $\beta$ 1.724(3), $\gamma$ 1.728(3) (for Na light), $2V_{meas.}$: 16(1)°, $2V_{calc.}$: 18(1)°, $Z\Lambda c$ = 26.5° in obtuse $\beta$, Y = b. On the Khibina specimens, an average of 12 electron-microprobe analyses gave CaO 0.39, SrO 1.55, BaO 47.39, $La_2O_3$ 6.61, $Ce_2O_3$ 15.30, $Pr_2O_3$ 1.19, $Nd_2O_3$ 4.26, $Y_2O_3$ 0.15, $CO_2$ 21.95 (calculated by stoichiometry), F 3.18, -O = $F_2$ 1.34, total 100.63. The ideal formula is $Ba_2Ce(CO_3)_3F$. The mineral is monoclinic, $P2_1/m$, with $a$ 13.396(7), $b$ 5.067(1), $c$ 6.701(1) Å, $\beta$ 106.58(1)°, $V$ 435.8(3) Å$^3$, $Z$ = 2. The strongest five X-ray powder diffraction lines [d in Å(I)(hkl)] are: 4.000(100)(201), 3.269(100)(310), 2.535(20)(020), 2.140(40)(221), 2.003(40)(402). The name kukharenkoite-(Ce) is given in honour of Professor A.A. Kukharenko (1914-1993; Department of Mineralogy, St-Petersburg University, Russia).

**Key-words:** kukharenkoite-(Ce), fluorocarbonate, new mineral, Khibina, Vuorijärvi, Mont Saint-Hilaire, Saint-Amable.

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## Introduction

In 1986, a monoclinic Ba-REE-Th-bearing fluorocarbonate mineral, designated as UK-65, was identified from the Mont Saint-Hilaire alkaline complex, Québec, Canada (Chao *et al.*, 1990). However, the small amount of material available for study precluded a complete investigation. In 1988, a mineral with similar crystallographic data to UK-65 was found in the Khibina and Vuorijärvi alkaline massifs, Kola peninsula, Russia. On the basis of its chemistry it was described as "zhonghuacerite-(Ce)", although a single crystal study showed the mineral to be monoclinic (Yakovenchuk *et al.*, 1991; Zaitsev, 1992). In 1993, a mineral with similar crystallographic and chemical data as those for the Mont Saint-Hilaire, Khibina and Vuorijärvi minerals was identified in specimens collected in 1976 from the Saint-Amable sill, near the village of Varennes, Québec, Canada. A joint investigation of this mineral from all its localities during 1993-1995 showed that it is a new Ba-REE fluorocarbonate with the formula $Ba_2REE(CO_3)_3F$ where Ce is the dominant rare-earth element. This new mineral has been named kukharenkoite-(Ce) (in accordance with the Levinson system of nomenclature of REE minerals) in honour of Professor Alexander A. Kukharenko (1914-1993; Department of Mineralogy, St-Petersburg University, Russia), in recognition of his outstanding contributions to the geology, petrology and mineralogy of ultrabasic-alkaline-carbonatite complexes from the Kola peninsula, Russia. Both the mineral and mineral name have been approved by the Commission on New Minerals and Mineral Names of the I.M.A. (proposal 95-040). The cotype specimens are deposited in the Mineralogical Museum, Department of Mineralogy, St-Petersburg University, Russia under catalogue numbers 1/18303 (Khibina) and at the Canadian Museum of Nature, Ottawa, Ontario, Canada, under catalogue numbers CMNI 81531 (Khibina), CMNI 81532 (Mont Saint-Hilaire) and CMNI 81533 (Saint-Amable).

## Mineral occurrences

Kukharenkoite-(Ce) is known from two alkaline massifs, Khibina and Vuorijärvi, which belong to the Kola alkaline province, Russia and from the Mont Saint-Hilaire alkaline complex and the Saint-Amable nepheline syenite sill which belong to the Monteregian Hills province, Canada.

The Khibina massif, covering an area of approximately 1327 $km^2$, is the largest intrusive complex of peralkaline nepheline syenites and foidolites in the world. It contains a wide variety of magmatic and metasomatic rocks that range from ultrabasics (pyroxenite) through alkaline rocks (foyaite, urtite, ijolite) to carbonatites (Kukharenko *et al.*, 1971; Kogarko *et al.*, 1995; Zaitsev, 1996). The Khibina massif is also well-known for its unique mineralogy, where, together with the nearby Lovozero massif, approximately 500 mineral species are known to occur, 110 of which are new species (Britvin *et al.*, 1995; Khomyakov, 1995). Kukharenkoite-(Ce) was discovered in the late REE-rich manganoan ankerite and ferroan rhodochrosite-manganoan ankerite carbonatites and REE-rich manganoan siderite-manganoan ankerite-natrolite rocks which are associated with foyaite (KH 1, KH 2, KH 3 samples), albite rock associated with fenite (KH 4 sample) and aegirine-feldspar rock associated with ijolite-urtite (KH 5 sample). The specimens were collected either from underground or from drill core sections. A compilation of associated species from the various locations within the Khibina massif include synchysite-(Ce), ewaldite, cordylite-(Ce), mckelveyite-(Y), orthoclase, barite, pyrite, sphalerite and galena (REE-rich carbonatites and carbonate-zeolite rocks), fluorite, zircon, burbankite and mckelveyite-(Y) (albite rock), natrolite, belovite, nenadkevichite, fluorite, ancylite-(Ce), calcite and ewaldite (aegirine-feldspar rock).

Vuorijärvi (20 $km^2$) is not as well-known an alkaline massif as Khibina. It is characterized by a lesser degree of rock alkalinity than Khibina and contains mainly ultrabasic rocks (dunite, pyroxenite) and foidolites (ijolite, melteigite). Veins of phoscorites and carbonatites cross-cut ultrabasic and alkaline rocks and are widespread throughout the massif (Kukharenko *et al.*, 1965; Kogarko *et al.*, 1995). Kukharenkoite-(Ce) was found in the dolomite-calcite carbonatite (V 1 sample) and was collected from drill core. Associated species include: vaterite, alstonite, ancylite-(Ce), cordylite-(Ce), mckelveyite-(Y), fluorapatite and barite.

Mont Saint-Hilaire is a roughly circular alkaline intrusion approximately 3 km in diameter, which rises 350 m above the surrounding flat-

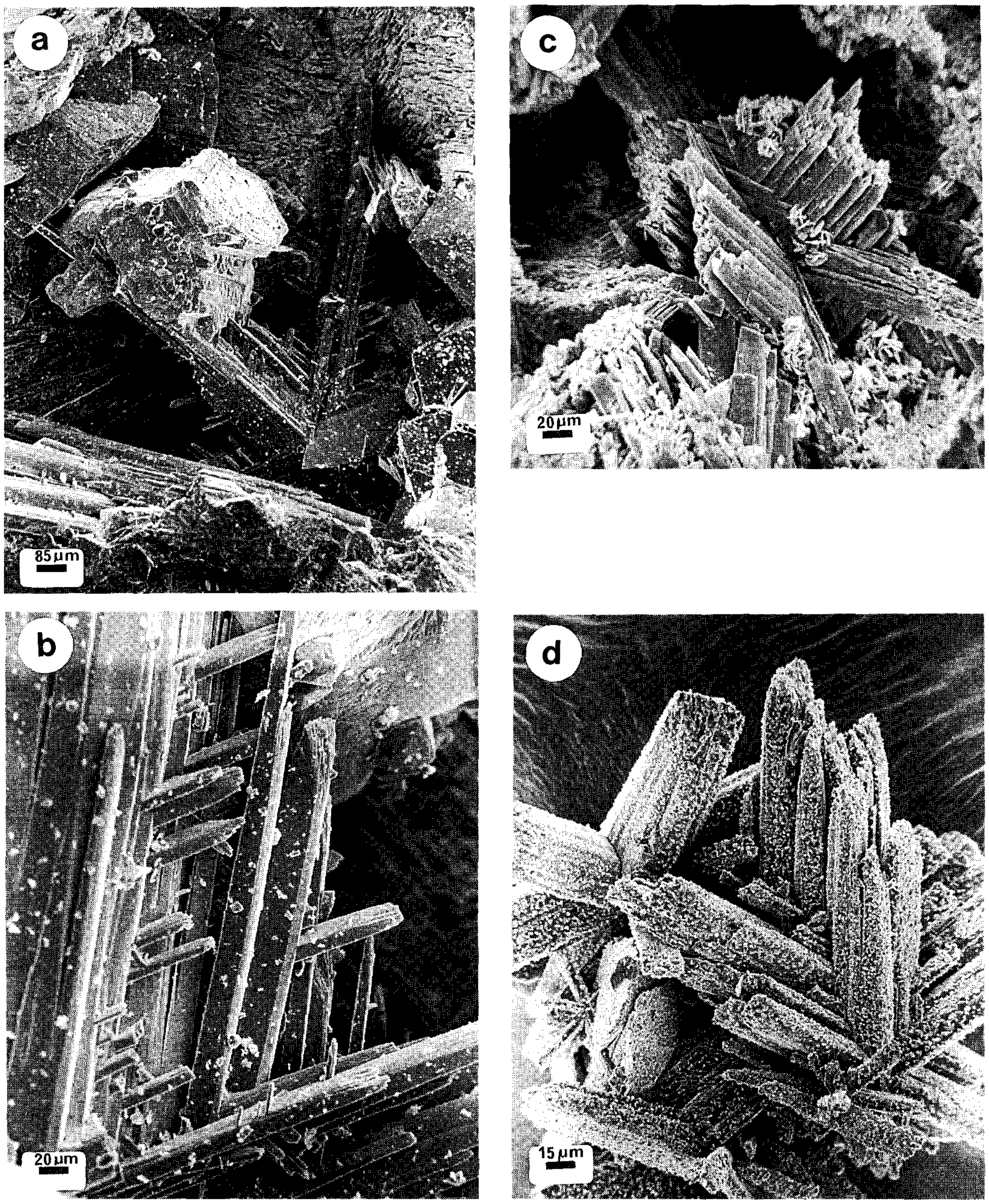


Fig. 1. Secondary electron images of kukharenkoite-(Ce) crystals. a - dendritic intergrowths (hexagonal crystal of ewaldite on left side of photograph), sample KH 1 (Khibina); b - detail of a; c - irregular intergrowths, sample KH 5 (Khibina); d - stellate intergrowths, sample V 1 (Vuoriyärvi).

lying Palaeozoic sedimentary rocks. The intrusion is Cretaceous in age and consists of 3 intrusions with different suites of igneous rocks ranging in composition from kaersutite-gabbro, to nepheline diorite and monzonite to peralkaline syenites, nepheline and sodalite syenites, phonolites and intrusive breccias (Currie *et al.*, 1986). A quarry on the east side of the mountain has exposed the most recent intrusion with nepheline syenite hosting pegmatitic veins, dykes and miarolitic cavities and numerous xenoliths of pre-existing igneous rock and hornfelsed sedimentary rock. It is from this quarry that over 300 mineral species have been identified, 29 of which are new species (Horváth & Gault, 1990). Kukharenkoite-(Ce) was found in thin seams in a hornfels xenolith associated with calcite, siderite, cordylite-(Ce), albite, quartz, pyrrhotite, pyrite and rutile (UK 65 sample).

The Saint-Amable alkaline sill is related to Mont Saint-Hilaire and other Cretaceous intrusions of the Monteregian Hills province. The sill, which is exposed by a large quarry, averages 15 m in thickness and forms at least part of a slightly elevated plateau approximately 100 $km^2$ in area. It consists mainly of fine-grained nepheline syenite with abundant natrolite. Tiny cavities in the syenite host a suite of some 100 minerals. Kukharenkoite-(Ce) occurs rarely as a late-stage mineral in the cavities, associated with microcline, natrolite, eudialyte, mangan-neptunite, aegirine, mosandrite, pyrite, zakharovite, yofortierite, låvenite, astrophyllite and calcite (VUK 12 sample).

## Physical properties

Kukharenkoite-(Ce) occurs as a late-stage mineral in tiny cavities. In Khibina, Vuorijärvi and Mont Saint-Hilaire it forms small (0.01-1 mm) prismatic crystals which are often in dendritic, stellate or irregular intergrowths up to 2-3 mm across (Fig. 1; KH 1, KH 4, KH 5, V 1 and UK 65 samples); rarely the mineral occurs as platy crystals (0.1-2 mm) or anhedral grains (0.05-0.2 mm in size), closely associated with manganoan siderite and natrolite (KH 2 and KH 3 samples). In Saint-Amable, kukharenkoite-(Ce) occurs as tapering, bladed crystals from 0.3 to 1 mm in length forming reticulated aggregates to 3 mm across or as fine needles forming fibrous aggregates (VUK 12 sample).

The mineral is yellow or reddish-brown (due to inclusions of Fe-bearing opaque phases) from Khibina and Vuorijärvi, and colourless to very pale white to silvery grey or pinkish grey from Mont Saint-Hilaire and Saint-Amable. The streak is white. It is transparent to translucent with a vitreous to greasy lustre, but the reddish-brown variety is opaque and earthy. Cleavage or parting were not observed. It is brittle with an uneven fracture. No fluorescence in long- or short-wave ultraviolet radiation was observed. The Mohs' hardness is about 4.5 and for KH 2 sample (platy crystals) micro-indentation: VHN load 25 g, mean 280(25) $kg/mm^2$, range 250-320 $kg/mm^2$ (22 measurements were made on a polished block using Mikromet II). The measured density, determined by the microburette method for KH 2 sample, is 4.7(1) $g/cm^3$, close to the values of 4.62-4.73 $g/cm^3$ calculated from empirical formulas and refined cell dimensions for KH 1, KH 5, UK 65 and VUK 12 samples. The mineral is soluble in HCl with effervescence.

The optical properties of kukharenkoite-(Ce) were determined in Na light (589 nm), using a spindle stage and crystals previously oriented by X-ray goniometry (Table 1).

Table 1. Optical properties for kukharenkoite-(Ce).

| Sample | KH 1 | KH 4 | UK-65 | VUK 12 |
|---|---|---|---|---|
| | biaxial (-) | | | |
| $\alpha$ | 1.584(1) | 1.586(3) | 1.594(1) | 1.593(1) |
| $\beta$ | 1.724(3) | not measured | 1.710(3) | ≈ 1.730 |
| $\gamma$ | 1.728(3) | 1.728(3) | 1.715(3) | ≈ 1.730 |
| $2V_{meas.}$ | 16(1)° | 10-20° | 16(1)° | 15(1)° |
| $2V_{calc.}$ | 18° | | 22° | |
| $Z \wedge c$ in obtuse $\beta$ | 26.5° | | 26.5° | 26.5° |
| | Y=b | | Y=b | Y=b |
| dispersion | | r > v, medium | | |

## Infra-red spectroscopy

The infrared-absorption spectrum of kukharenkoite-(Ce) was obtained utilizing a UR-20 Carl Zeiss spectrophotometer (Geological Institute, Apatity). About 2-3 mg of the mineral from KH 1, KH 2 and KH 5 samples, were ground and pressed into KBr pellets, and the infrared-absorption spectra were recorded over the region 400-3800 $cm^{-1}$. IR spectra obtained from the KH 1, KH 3 and KH 5 samples are identical in positions of absorption bands as well as in their intensities. The spectrum of kukharenkoite-(Ce) (Fig. 2) is characterised by strong absorption in the regions 675-745, 850-900, 1060-1100 and 1200-1600 $cm^{-1}$

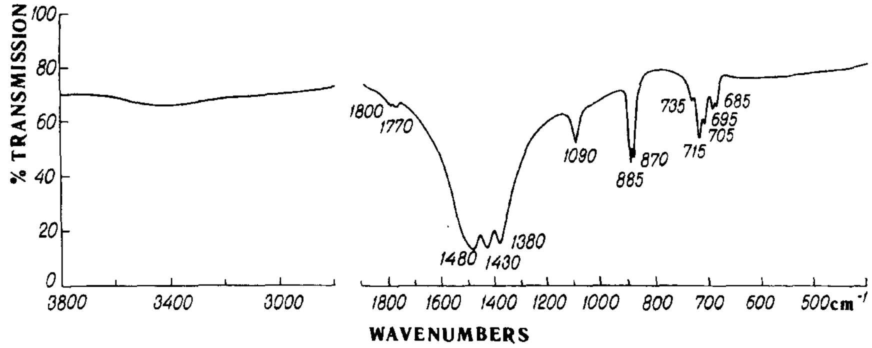


Fig. 2. Infra-red spectrum of kukharenkoite-(Ce).

which indicate that the mineral contains a carbonate group, but no OH or $H_2O$ groups (White, 1974).

The free anion $(CO_3)^{2-}$ has been known to have four normal IR-active vibration modes; in the infrared spectrum of the kukharenkoite-(Ce) the relevant wavenumbers have the following values: $\nu_4$ 685-695-705-715-735; $\nu_2$ 870-885; $\nu_1$ 1090; $\nu_3$ 1380-1430-1480 $cm^{-1}$. The splitting of the $\nu_3$ and $\nu_4$ vibration modes suggest the presence of at least two non-equivalent carbonate groups in the cell.

Table 2. Chemical composition of kukharenkoite-(Ce).

| Sample | KH1 | KH2 | KH3 | KH5 | UK 65 | VUK 12 |
|---|---|---|---|---|---|---|
| Number of analyses | 12 | 3 | 17 | 2 | 1 | 1 |
| $Na_2O$ | bd | bd | 0.08 | bd | 0.14 | bd |
| CaO | 0.39 | 0.06 | 0.05 | 0.43 | 0.38 | 0.06 |
| MnO | - | bd | 0.26 | - | - | - |
| FeO | - | 0.42 | bd | - | 0.10 | bd |
| SrO | 1.55 | 0.62 | 0.42 | 2.04 | 2.29 | 0.05 |
| BaO | 47.39 | 49.82 | 48.93 | 48.80 | 47.63 | 50.07 |
| $La_2O_3$ | 6.61 | 6.32 | 6.16 | 10.44 | 5.77 | 10.27 |
| $Ce_2O_3$ | 15.30 | 13.57 | 15.12 | 10.34 | 9.91 | 14.32 |
| $Pr_2O_3$ | 1.19 | 1.25 | 1.49 | bd | bd | 0.37 |
| $Nd_2O_3$ | 4.26 | 3.41 | 4.08 | 1.74 | 1.31 | 1.47 |
| $Sm_2O_3$ | bd | 0.11 | bd | bd | bd | bd |
| $Gd_2O_3$ | - | - | - | - | 0.20 | bd |
| $Y_2O_3$ | 0.15 | bd | bd | 0.72 | bd | bd |
| $ThO_2$ | - | 0.76 | 0.10 | - | 7.61 | bd |
| F | 3.18 | 2.98 | 3.20 | 3.05 | 3.31 | 3.14 |
| $CO_2$ | 21.95 | 21.57 | 21.73 | 21.17 | 20.72 | 21.45 |
| $-O=F_2$ | 1.34 | 1.25 | 1.35 | 1.28 | 1.39 | 1.32 |
| Total | 100.63 | 99.64 | 100.27 | 97.45 | 97.98 | 99.88 |

Structural formulas calculated on the basis of 3 atoms of C

| | |
|---|---|
| KH 1 | $(Ba_{1.86}Sr_{0.09}Ca_{0.04})_{\Sigma 1.99}(Ce_{0.56}La_{0.24}Nd_{0.15}Pr_{0.04}Y_{0.01})_{\Sigma 1.00}(CO_3)_3F_{1.01}$ |
| KH 2 | $(Ba_{1.99}Sr_{0.04})_{\Sigma 2.03}(Ce_{0.51}La_{0.24}Nd_{0.12}Pr_{0.05}Fe_{0.04}Th_{0.02}Ca_{0.01})_{\Sigma 0.99}(CO_3)_3F_{0.96}$ |
| KH 3 | $(Ba_{1.94}Sr_{0.03}Mn_{0.02}Ca_{0.01})_{\Sigma 2.00}(Ce_{0.56}La_{0.23}Nd_{0.15}Pr_{0.06})_{\Sigma 1.00}(CO_3)_3F_{1.02}$ |
| KH 5 | $(Ba_{1.99}Sr_{0.12})_{\Sigma 2.11}(La_{0.40}Ce_{0.39}Nd_{0.06}Ca_{0.05}Y_{0.04})_{\Sigma 0.94}(CO_3)_3F_{1.00}$ |
| UK 65 | $(Ba_{1.98}Sr_{0.14})_{\Sigma 2.12}(Ce_{0.38}La_{0.23}Th_{0.18}Nd_{0.05}Ca_{0.04}Na_{0.03}Gd_{0.01}Fe_{0.01})_{\Sigma 0.93}(CO_3)_3F_{1.11}$ |
| VUK 12 | $Ba_{2.01}(Ce_{0.54}La_{0.39}Nd_{0.05}Pr_{0.01}Ca_{0.01})_{\Sigma 1.00}(CO_3)_3F_{1.02}$ |

bd = below detection limit, - = not sought.

Table 3. X-ray powder diffraction data for kukharenkoite-(Ce).

| KH 1 | | | KH 5 | | | UK 65 | | | VUK 12 | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| I | $d_{meas.}$ | $d_{calc.}$ | I | $d_{meas.}$ | $d_{calc.}$ | I | $d_{meas.}$ | $d_{calc.}$ | I | $d_{meas.}$ | $d_{calc.}$ | hkl |
| 100 | 4.000 | 4.0052 | 90 | 4.000 | 3.9933 | 100 | 4.015 | 4.0129 | 100 | 3.995 | 3.9967 | $\bar{1}11$ |
| | | 4.0047 | | | 3.9932 | | | 4.0127 | | | 3.9966 | 201 |
| 100 | 3.269 | 3.2693 | 100 | 3.264 | 3.2604 | 100 | 3.273 | 3.2751 | 100 | 3.261 | 3.2627 | 310 |
| | | 3.2694 | | | 3.2597 | | | 3.2753 | | | 3.2624 | $\bar{2}02$ |
| | | 3.2682 | | | 3.2594 | | | 3.2735 | | | 3.2611 | $\bar{4}01$ |
| 20 | 2.535 | 2.5330 | 70 | 2.527 | 2.5260 | 20 | 2.539 | 2.5377 | 50 | 2.526 | 2.5282 | 020 |
| | | 2.5331 | | | 2.5257 | | | 2.5381 | | | 2.5280 | 112 |
| 40 | 2.140 | 2.1408 | 50 | 2.138 | 2.1348 | 40 | 2.143 | 2.1448 | 60 | 2.135 | 2.1366 | 221 |
| | | 2.1407 | | | 2.1344 | | | 2.1452 | | | 2.1364 | 003 |
| | | 2.1399 | | | 2.1339 | | | 2.1435 | | | 2.1353 | $\bar{5}12$ |
| | | 2.1398 | | | 2.1342 | | | 2.1436 | | | 2.1353 | 600 |
| 40 | 2.003 | 2.0024 | 60 | 1.997 | 1.9967 | 50 | 2.007 | 2.0064 | 80 | 1.998 | 1.9983 | 402 |
| | | 2.0021 | | | 1.9966 | | | 2.0059 | | | 1.9980 | 511 |
| | | 2.0024 | | | 1.9966 | | | 2.0060 | | | 1.9984 | $\bar{2}22$ |
| | | 2.0022 | | | 1.9963 | | | 2.0058 | | | 1.9980 | $\bar{3}13$ |
| | | 2.0021 | | | 1.9966 | | | 2.0056 | | | 1.9981 | $\bar{4}21$ |
| 5 | 1.790 | 1.7903 | 30 | 1.783 | 1.7852 | 10 | 1.792 | 1.7933 | 10 | 1.786 | 1.7864 | $\bar{6}03$ |
| | | 1.7902 | | | 1.7855 | | | 1.7933 | | | 1.7865 | $\bar{7}11$ |
| 10 | 1.635 | 1.6350 | 30 | 1.631 | 1.6305 | 30 | 1.637 | 1.6380 | 20 | 1.631 | 1.6319 | $\bar{1}31$ |
| | | 1.6346 | | | 1.6302 | | | 1.6376 | | | 1.6313 | 620 |
| | | 1.6351 | | | 1.6304 | | | 1.6384 | | | 1.6318 | 313 |
| | | 1.6341 | | | 1.6297 | | | 1.6368 | | | 1.6306 | $\bar{8}02$ |
| | | 1.6347 | | | 1.6299 | | | 1.6377 | | | 1.6312 | $\bar{4}04$ |
| 5 | 1.571 | 1.5709 | 20 | 1.571 | 1.5662 | 10 | 1.574 | 1.5740 | 10 | 1.568 | 1.5677 | $\bar{1}14$ |
| | | 1.5708 | | | 1.5664 | | | 1.5739 | | | 1.5677 | 422 |
| 10 | 1.373 | 1.3732 | 25 | 1.369 | 1.3694 | 20 | 1.376 | 1.3755 | 20 | 1.369 | 1.3703 | $\bar{8}22$ |
| | | 1.3732 | | | 1.3693 | | | 1.3755 | | | 1.3702 | $\bar{7}14$ |
| | | 1.3732 | | | 1.3695 | | | 1.3756 | | | 1.3703 | 910 |
| | | 1.3735 | | | 1.3697 | | | 1.3759 | | | 1.3707 | $\bar{5}32$ |
| | | 1.3735 | | | 1.3695 | | | 1.3760 | | | 1.3707 | $\bar{4}24$ |
| | | 1.3735 | | | 1.3697 | | | 1.3761 | | | 1.3707 | 712 |
| | | | 15 | 1.330 | 1.3307 | | | | | | | $\bar{10}.01$ |
| | | | | | 1.3311 | | | | | | | $\bar{3}33$ |
| | | | | | 1.3311 | | | | | | | 603 |
| | | | | | 1.3309 | | | | | | | $\bar{2}05$ |
| | | | | | 1.3312 | | | | | | | $\bar{5}31$ |
| | | | | | 1.3307 | | | | | | | $\bar{9}13$ |
| | | | 10 | 1.263 | 1.2627 | | | | | | | $\bar{7}31$ |
| | | | | | 1.2628 | | | | | | | 821 |
| | | | | | 1.2625 | | | | | | | $\bar{5}15$ |
| | | | | | 1.2629 | | | | | | | 224 |
| | | | | | 1.2630 | | | | | | | 040 |
| | | | 5 | 1.208 | 1.2076 | | | | | | | $\bar{11}.01$ |
| | | | | | 1.2080 | | | | | | | $\bar{3}41$ |

## Chemical composition

Both energy- and wavelength-dispersion analyses of kukharenkoite-(Ce) were made using a Cameca MS-46 electron microprobe at 20 kV and 20 nA (Geological Institute, Apatity), a JEOL 733 Superprobe with Tracor-Northern automation at 15 kV, 20 nA and 30 μm beam (Canadian Museum of Nature, Ottawa) and a Cameca SX 50 electron microprobe at 15 kV, 10 nA and 20 μm beam (The Natural History Museum, London). The following standards were used: lorenzenite (Na), diopside (Ca), celestine (Sr), barite (Ba), synthetic phases (La,Ce)S (La, Ce), $LiPr(WO_4)_2$ (Pr), $LiNd(MoO_4)_2$ (Nd), $LiSm(MoO_4)_2$ (Sm), $YAl_5O_{13}$ (Y) and $ThO_2$ (Th) (Geological Institute, Apatity); vlasovite (Na), calcite and gehlenite (Ca), celestine (Sr), sanbornite and barite (Ba), synthetic phases $LaPO_4$ (La), $CePO_4$ (Ce), $PrPO_4$ (Pr), $NdPO_4$ (Nd), $GdPO_4$(Gd), $BaFe_{12}O_{19}$ (Fe), LiF and synthetic $LaCO_3F$ (F) and $ThO_2$ (Th) (Canadian Museum of Nature, Ottawa); jadeite (Na), apatite (Ca), celestine (Sr), synthetic calcium aluminium silicate glasses obtained from the University of Edinburgh (REE), pure Mn (Mn), Fe (Fe), Th (Th) and $BaF_2$ (Ba, F) (The Natural History Museum, London). F determinations in the Khibina KH 1, KH 2 and KH 5 samples were made by wet micro-chemical analysis and confirmed by microprobe. It was unfortunately not possible to obtain enough material for direct determination of $CO_2$ content.

The analytical results are given in Table 2. They show that kukharenkoite-(Ce) contains Ba, REE and F as major elements and Sr, Ca, Th and Fe as minor elements. An exception to this is the mineral from Mont Saint-Hilaire which is characterized by a high Th content (7.61 wt.% $ThO_2$). The atomic ratios of Ba, REE and F are near 2:1:1, which requires 3 $(CO_3)^{2-}$ groups per formula unit. Calculated empirical formulas (Table 2) suggest that the ideal formula for the mineral is $Ba_2REE(CO_3)_3F$.

The mineral is strongly light-REE-enriched with Ce as a dominant element and Y content near the detection limit. For the mineral from the aegirine-feldspar rock (KH 5 sample) it is established that both La and Ce are present in similar amounts, atomic proportions being 0.40 for La and 0.39 for Ce. However, having taken into account the imprecision of the high overlap correction for Ba on Ce we conclude that the mineral from this sample cannot be designated as 'kukharenkoite-(La)'.

Using the Gladstone-Dale constants (Mandarino, 1976) and the analysis for KH 1, 1-(Kp/Kc) = 0.001, which indicates superior compatibility between the chemical and physical data.

## X-ray crystallography

Precession X-ray studies of crystals from KH 1, KH 5 and UK 65 samples show that kukharenkoite-(Ce) belongs to the monoclinic system with space group $P2_1/m$ or $P2_1$. Structural analysis of synthetic $Ba_2Ce(CO_3)_3F$ (Mercier & Leblanc, 1993b) confirmed the space group $P2_1/m$.

The cell parameters for both KH 1 and UK 65 samples were obtained from precession photographs and then refined by the least-squares method using powder diffraction lines (Gandolfi 114.6 mm camera, filtered Cu$K\alpha$ radiation). Indexing was based on precession photographs, using only strong reflections. Cell parameters for the KH 5 sample were refined by the least-squares method using DRON powder diffraction lines (DRON 2.0 diffractometer, filtered Cu$K\alpha$ radiation) and those for VUK 12 sample were refined from powder data. X-ray powder diffraction data and unit cell parameters for kukharenkoite-(Ce) are given in Table 3 and Table 4 respectively.

Table 4. Crystallographic data for kukharenkoite-(Ce).

| Sample | KH 1 | KH 5 | UK 65 | VUK 12 |
|---|---|---|---|---|
| Crystal system | monoclinic | | | |
| Space group | $P2_1/m$ | | | |
| a, Å | 13.396(7) | 13.360(9) | 13.418(9) | 13.367(9) |
| b, Å | 5.067(1) | 5.052(1) | 5.077(1) | 5.056(1) |
| c, Å | 6.701(1) | 6.681(2) | 6.714(2) | 6.687(2) |
| β, ° | 106.58(1) | 106.58(2) | 106.56(2) | 106.57(2) |
| V, Å$^3$ | 435.8(3) | 432.2(4) | 438.3(4) | 433.2(5) |
| Z | 2 | 2 | 2 | 2 |
| $D_{calc.}$, g/cm$^3$ | 4.62 | 4.67 | 4.73 | 4.71 |

The crystallographic data for kukharenkoite-(Ce) are similar to those for the synthetic phase $Ba_2Ce(CO_3)_3F$, prepared by hydrothermal growth at T = 750°C and P = 200 MPa for 30 hours (Mercier & Leblanc, 1993a and b). The data for synthetic $Ba_2Ce(CO_3)_3F$ are included in Table 5 for comparison. The structure of synthetic $Ba_2Ce(CO_3)_3F$ has been solved by Mercier & Leblanc (1993b) ($R$ = 0.019, $R$w = 0.021) and it consists of $CeO_9F$, $BaO_{11}$ and $BaO_7F_3$ coordination polyhedra. The cerium polyhedra form infinite isolated chains parallel to the **b**-axis. The barium polyhedra form double chains along [010] and these double chains form infinite layers parallel to the (100) plane.

## Discussion

The Ba-REE fluorocarbonates include the following four minerals: *the new species* and subject of this report, *kukharenkoite-(Ce)*, $Ba_2Ce(CO_3)_3F$, *huanghoite-(Ce)*, $BaCe(CO_3)_2F$ (Semenov & Zhang, 1961; Kapustin, 1973; Yang & Pertlik, 1993), *cordylite-(Ce)*, $BaCe_2(CO_3)_3F_2$ (Flink, 1901; Chen & Chao, 1975) and *cebaite-(Ce)*, $Ba_3Ce_2(CO_3)_5F_2$ (Zhang & Tao, 1983; Dunn *et al.*, 1985; Yang, 1995). Three other reported Ba-REE fluorocarbonate phases are not accepted by IMA: "*zhonghuacerite-(Ce)*" (Zhang & Tao, 1981, 1986), although published, was never submitted to IMA and important discrepancies were noted by Fleischer *et al.* (1982); "*cebaite-(Nd)*" was found to equal cebaite-(Ce) (Jambor *et al.*, 1988); "*baiyuneboite-(Ce)*" (Fu *et al.*, 1987; Fu & Su, 1988) was rescinded before its publication,

Table 5. Comparison of data for kukharenkoite-(Ce), "zhonghuacerite-(Ce)" and synthetic $Ba_2Ce(CO_3)_3F$.

| | Kukharenkoite-(Ce) Khibina | "Zhonghuacerite-(Ce)"* Bayan-Obo | Synthetic** |
|---|---|---|---|
| Formula | $Ba_2(Ce,La)(CO_3)_3F$ | $Ba_2(Ce,La)(CO_3)_3F$ | $Ba_2Ce(CO_3)_3F$ |
| Crystallography | monoclinic | trigonal | monoclinic |
| Space group | $P2_1/m$ | | $P2_1/m$ |
| Parameters | | | |
| a, Å | 13.396 | 5.07 | 13.365 |
| b, Å | 5.067 | | 5.097 |
| c, Å | 6.701 | 9.82 | 6.638 |
| β,° | 106.58 | | 106.45 |
| V, Å$^3$ | 435.8 | 218.6 | 433.5 |
| Z | 2 | 1 | 2 |
| Strongest lines in the powder pattern, $d_{meas}$(I) | 4.000 (100), 3.269 (100), 2.535 (20), 2.140 (40), 2.003 (40) | 3.92 (8), 3.419 (4), 3.216 (10), 2.512 (6), 2.123 (3), 2.103 (10), 1.979 (10), 1.638 (3), 1.572 (3) | |
| Physical properties | | | |
| Colour | yellow | pale yellowish | |
| Lustre | vitreous | vitreous or greasy | |
| $D_{meas.}$, g/cm$^3$ | 4.7 | 4.20-4.40 | |
| $D_{calc.}$, g/cm$^3$ | 4.62 | 4.66 | 4.702 |
| Hardness (Mohs) | 4.5 | 4.6 | |
| VHN | 280 | 289-309 | |
| Optical data | | | |
| | Biaxial (-) | Unaxial (-) | |
| | α 1.584 | ε 1.568 | |
| | β 1.724 | | |
| | γ 1.728 | ω 1.745 | |
| | $2V_{meas.}$ 16° | | |
| | $2V_{calc.}$ 18° | | |

* Zhang & Tao (1981). ** Mercier & Leblanc (1993a).

after it was found to equal cordylite-(Ce) whose original formula was incorrect (Jambor & Grew, 1990). A corrected formula for cordylite-(Ce), which contains essential Na, is not reported here pending a redefinition of the mineral (J. Zemann, pers. comm., 1996). Although there are a number of publications describing Ba-REE fluorocarbonate minerals, some mineral data (physical properties, chemical composition, X-ray diffraction data) are, however, often incomplete and sometimes inconsistent.

Kukharenkoite-(Ce) has a very strong rhombohedral subcell ($a'$ = 5.076(1), $c'$ = 9.821(9) Å for UK-65) which is very close to the subcell of cebaite-(Ce) ($a'$ = 5.071, $c'$ = 9.740 Å) and huanghoite-(Ce) ($a'$ = 5.026, $c'$ = 9.747 Å; Peng & Shen, 1980). As only the strong sublattice reflections are recordable by the powder diffraction method, the powder pattern of kukharenkoite-(Ce), cebaite-(Ce) and huanghoite-(Ce) are therefore similar. This suggests a strong structural relationship among the three species which was discussed by Mercier & Leblanc (1993b).

"Zhonghuacerite-(Ce)" was described and published (Zhang & Tao, 1981, 1986; Fleischer *et al.*, 1982) without approval of CNMMN of the IMA. The mineral was originally described as trigonal and uniaxial (-) (Table 5) and later revised as trigonal with a monoclinic superstructure and optically biaxial (-) with small 2V = 5°, α 1.565, β 1.732 and γ 1.745 (Zhang & Tao, 1986). "Zhonghuacerite-(Ce)" is almost certainly identical with kukharenkoite-(Ce). Unfortunately, we did not have any possibility of studying "zhonghuacerite-(Ce)" from Bayan Obo, because all the available material was used for previous investigations (P. Zhang, pers. comm. to A. Zaitsev, 1992).

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