THE CRYSTAL STRUCTURE OF KUKHARENKOITE-(Ce), Ba$_2$*REE*(CO$_3$)$_3$F, AND AN INTERPRETATION BASED ON CATION-COORDINATED F TETRAHEDRA

SERGEY V. KRIVOVICHEV* AND STANISLAV K. FILATOV

Department of Crystallography, St. Petersburg University, University Emb. 7/9, St. Petersburg 199034, Russia

ANATOLY N. ZAITSEV

Department of Mineralogy, St. Petersburg University, University Emb. 7/9, St. Petersburg 199034, Russia

ABSTRACT

The crystal structure of kukharenkoite-(Ce), Ba$_2$*REE*(CO$_3$)$_3$F, from the Khibina carbonatite, Kola Peninsula, Russia, has been refined to $R = 0.044$ ($wR = 0.112$) using 2296 reflections. The mineral is monoclinic, space group $P2_1/m$, with a 13.374(3), b 5.1011(8), c 6.653(1) Å, ß 106.56(1)°, V 435.1(1) Å^3, $Z = 2$. The structure is similar to that determined by Mercier & Leblanc (1993) for synthetic Ba$_2$Ce(CO$_3$)$_3$F. The F$^-$ anion is tetrahedrally coordinated by three Ba and one Ce cations. F-centered [FCeBa$_3$] tetrahedra are linked through shared edges to form double chains {**uB**, 2$_\infty^1$}[FCeBa] along the b axis. C(3)O$_3$ carbonate groups are positioned on the faces of the [FCeBa$_3$] tetrahedra, resulting in complex [FCeBa](CO$_3$) chains. These chains are positioned in sheets parallel to (001) (layer A) and alternating along [001] with sheets formed by C(1)O$_3$ and C(2)O$_3$ groups and Ba atoms that do not bond with fluorine (layer B). The structures of other fluorocarbonates with fluorine-centered tetrahedra contain the following tetrahedral complexes: double chains {**uB**, 2$_\infty^1$} [F$_2$$M_5$] in cebaite-(Ce), Ba$_3Ce_2$(CO$_3$)$_5F_2$, and Ba$_3La_2$(CO$_3$)$_5F_2$, layers {**uB**, 1$_\infty^2$}[F$_2$$M_3$] in huanghoite-(Ce), BaCe(CO$_3$)$_2$F, and BaSm(CO$_3$)$_2$F, layers {**uB**, 1$_\infty^2$}[FM] in kettnerite, CaBiOF(CO$_3$), frameworks {$_\infty^3$}[FM] in brenkite, Ca$_2$F$_2$(CO$_3$), and Pb$_2$F$_2$(CO$_3$), frameworks {$_\infty^3$}[FM] in BaCu(CO$_3$)$_2$F$_2$, and frameworks {$_\infty^3$}[FM_4] in horváthite-(Y), NaY(CO$_3$)F$_2$. Topologically similar structural units composed of [OM_4] tetrahedra have been described in oxysalts with "additional" oxygen atoms.

Keywords: kukharenkoite-(Ce), fluorocarbonate, Khibina, crystal structure, fluorine-centered tetrahedra.

SOMMAIRE

Nous avons affiné la structure cristalline de la kukharenkoite-(Ce), Ba$_2$*TR*(CO$_3$)$_3$F (*TR*: terres rares) provenant d'une carbonatite du complexe de Khibina, dans la péninsule de Kola, en Russie, jusqu'à un résidu R de 0.044 ($wR = 0.112$) en utilisant 2296 réflexions. Il s'agit d'un minéral monoclinique, groupe spatial $P2_1/m$, a 13.374(3), b 5.1011(8), c 6.653(1) Å, ß 106.56(1)°, V 435.1(1) Å^3, $Z = 2$. La structure ressemble à celle qu'ont déterminé Mercier et Leblanc (1993) pour le composé synthétique Ba$_2$Ce(CO$_3$)$_3$F. L'anion F$^-$ est en coordinence tétraédrique avec trois atomes de Ba et un de Ce. Des tétraèdres [FCeBa$_3$] sont liés par arêtes partagées pour former des chaînes doubles {**uB**, 2$_\infty^1$}[FCeBa] le long de l'axe b. Des groupes C(3)O$_3$ sont disposés sur les faces de ces tétraèdres pour donner des chaînes complexes de stoechiométrie [FCeBa](CO$_3$). Ces chaînes sont disposées en feuillets parallèles à (001) (couche A) et alternent le long de [001] avec des feuillets formés de groupes C(1)O$_3$ et C(2)O$_3$ et d'atomes de Ba non liés au fluor (couche B). Les structures d'autres fluorocarbonates contenant des tétraèdres centrés sur le fluor contiennent les complexes tétraédriques suivants: des chaînes doubles {**uB**, 2$_\infty^1$}[F$_2$$M_5$] dans la cébaïte-(Ce), Ba$_3$Ce$_2$(CO$_3$)$_5$F$_2$, et Ba$_3$La$_2$(CO$_3$)$_5$F$_2$, des couches {**uB**, 1$_\infty^2$}[F$_2$$M_3$] dans la huanghoite-(Ce), BaCe(CO$_3$)$_2$F, et BaSm(CO$_3$)$_2$F, des couches {**uB**, 1$_\infty^2$}[FM] dans la kettnerite, CaBiOF(CO$_3$), des trames {$_\infty^3$}[FM] dans la brenkite, Ca$_2$F$_2$(CO$_3$), et Pb$_2$F$_2$(CO$_3$), des trames {$_\infty^3$}[FM] dans le composé BaCu(CO$_3$)$_2$F$_2$, et des trames {$_\infty^3$}[FM_4] dans la horváthite-(Y), NaY(CO$_3$)F$_2$. Des modules structuraux topologiquement semblables composés de tétraèdres [OM_4] ont été décrits dans les oxysels contenant des atomes d'oxygène "additionnels".

Mots-clés: kukharenkoite-(Ce), fluorocarbonate, Khibina, structure cristalline, tétraèdres centrés sur le fluor.

* To whom correspondence should be addressed. *E-mail address:* flt@cryst.geol.pu.ru

INTRODUCTION

The new mineral kukharenkoite-(Ce) has been described recently from a number of localities, including the Khibina and Vuorijärvi massifs, Kola Peninsula, Russia and the Mont Saint-Hilaire and Saint-Amable massifs, Quebec (Zaitsev *et al.* 1996). It is a Ba–*REE* fluorocarbonate with the formula Ba$_2$*REE*(CO$_3$)$_3$F, where Ce is the dominant rare-earth element (*REE*). Here, we report on the crystal structure of this species.

The kukharenkoite-(Ce) crystal used for structure analysis was taken from manganoan ankerite carbonatite (Khibina) and referred to as sample KH 1 in Zaitsev *et al.* (1996). Kukharenkoite-(Ce) occurs as yellow, prismatic crystals to 1 mm in length, which commonly occur in dendritic intergrowths. An electron-microprobe analysis of the mineral yields the empirical formula (Ba$_{1.86}$Sr$_{0.09}$Ca$_{0.04}$)$_{\Sigma1.99}$(Ce$_{0.56}$La$_{0.24}$Nd$_{0.15}$Pr$_{0.04}$Y$_{0.01}$)$_{\Sigma1.00}$(CO$_3$)$_3$F$_{1.01}$.

On the basis of its chemistry, it was originally described as "zhonghuacerite-(Ce)". The latter was described and published (Zhang & Tao 1981, 1986, Fleischer *et al.* 1982) without approval of CNMMN of the IMA. The crystallographic data for kukharenkoite-(Ce) were found to be similar to those for the synthetic phase Ba$_2$Ce(CO$_3$)$_3$F, prepared by hydrothermal growth at 750°C and 200 MPa (Mercier & Leblanc 1993b).

EXPERIMENTAL

The single crystal used for collection of the X-ray-diffraction data is an elongate plate measuring $0.05 \times 0.1 \times 0.4$ mm^3. It was first examined by Laue and oscillation methods using CuKα radiation. Intensities were collected on an automated four-circle Syntex P2$_1$ diffractometer (details in Table 1). Integral intensities were measured by ω–2θ scan and were converted to structure factors by applying Lorentz and polarization corrections using the AREN package of

crystallographic programs (Andrianov 1987). Using the initial parameters of the structure given for synthetic Ba$_2$Ce(CO$_3$)$_3$F by Mercier & Leblanc (1993b), the structure was refined to $R = 0.044$ ($wR = 0.112$) by means of the SHELXL–93 program (Sheldrick 1993). The absorption correction was done using DIFABS (Walker & Stuart 1983). Fractional atomic coordinates and displacement parameters are given in Table 2, and selected interatomic distances and angles in Table 3. These values are in good agreement with those of

TABLE 2. FRACTIONAL ATOMIC COORDINATES AND DISPLACEMENT PARAMETERS (Å^2) FOR KUKHARENKOITE-(Ce)

Atom	x	y	z	U$_{eq}$	U$_{11}$	U$_{22}$	U$_{33}$	U$_{23}$	U$_{13}$	U$_{12}$
								U$_{ij}$ (× 10^{-4})		
Ba1	0.07490(4)	0.25	0.2900(1)	0.0175(1)	181	172	168	0	42	0
Ba2	0.41615(4)	0.25	0.6888(1)	0.0170(1)	206	142	152	0	34	0
Ce	0.76096(4)	0.25	0.9884(1)	0.0146(1)	177	113	142	0	36	0
F	0.9283(5)	0.25	0.911(1)	0.027(1)	320	240	230	0	40	0
C1	0.7259(7)	0.25	0.509(1)	0.018(1)	200	120	210	0	0	0
C2	0.4268(7)	0.25	0.174(1)	0.019(2)	240	120	220	0	90	0
C3	0.1273(7)	0.25	0.794(1)	0.019(1)	190	220	160	0	40	0
O1	0.1826(6)	0.25	0.991(1)	0.025(1)	370	200	130	0	10	0
O2	0.6996(7)	0.25	0.310(1)	0.030(1)	380	380	140	0	70	0
O3	0.4899(6)	0.25	0.358(1)	0.024(1)	320	210	170	0	30	0
O4	0.3993(4)	0.031(1)	0.077(1)	0.026(1)	300	190	290	–50	90	–30
O5	0.2625(4)	0.965(1)	0.386(1)	0.026(1)	320	140	270	30	0	0
O6	0.8969(4)	0.970(1)	0.300(1)	0.025(1)	370	150	220	–40	40	–50

$U_{eq} = (1/3)\Sigma_i\Sigma_j U_{ij} a_i^* a_j^* \mathbf{a}_i \mathbf{a}_j$

TABLE 3. SELECTED INTERATOMIC DISTANCES (Å) AND ANGLES (°) IN KUKHARENKOITE-(Ce)

Ba1 – F	2.717(6)	Ba2 – O3	2.659(6)	Ce – F	2.434(7)
– O1	2.769(8)	– O5 2×	2.835(5)	– O2	2.503(7)
– O6 2×	2.793(5)	– O4 2×	2.883(5)	– O4 2×	2.511(5)
– O5 2×	2.811(5)	– O4 2×	2.894(6)	– O1 2×	2.652(2)
– O6 2×	2.873(5)	– O3 2×	2.898(4)	– O5 2×	2.657(5)
– F 2×	2.875(3)	– O2 2×	2.984(5)	– O6 2×	2.738(5)

C1 – O2	1.27(1)	C2 – O3	1.27(1)	C3 – O1	1.31(1)
– O5 2×	1.284(7)	– O4 2×	1.291(7)	– O6 2×	1.282(6)
O2 – C1 – O5		O3 – C2 – O4		O1 – C3 – O6	
	2× 121.4(4)		2× 119.8(4)		2× 118.8(4)
O5 – C1– O5		O4 – C2 – O4		O6 – C3 – O6	
	117.2(8)		120.1(9)		122.2(8)

F – Ce		Ce – F – Ba1^a		Ba1^a – F – Ba1^b	
	2.434(7)		105.6(2)		2× 110.0(1)
– Ba1^a		Ce – F – Ba1^b		Ba1^b – F – Ba1^b	
	2.717(6)		2× 101.9(2)		125.0(2)
– Ba1^b		<M – F – M>			
	2× 2.875(3)		109.1		

TABLE 1. DETAILS OF THE CRYSTAL DATA, X-RAY DATA COLLECTION, AND THE STRUCTURE REFINEMENT: KUKHARENKOITE-(Ce)

Chemical formula	Ba$_2$Ce(CO$_3$)$_3$F	Diffractometer	Syntex P2$_1$
Formula weight	613.83 g.mol^{-1}	Scan mode	ω – 2θ
Crystal system	Monoclinic	Independent	
Space group; Z	P2$_1$/m; 2	reflections	2321
Unit-cell constants	a 13.374(3) Å	Observed reflections	
at 293(2) K	b 5.1011(8) Å	[I > 2σ(I)]	2296
	c 6.653(1) Å	Index ranges	–27 ≤ h ≤ 26
	β 106.56(1)°		0 ≤ k ≤ 10
			0 ≤ l ≤ 14
Unit-cell volume	435.1(1) Å^3		
Density (calculated)	4.69 g cm^{-3}	Range of 2θ	1.5 – 64.0°
Radiation	MoKα (λ =	μ	14.150 mm^{-1}
	0.71069 Å)	R(F)	0.044
		wR(F^2)	0.112
		Goodness-of-fit S	1.134
		Parameters refined	89
		Δρ$_{min}$, Δρ$_{max}$	–2.67, 3.72 e Å^{-3}

Mercier & Leblanc (1993b). A table of observed and calculated structure-factors is available from the Depository of Unpublished Data, CISTI, National Research Council of Canada, Ottawa, Ontario K1A 0S2, Canada.

DISCUSSION

Cation coordination

The structure of synthetic Ba$_2$Ce(CO$_3$)$_3$F from the perspective of Ba and *REE* coordination was described in detail by Mercier & Leblanc (1993b) [see also recent reviews of fluorocarbonates by Mercier & Leblanc (1997) and Yang *et al.* (1996)]. Two distinct Ba polyhedra [Ba(1)O$_7$F$_3$ and Ba(2)O$_{11}$] and one *REE*O$_9$F polyhedron are present. The three CO$_3$ groups have the usual values of bond lengths and bond angles.

Fluorine coordination

As part of our continuing research into the coordination of "additional" anions in inorganic compounds and their crystal-chemical role in structural hierarchies (Filatov *et al.* 1992, Krivovichev *et al.* 1998), we consider here the coordination of fluorine in kukharenkoite-(Ce). There is one F$^-$ tetrahedrally coordinated by three Ba atoms and one *REE* atom, forming a [FCeBa$_3$] tetrahedron. Each [FCeBa$_3$] tetrahedron shares two Ba–Ba edges with two others, so that infinite chains along [010] are formed (Fig. 1). Using terminology developed by Liebau (1985) for silicates and reconsidered

FIG. 1. Fluorine-centered chains in kukharenkoite-(Ce) in "ball-and-stick" (*a*) and polyhedral (*b*) representations. C(3)O$_3$ groups are attached to the bases of [FCeBa$_3$] tetrahedra.

for structures based on the edge- and face-sharing tetrahedral polyions by Krivovichev *et al.* (1997) and Krivovichev (1997), we can describe these as unbranched double *einer* chains {**uB**, 2$_\infty^1$} [FBaCe] composed of topologically and configurationally distinct tetrahedra. In Figure 1, this chain is shown in both "ball and stick" (*a*) and polyhedral (*b*) representations.

The chains {**uB**, 2$_\infty^1$}[FCeBa] composed of fluorine-centered tetrahedra are parallel to the *b* axis (Fig. 2). The C(3)O$_3$ groups are positioned on the bases of [FCeBa$_3$] tetrahedra [Ba – O = 2.793 (2×), 2.769 Å], so that a complex chain {$_\infty^1$}[FCeBa](CO$_3$) is formed along [010]. The "face-to-face" relationships between anion-centered tetrahedra and cation-centered tetrahedral or triangular groups [(VO$_4$), (SO$_4$), (SeO$_3$), *etc.*] have commonly been observed in structures based on the oxygen-centered tetrahedra [O*M*$_4$] (*e.g.*, Starova *et al.* 1997). The {$_\infty^1$}[FCeBa](CO$_3$) chains lie in the (001) plane forming the **A** layers (Fig. 2). These layers are subdivided by the **B** layers composed of groups of C(1)O$_3$, C(2)O$_3$ and Ba(2) atoms, which do not bond with fluorine. The **A** and **B** layers are linked through Ce–O bonds. If we consider the kukharenkoite-(Ce) structure in light of the bond-valence theory, layers **A** and **B** represent the principal structural units, linked by strong Ce–O bonds.

It should be emphasized that the chains of F-centered polyhedra are not the strongest structural units because of the relatively weak Ba–F bonds (Mercier & Leblanc 1993b), such that their contribution to the topology of chemical bonds is relatively minor. However, the role of F$^-$ bonding in structural organization cannot be ignored because of the concentration of bonds around the fluorine-centered chains. In addition, F-centered complexes exist in gaseous and liquid phases. Pb$_2$F$^+$ complexes in melts were investigated by Bengtsson & Holmberg (1989a, b, c) using X-ray scattering and Raman spectroscopy (F–Pb in the range 2.03–2.56 Å, Pb–F–Pb in the range 81–84°). Bengtsson & Holmberg (1989a) also discussed [FPb$_4$]$^{7+}$ tetrahedra in solids. In molten nitrate media, Ba$_2$F^{3+} and Sr$_2$F^{3+} complexes were encountered by Bengtsson *et al.* (1991) (Ba–Ba in the range 4.1–4.3 Å, Ba–F–Ba = 107°), Bi$_2$F^{5+}, by Frostemark *et al.* (1994a), and Mg$_2$F^{3+}, by Frostemark *et al.* (1994b).

Fluorine-centered tetrahedra in fluorocarbonates

There are a number of fluorocarbonates containing tetrahedrally coordinated F$^-$ ions. These fluorine-centered tetrahedra show seven types of polyions based on the [F*M*$_4$] groups (Figs. 3, 4, Table 4). In Table 4, their crystal-chemical formulae are given in the form: {**B**, **M**$_\infty^D$}[F$_n$*M*$_m$], where **B**, **M** and **D** are branchedness, multiplicity and dimensionality, respectively; for details, see Liebau (1985) and Krivovichev *et al.* (1997). In
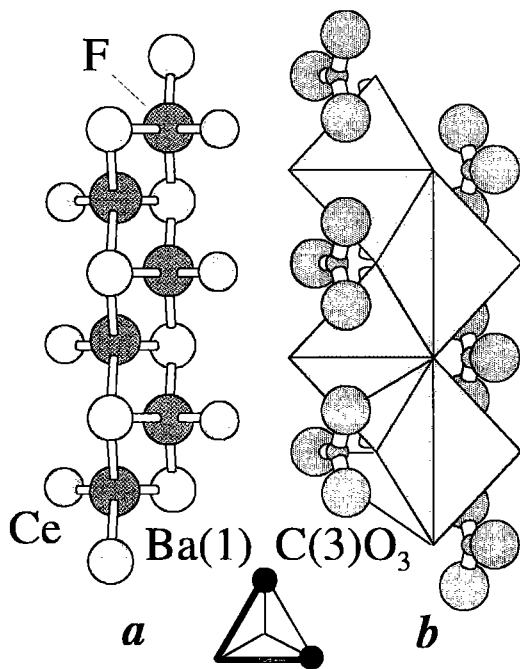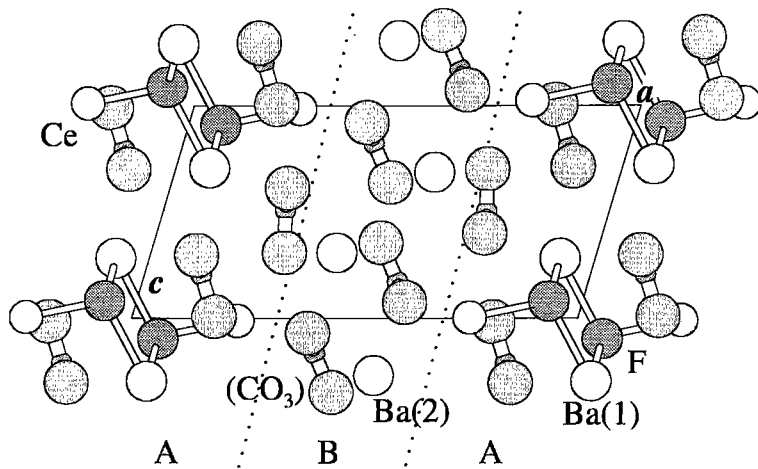
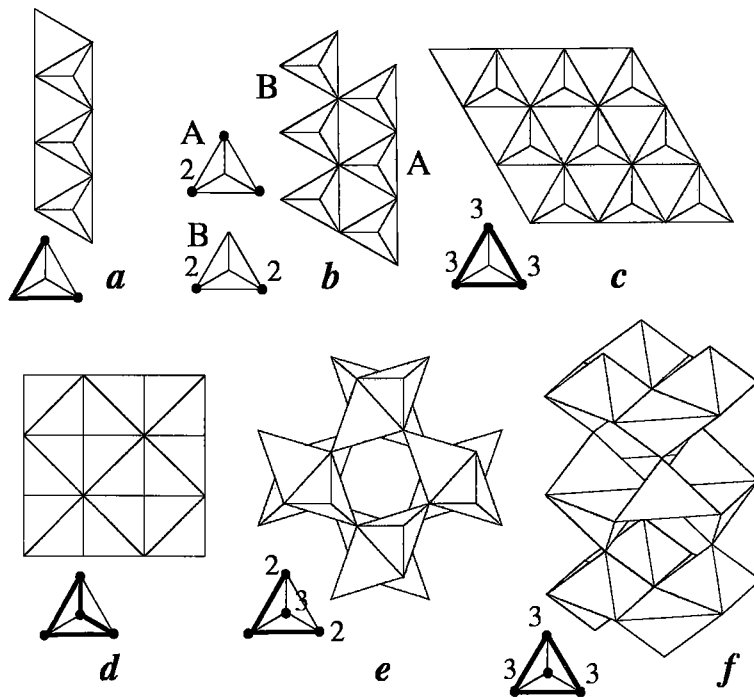FIG. 2. The crystal structure of kukharenkoite-(Ce) in (010) projection.

FIG. 3. Cationic complexes on the basis of fluorine-centered tetrahedra in fluorocarbonates (details in text and Table 4).
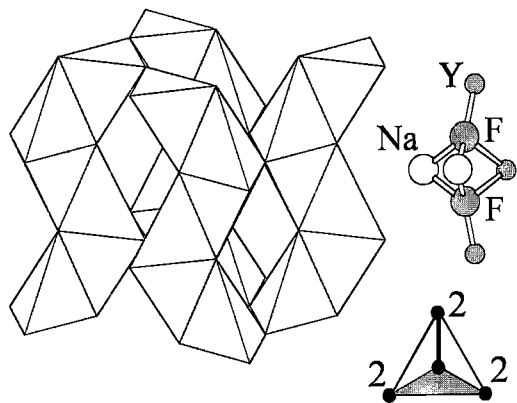
FIG. 4. Framework of F-centered tetrahedra in horváthite-(Y), $NaY(CO_3)F_2$: an exceptional case of two tetrahedra sharing a common face.

TABLE 4. CATIONIC COMPLEXES ON THE BASE OF F-CENTERED TETRAHEDRA IN FLUOROCARBONATES

General formula	Crystal-chemical formula	Figure	Compound	Ref.
$\{uB, 2_\infty^1\}[FM_2]$	$\{uB, 2_\infty^1\}[FCeBa]$	3a	$Ba_3Ce(CO_3)_3F$ kukharenkoite-(Ce)	1
$\{uB, 2_\infty^1\}[F_2M_5]$	$\{uB, 2_\infty^1\}[F_2Ba_3Ce_2]$	3b	$Ba_3Ce_2(CO_3)_5F_2$ cebaite-(Ce)	2
	$\{uB, 2_\infty^1\}[F_2Ba_3La_2]$		$Ba_3La_2(CO_3)_5F_2$	3
$\{uB, 1_\infty^2\}[F_2M_3]$	$\{uB, 1_\infty^2\}[F_2BaCe_2]$	3c	$BaCe(CO_3)_2F$ huanghoite-(Ce)	4
	$\{uB, 1_\infty^2\}[F_2BaSm_2]$		$BaSm(CO_3)_2F$	3
$\{uB, 1_\infty^2\}[FM]$	$\{uB, 1_\infty^2\}[FCa]$	3d	$CaBiOF(CO_3)$ kettnerite	5
$\{_\infty^3\}[FM]$	$\{_\infty^3\}[FCa]$	3e	$Ca_2F_2(CO_3)$ brenkite	6
	$\{_\infty^3\}[FPb]$		$Pb_2F_2(CO_3)$	7
$\{_\infty^3\}[FM]$	$\{_\infty^3\}[F_2BaCu]$	3f	$BaCu(CO_3)F_2$	8
$\{_\infty^3\}[FM]$	$\{_\infty^3\}[F_2NaY]$	4	$NaY(CO_3)F_2$ horváthite-(Y)	9

Ref.: 1 Mercier & Leblanc (1993b), this work, 2 Shen & Mi (1992), 3 Mercier & Leblanc (1993a), 4 Yang & Pertlik (1993), 5 Syneček & Žák (1960), 6 Leufer & Tillmanns (1980), 7 Aurivillius (1983), 8 Mercier & Leblanc (1993c), 9 Grice & Chao (1997).

Figure 3a, a double chain of kukharenkoite-(Ce) is shown from an aspect different than in Figure 1. The analogous double anion-centered chains have been described in many inorganic compounds with anion-centered tetrahedra. Recently, in a review on $[NM_4]$ tetrahedra in nitride sulfides and chlorides of trivalent lanthanides, Schleid (1996) described such chains in the compound $M_4N_2S_3$ (M is a trivalent lanthanide). Similar chains of $[OM_4]$ tetrahedra were analyzed by Krivovichev et al. (1998) and subdivided, in particular, in the minerals of the cuspidine, warwickite and lomonosovite groups. The structural analogy between cuspidine and warwickite has been pointed out by Belov (1976) and Hawthorne (1986). In both these structure-types, there are additional oxygen (or fluorine) atoms surrounded tetrahedrally by metal cations, M. Traditionally, this means that four coordination polyhedra of cations share one corner, and these complexes are arranged in infinite chains. Using the anion-centered approach, we can describe such structural units as composed of $[AM_4]$ tetrahedra, where A is an anion in the center of the tetrahedron. Thus $[AM_4]$ tetrahedra are linked together in double chains such as $[FCeBa]$ in kukharenkoite-(Ce). Figure 3b represents the double chain $\{uB, 2_\infty^1\}[F_2M_5]$ of cebaite-(Ce), $Ba_3Ce_2(CO_3)_5F_2$ (Shen & Mi 1992), and of $Ba_3La_2(CO_3)_5F_2$ (Mercier & Leblanc 1993a). It consists of two types of topologically and configurationally distinct tetrahedra. Figure 3c shows the layer $\{uB, 1_\infty^2\}[F_2M_3]$ of huanghoite-(Ce), $BaCe(CO_3)_2F$ (Yang & Pertlik 1993) and of $BaSm(CO_3)_2F$ (Mercier & Leblanc 1993a). In Figure 3d, the layer $\{uB, 1_\infty^2\}[FM]$ of kettnerite, $CaBiOF(CO_3)$ (Syneček & Žák 1960) is represented. Figure 3e shows a framework of F-centered tetrahedra observed in brenkite, $Ca_2F_2(CO_3)$ (Leufer & Tillmanns

1980), and in $Pb_2F_2(CO_3)$ (Aurivillius 1983). Figure 3f represents a framework $\{_\infty^3\}[FM]$ of $BaCu(CO_3)F_2$ (Mercier & Leblanc 1993c), which is topologically similar to that composed of $[OM_4]$ tetrahedra in delafossite, $CuFeO_2$, and crednerite, $CuMnO_2$ (Krivovichev et al. 1998). Finally, Figure 4 shows an exceptional framework of $[FM_4]$ tetrahedra in horváthite-(Y), $NaY(CO_3)F_2$, a new mineral recently described by Grice & Chao (1997). In this structure, two F-centered tetrahedra share one face because of the small absolute charge of F^- ions and large ionic radii of Na^+ and Y^{3+}, which reduce the repulsive forces between the centers of tetrahedra. As far as we know, this is a unique case of face-sharing in tetrahedral polyions.

REFERENCES

ANDRIANOV, V.I. (1987): AREN-85 – development of crystallographic program system RENTGEH for NORD, SM-4 and ES. Kristallographiya 32, 228-231 (in Russ.).

AURIVILLIUS, B. (1983): The crystal structure of lead carbonate fluoride, Pb₂F₂CO₃. *Acta Chem. Scand.* **A37**, 159-171.

BELOV, N.V. (1976): *Outline of Structural Mineralogy.* Nedra, Moscow, Russia (in Russ.).

BENGTSSON, L., FROSTEMARK, F., HOLMBERG, B. & ULVELUND, S. (1991): Thermodynamics of formation and the structure of polymetal alkaline-earth-metal (II) fluoride complexes in molten-nitrate media. *J. Chem. Soc., Faraday Trans.* **87**, 1141-1147.

_____ & HOLMBERG, B. (1989a): Cationic lead(II) halide complexes in molten alkali-metal nitrate. 1. A thermodynamic investigation of the fluoride system. *J. Chem. Soc., Faraday Trans. I* **85**, 305-316.

_____ & _____ (1989b): Cationic lead(II) halide complexes in molten alkali-metal nitrate. 2. A thermodynamic investigation of the chloride, bromide and iodide systems. *J. Chem. Soc., Faraday Trans. I* **85**, 317-329.

_____ & _____ (1989c): Cationic lead(II) halide complexes in molten alkali-metal nitrate. 3. The structure of Pb₂X³⁺ and the solvated Pbᴵᴵ ion, determined by liquid X-ray scattering and Raman spectroscopy. *J. Chem. Soc., Faraday Trans. I* **85**, 2917-2930.

FILATOV, S.K., SEMENOVA, T.F. & VERGASOVA, L.P. (1992): Types of polymerization of [OCu₄]⁶⁺ tetrahedra in inorganic compounds with "additional" oxygen atoms. *Dokl. Akad. Nauk SSSR* **322**, 536-539 (in Russ.).

FLEISCHER, M., CABRI, L.J., CHAO, G.Y., MANDARINO, J.A. & PABST, A. (1982): New mineral names. *Am. Mineral.* **67**, 1074-1082.

FROSTEMARK, F., BENGTSSON, L.A. & HOLMBERG, B. (1994a): Formation and structure of mono- and di-bismuth hydroxide and fluoride complexes in molten NH₄NO₃•1.5H₂O at 50°C. *J. Chem. Soc., Faraday Trans.* **90**, 2401-2412.

_____, MALMQUIST, P., BENGTSSON, L. & HOLMBERG, B. (1994b): Alkaline-earth-metal (II) complexes with hydroxide and fluoride in molten NH₄NO₃•1.5H₂O at 50°C. *J. Chem. Soc., Faraday Trans.* **90**, 3539-3544.

GRICE, J.D. & CHAO, G.Y. (1997): Horváthite-(Y), rare-earth fluorocarbonate, a new mineral species from Mont Saint-Hilaire, Québec. *Can. Mineral.* **35**, 743-749.

HAWTHORNE, F.C. (1986): Structural hierarchy in ⱽᴵMₓᴵᴵᴵTᵧφᵤ minerals. *Can. Mineral.* **24**, 625-642.

KRIVOVICHEV, S.V. (1997): On the using of Schlegel diagram for description and classification of minerals' crystal structures. *Zap. Vses. Mineral. Obshchest.* **126**(2), 37-46 (in Russ.).

_____, FILATOV, S.K. & SEMENOVA, T.F. (1997): On the systematics of polyions of linked polyhedra. *Z. Kristallogr.* **212**, 411-417.

_____, _____ & _____ (1998): Types of cationic complexes on the base of [OM₄] tetrahedra in crystal structures of inorganic compounds. *Russ. Chem. Reviews* **67**, 137-155.

LEUFER, U. & TILLMANNS, E. (1980): Die Kristallstruktur von Brenkit, Ca₂F₂(CO₃). *Tschermaks Mineral. Petrogr. Mitt.* **27**, 261-266.

LIEBAU, F. (1985): *Structural Chemistry of Silicates: Structure, Bonding and Classification.* Springer, Berlin, Germany.

MERCIER, N. & LEBLANC, M. (1993a): Crystal growth and structures of rare earth fluorocarbonates. I. Structures of BaSm(CO₃)₂F and Ba₃La₂(CO₃)₅F₂: revision of the corresponding huanghoite and cebaite type structures. *Eur. J. Solid State Inorg. Chem.* **30**, 195-205.

_____ & _____ (1993b): Crystal growth and structures of rare earth fluorocarbonates. II. Structures of zhonghuacerite Ba₂Ce(CO₃)₃F. Correlations between huanghoite, cebaite and zhonghuacerite type structures. *Eur. J. Solid State Inorg. Chem.* **30**, 207-216.

_____ & _____ (1993c): Existence of 3d transition metal fluorocarbonates: synthesis, characterization of BaM(CO₃)F₂ (M = Mn, Cu) and crystal structure of BaCu(CO₃)F₂. *Eur. J. Solid State Inorg. Chem.* **30**, 217-225.

_____ & _____ (1997): Structural correlations in fluoride carbonates. *Eur. J. Solid State Inorg. Chem.* **34**, 251-256.

SCHLEID, T. (1996): [NM₄] tetrahedra in nitride sulfides and chlorides of the trivalent lanthanides. *Eur. J. Solid State Inorg. Chem.* **33**, 227-240.

SHELDRICK, G.M. (1993): SHELXL–93. Program for the refinement of crystal structures. Univ. of Göttingen, Göttingen, Germany.

SHEN, JINCHUAN & MI, JINXIAO (1992): New advances in structural studies of barium rare-earth fluor-carbonate minerals. *J. China Univ. Geosci.* **3**, 17-24.

STAROVA, G.L., KRIVOVICHEV, S.V., FUNDAMENSKY, V.S. & FILATOV, S.K. (1997): The crystal structure of averievite Cu₅O₂(VO₄)₂•nMX: comparison with related compounds. *Mineral. Mag.* **61**, 441-446.

SYNEČEK, V. & ŽÁK, L. (1960): The crystal structure of kettnerite, (BiO)(CaF)CO₃. *Czech. J. Phys.* **10**, 195-207.

WALKER, N. & STUART, D. (1983): An empirical method for correcting diffractometer data for absorption effects. *Acta Crystallogr.* **A39**, 158-166.

YANG, ZHUMING & PERTLIK, F. (1993): Huanghoite-(Ce), BaCe(CO₃)₂F, from Khibina, Kola Peninsula, Russia: redetermination of the crystal structure with a discussion on space group symmetry. *Neues Jahrb. Mineral., Monatsh.*, 163-171.

_____, TAO, KEJIE & ZHANG, PEISHAN (1996): Polysomatic features of huanghoite – zhonghuacerite series minerals. *Neues Jahrb. Mineral., Monatsh.,* 264-270.

ZAITSEV, A.N., YAKOVENCHUK, V.N., CHAO, G.Y., GAULT, R.A., SUBBOTIN, V.V., PAKHOMOSKY, Y.A. & BOGDANOVA, A.N. (1996): Kukharenkoite-(Ce), $Ba_2Ce(CO_3)_3F$, a new mineral from Kola Peninsula, Russia and Québec, Canada. *Eur. J. Mineral.* **8**, 1327-1336.

ZHANG, PEISHAN & TAO, KEJIE (1981): Zhonghuacerite $Ba_2Ce(CO_3)_3F$ – a new mineral. *Scientia Geol. Sinica* **4**, 195-196 (in Chinese with English abstract).

_____ & _____ (1986): *Mineralogy of Bayan Obo.* Science Press, Beijing, China (in Chinese, with English abstr.).