

Article

Single Crystals of the Isotypic Series BaLu_2Ch_4 ($\text{Ch} = \text{S}, \text{Se}$ and Te) with CaFe_2O_4 -Type Structure

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Abstract: Single crystals of ternary chalcogenides with the composition BaLu_2Ch_4 ($\text{Ch} = \text{S}, \text{Se}$ and Te ; orthorhombic, $Pnma$; $a = 1211.4$ – 1353.6 , $b = 395.6$ – 438.5 , $c = 1427.8$ – 1593.6 pm) could be obtained after attempts to synthesize ternary lutetium(III) nitride chalcogenides using the elements (Lu and Ch) along with BaN_3Cl as a nitrogen source. Their crystal structures are isotypic with CaFe_2O_4 containing two sorts of ${}^1_{\infty}\{[\text{LuCh}_{4/4}\text{Ch}_{2/2}]^{8-}\}$ chains built up of edge-linked $[(\text{Lu}1)(\text{Ch}2)(\text{Ch}3)_3(\text{Ch}4)_2]^{9-}$ and $[(\text{Lu}2)(\text{Ch}1)_3(\text{Ch}2)_2(\text{Ch}4)]^{9-}$ octahedra, respectively. A further interconnection via the chalcogenide anions $(\text{Ch}3)^{2-}$ and $(\text{Ch}1)^{2-}$ leads to double chains, where either $(\text{Lu}1)^{3+}$ or $(\text{Lu}2)^{3+}$ coordinates these chalcogenide anions as well. The three-dimensional framework ${}^3_{\infty}\{[\text{Lu}_2\text{Ch}_4]^{2-}\}$ emerges from the corner-linkage of the two kinds of double chains forming large channels apt to take up the Ba^{2+} cations. These divalent cations exhibit eight contacts to chalcogenide anions resulting in the formation of bicapped trigonal prisms $[\text{BaCh}_8]^{14-}$.

Keywords: Lutetium; Chalcogenides; Barium; Crystal Structures

1. Introduction

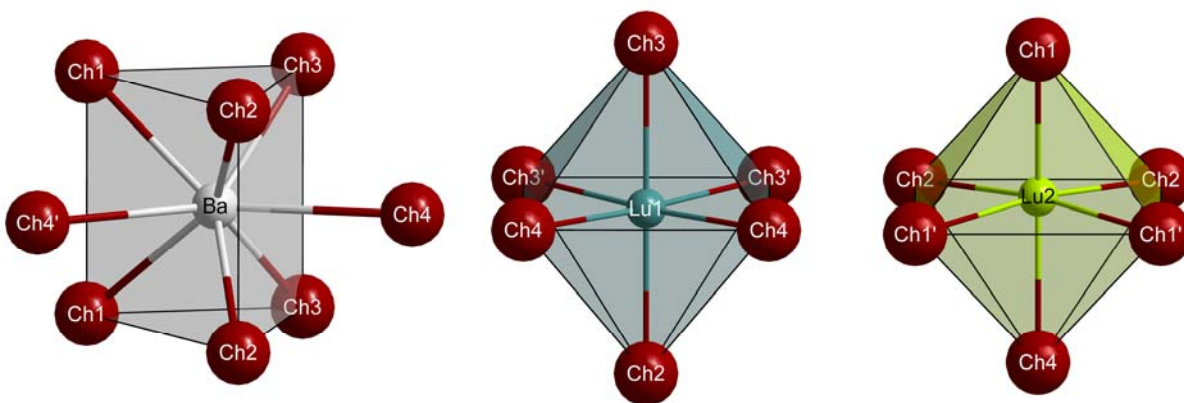
Up until now many nitride chalcogenides of the lanthanides with the formulae Ln_3NCh_3 ($\text{Ch} = \text{S}, \text{Se}$) [1–5] and $\text{Ln}_4\text{N}_2\text{Ch}_3$ ($\text{Ch} = \text{S}, \text{Se}, \text{Te}$) [4,6–10] are known in the literature, mainly as compounds with the lighter representatives ($\text{Ln} = \text{La}$ – Ho). Thus, the quest for a possible formation of nitride chalcogenides of the heaviest lanthanoid leads to formulation of the question, which nitrogen source would be most suitable for their synthesis? In order to test new educts for such experiments, the

recently described barium azide chloride BaN_3Cl [11] offers a promising option. Unfortunately, these experiments failed in the case of lutetium and ternary chalcogenides with the general composition BaLu_2Ch_4 were obtained instead of the primary target products Lu_3NCh_3 or $\text{Lu}_4\text{N}_2\text{Ch}_3$ ($\text{Ch} = \text{S}, \text{Se}, \text{Te}$). This type of compound $(\text{M}^{2+})(\text{M}^{3+})_2(\text{Ch}^{2-})_4$ has been known for quite a long time with a huge range of combinations for chalcogenide anions (Ch^{2-}), divalent (M^{2+}) and trivalent cations (M^{3+}), even for the lanthanides as rather large trivalent species (Ln^{3+}). First studies within the systems alkaline-earth metals, rare-earth metals and chalcogens were carried out by Flahaut *et al.* [12] in the early 1960s. Since this time further groups have published many reports dealing with this class of compounds. Although several examples for lutetium-bearing chalcogenides were characterized, the combination of barium as divalent (Ba^{2+}) and lutetium as trivalent cation (Lu^{3+}) was barely investigated. The so far identified compounds $\text{M}^{\text{II}}\text{Lu}_2\text{Ch}_4$ crystallize in three different structure types: MgAl_2O_4 (for $\text{M}^{\text{II}} = \text{Mg}, \text{Mn}, \text{Fe}$ and $\text{Ch} = \text{S}$) [13–17], CaFe_2O_4 (for $\text{M}^{\text{II}} = \text{Ca}, \text{Eu}, \text{Pb}$ and $\text{Ch} = \text{O}, \text{S}, \text{Se}$) [18–23] and Th_3P_4 (for $\text{M}^{\text{II}} = \text{Eu}$ and $\text{Ch} = \text{S}$) [24]. Furthermore, besides BaY_2S_4 [25] and the defective crystal structure of $\text{Ba}_{0.9}\text{Sm}_2\text{S}_{3.9}$ [26] no other examples for sulfide-containing compounds with barium and rare-earth metal cations are known with the CaFe_2O_4 -type arrangement hitherto, while many representatives for the compositions BaLn_2Se_4 [27] and BaLn_2Te_4 [28] could be synthesized. In this short paper the crystal structures of the three isotypic barium lutetium chalcogenides BaLu_2Ch_4 ($\text{Ch} = \text{S}, \text{Se}$ and Te) will be presented and discussed.

2. Results and Discussion

Initially, nitride chalcogenides of the heavy lanthanoids should be synthesized by using barium azide chloride BaN_3Cl as a nitrogen source and fluxing agent. Instead of the target compounds several ternary chalcogenides with the formula type BaLn_2Ch_4 ($\text{Ln} = \text{Gd}, \text{Tb}, \text{Er}, \text{Tm}, \text{Lu}$; $\text{Ch} = \text{S}, \text{Se}$ and Te) could be isolated and identified by X-ray single crystal and powder diffraction after washing the products with water. Although the first attempts to synthesize almost all of the compounds BaLn_2Ch_4 were successful and described by Bugaris and Ibers [27] and Narducci *et al.* [28], the lutetium representatives were not described in their papers.

Figure 1. View at the coordination sphere of the Ba^{2+} (left), $(\text{Lu}1)^{3+}$ (mid) and $(\text{Lu}2)^{3+}$ cations (right) in the crystal structure of the BaLu_2Ch_4 series ($\text{Ch} = \text{S}, \text{Se}$ and Te).



The ternary chalcogenides BaLu_2Ch_4 crystallize in the orthorhombic system with the space group $Pnma$ ($\text{Ch} = \text{S}$: $a = 1211.43(6)$, $b = 395.56(2)$, $c = 1427.81(4)$ pm; $\text{Ch} = \text{Se}$: $a = 1261.32(4)$, $b = 410.89(1)$, $c = 1487.74(4)$ pm; $\text{Ch} = \text{Te}$: $a = 1353.58(8)$, $b = 438.47(3)$, $c = 1593.62(8)$ pm) and four formula units per unit cell representing the CaFe_2O_4 -structure type (see Table 1 for atomic coordinates). All seven crystallographically independent atoms reside at Wyckoff positions 4c with the site symmetry m . The two trivalent lutetium cations are surrounded by six chalcogenide anions forming slightly distorted $[(\text{Lu}1)(\text{Ch}2)(\text{Ch}3)_3(\text{Ch}4)_2]^{9-}$ and $[(\text{Lu}2)(\text{Ch}1)_3(\text{Ch}2)_2(\text{Ch}4)]^{9-}$ octahedra (Figure 1, *mid* and *right*), while the divalent barium cations are coordinated by eight chalcogenide anions in the shape of bicapped trigonal prisms (Figure 1, *left*). Each of the four crystallographically different chalcogenide anions shows three contacts to lutetium and just two bonds to barium. The polyhedra can be described as more or less distorted square pyramids for $(\text{Ch}1)^{2-}$, $(\text{Ch}2)^{2-}$ and $(\text{Ch}3)^{2-}$ as well as distorted trigonal bipyramids for $(\text{Ch}4)^{2-}$.

Table 1. Atomic coordinates and equivalent isotropic displacement coefficients ($U_{\text{eq}}/\text{pm}^2$) for the three BaLu_2Ch_4 representatives ($\text{Ch} = \text{S}$, Se and Te).

Atom	Wyckoff site	x/a	y/b	z/c	$U_{\text{eq}}^{\text{a)}$	Ch
Ba	4c	0.24128(12)	$1/4$	0.66285(11)	154(4)	S
		0.23994(5)	$1/4$	0.66557(4)	64(2)	Se
		0.23844(13)	$1/4$	0.66986(11)	143(4)	Te
Lu1	4c	0.07937(8)	$1/4$	0.39920(7)	140(3)	S
		0.07980(4)	$1/4$	0.40077(3)	47(1)	Se
		0.08131(9)	$1/4$	0.40350(7)	137(3)	Te
Lu2	4c	0.56482(8)	$1/4$	0.60849(8)	146(3)	S
		0.56246(4)	$1/4$	0.60870(3)	49(1)	Se
		0.55812(9)	$1/4$	0.60972(7)	130(3)	Te
Ch1	4c	0.0822(5)	$1/4$	0.0759(4)	142(12)	S
		0.08590(7)	$1/4$	0.07604(6)	45(2)	Se
		0.09048(14)	$1/4$	0.07529(12)	125(4)	Te
Ch2	4c	0.2929(5)	$1/4$	0.3412(5)	149(12)	S
		0.29430(7)	$1/4$	0.34133(6)	61(2)	Se
		0.29558(14)	$1/4$	0.34259(12)	140(4)	Te
Ch3	4c	0.3766(5)	$1/4$	0.0236(4)	132(12)	S
		0.37538(7)	$1/4$	0.02521(6)	46(2)	Se
		0.37455(14)	$1/4$	0.02823(12)	125(4)	Te
Ch4	4c	0.4772(5)	$1/4$	0.7830(4)	137(12)	S
		0.47488(7)	$1/4$	0.78338(6)	58(2)	Se
		0.47228(14)	$1/4$	0.78407(12)	138(4)	Te

$$^{\text{a)}} U_{\text{eq}} = 1/3(U_{11} + U_{22} + U_{33}) [29].$$

All bond lengths between Ba^{2+} and its eight Ch^{2-} ligands (315–333 pm for $\text{Ch} = \text{S}$, 327–349 pm for $\text{Ch} = \text{Se}$, and 350–367 pm for $\text{Ch} = \text{Te}$, for details see Table 2) are similar to those obtained for the other representatives of the ternary barium sulfides BaLn_2S_4 (318–343 pm for $\text{Ln} = \text{Sm}$, Y) [25,26], selenides BaLn_2Se_4 (327–346 pm for $\text{Ln} = \text{Er}$ – Yb) [28] and tellurides BaLn_2Te_4 (350–375 pm for $\text{Ln} = \text{Sm}$ – Tm , Y) [27]. Comparable short distances between Lu^{3+} and Ch^{2-} as in the BaLu_2Ch_4 series

(264–272 pm for $Ch = S$, 277–285 pm for $Ch = Se$, 298–306 pm for $Ch = Te$) can also be observed in Lu_2S_3 (E-type: 264–274 pm) [30], $CaLu_2S_4$ (265–277 pm) [19], Lu_2Se_3 (Z-type: 279–286 pm) [31], $EuLu_2Se_4$ (275–282 pm) [21], $CsCdLuTe_3$ (307–311 pm) [32] and $CsCuLu_2Te_4$ (297–314 pm) [33]. A periodic effect regarding ionic radii and volume increments can be stated by a comparison of their influence on the molar volumes V_m of the title compounds in the order of increasing radii of the chalcogenide anions: sulfide ($r = 184$ pm), selenide ($r = 198$ pm) and telluride ($r = 221$ pm) [34]. The difference of the volume increments of these chalcogenide anions ($16 \text{ cm}^3/\text{mol}$ between $4 \times S^{2-}$ and $4 \times Se^{2-}$ as well as $30 \text{ cm}^3/\text{mol}$ between $4 \times Se^{2-}$ and $4 \times Te^{2-}$) [35] are very similar to the obtained V_m differences of the ternary compounds ($13 \text{ cm}^3/\text{mol}$ between $BaLu_2S_4$ and $BaLu_2Se_4$, $26 \text{ cm}^3/\text{mol}$ between $BaLu_2Se_4$ and $BaLu_2Te_4$).

Table 2. Selected internuclear distances (d/pm) for the three $BaLu_2Ch_4$ representatives ($Ch = S$, Se and Te).

			$Ch = S$	$Ch = Se$	$Ch = Te$
Ba	– $Ch3$	(2×)	314.7(5)	327.1(1)	349.8(2)
	– $Ch1$	(2×)	316.7(5)	329.0(1)	352.7(2)
	– $Ch2$	(2×)	325.1(5)	335.3(1)	354.9(2)
	– $Ch4$	(1×)	329.1(6)	342.8(1)	365.1(3)
	– $Ch4'$	(1×)	333.3(6)	344.3(1)	367.7(3)
Lu1	– $Ch4$	(2×)	267.2(4)	278.3(1)	299.3(1)
	– $Ch3$	(1×)	269.2(6)	280.4(1)	300.3(2)
	– $Ch3'$	(2×)	271.1(4)	282.3(1)	301.9(1)
	– $Ch2$	(1×)	271.7(6)	284.6(1)	305.8(2)
Lu2	– $Ch1$	(1×)	264.0(6)	276.4(1)	298.1(2)
	– $Ch4$	(1×)	270.8(6)	282.1(1)	301.2(2)
	– $Ch1'$	(2×)	270.2(4)	282.4(1)	302.5(2)
	– $Ch2$	(2×)	272.0(4)	283.5(1)	305.1(2)

The different surrounding of the two crystallographically distinct lutetium cations is manifested in the crystal structure as the $[(Lu1)(Ch2)(Ch3)_3(Ch4)_2]^{9-}$ and $[(Lu2)(Ch1)_3(Ch2)_2(Ch4)]^{9-}$ octahedra form two different kinds of $\infty \{[(Lu)Ch_{4/4}^e Ch_{2/2}^t]^{8-}\}$ chains by edge linkage. Interestingly, the chalcogenide anions $(Ch3)^{2-}$ connect two $\infty \{[(Lu1)Ch_{4/4}^e Ch_{2/2}^t]^{8-}\}$ strands to double chains running parallel to the $[010]$ direction (Figure 2, left). The same holds for the $(Ch1)^{2-}$ anions in the case of the $(Lu2)^{2+}$ -bearing congeners (Figure 2, right) and so, besides two extra Ba^{2+} contacts for all chalcogenide anions, $(Ch1)^{2-}$ and $(Ch3)^{2-}$ exhibit three contacts to only one sort of trivalent lutetium cation, while the $(Ch2)^{2-}$ and $(Ch4)^{2-}$ anions are bonded to both types of Lu^{3+} . Both kinds of double chains are finally corner-connected according to the pattern in Figure 3, forming a three-dimensional framework $\infty \{[Lu_2Ch_4]^{2-}\}$ with channels that are occupied by the octacoordinated barium cations.

Figure 2. View of the $\frac{1}{\infty} \{[(\text{Lu}1)\text{Ch}_{4/4}^e \text{Ch}_{2/2}^t]^{8-}\}$ (left) and $\frac{1}{\infty} \{[(\text{Lu}2)\text{Ch}_{4/4}^e \text{Ch}_{2/2}^t]^{8-}\}$ chains (right), which both form double chains (below) of edge-connected $[\text{LuCh}_6]^{9-}$ octahedra in the crystal structure of the BaLu_2Ch_4 series ($\text{Ch} = \text{S}, \text{Se}$ and Te).

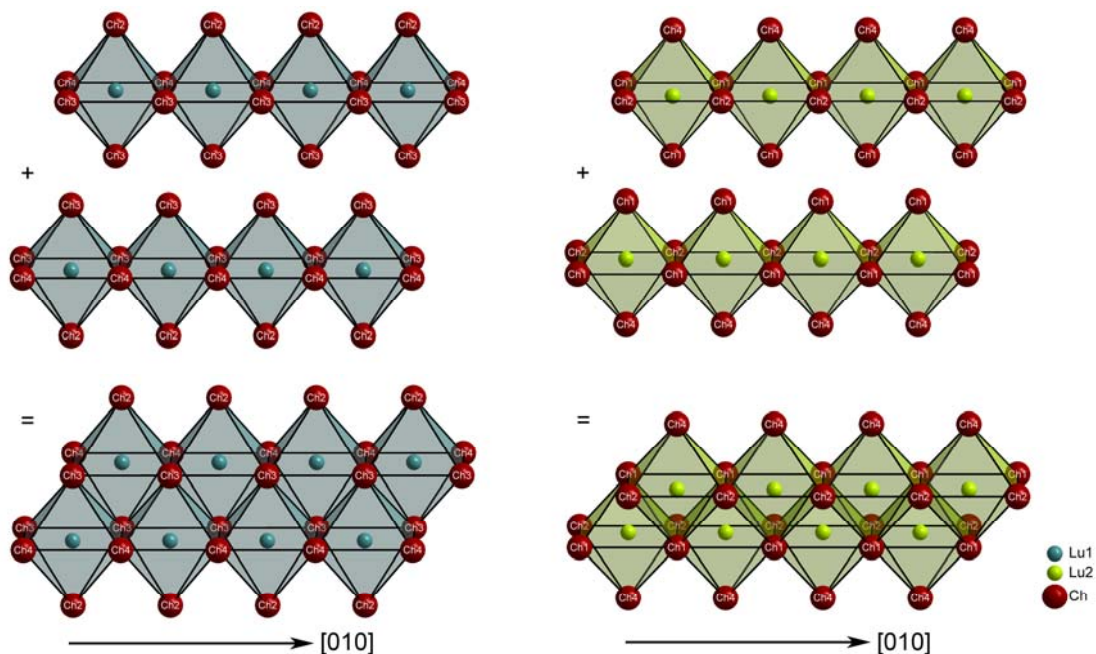
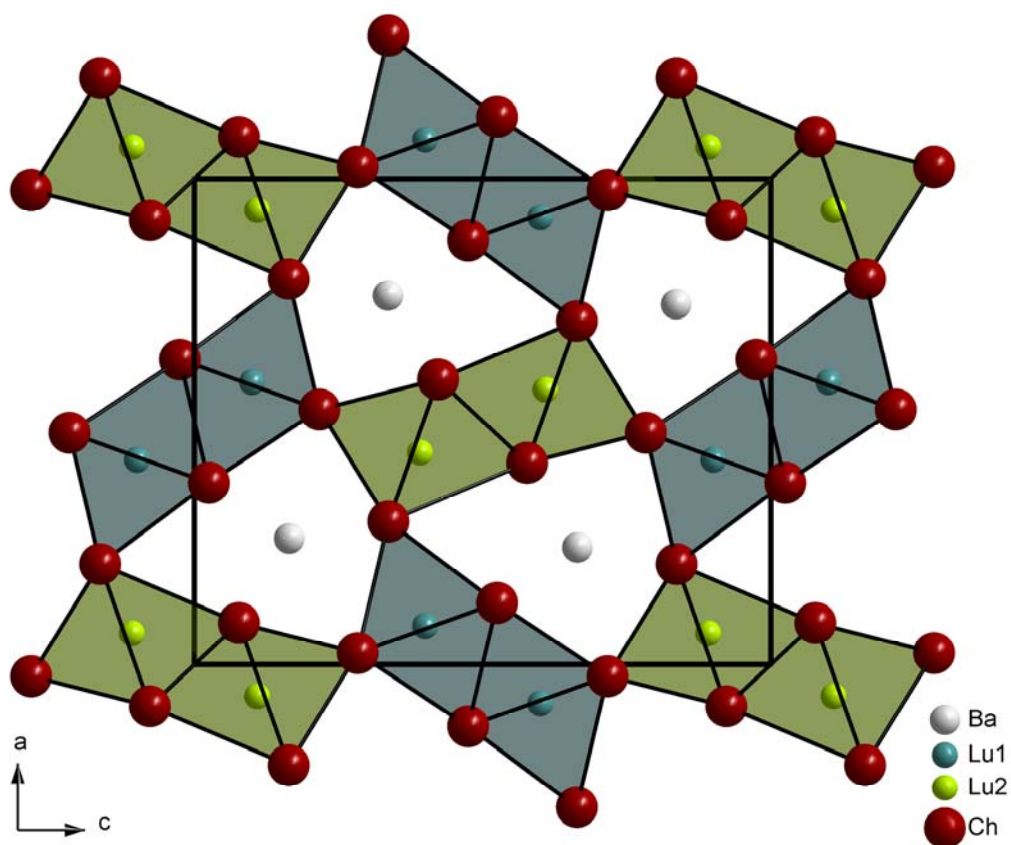


Figure 3. View of the crystal structure of the BaLu_2Ch_4 series ($\text{Ch} = \text{S}, \text{Se}$ and Te), where the $\frac{3}{\infty} \{[\text{Lu}_2\text{Ch}_4]^{2-}\}$ framework with channels is filled up by barium cations.



3. Experimental Section

Single crystals of BaLu₂S₄, BaLu₂Se₄ and BaLu₂Te₄ were accidentally (but reproducible) obtained after heating mixtures of lutetium metal, its trichloride, chalcogen and barium azide chloride in molar ratios of 26:2:27:6 designed to produce Lu₃NCh₃ [1-5] or Lu₄N₂Ch₃ [4,6-10] along with an excess of barium chloride as flux at 920 °C for ten days.

Table 3. Crystallographic data for the three BaLu₂Ch₄ representatives (Ch = S, Se and Te).

BaLu ₂ Ch ₄	Ch = S	Ch = Se	Ch = Te
Crystal system	orthorhombic	orthorhombic	Orthorhombic
Space group	<i>Pnma</i>	<i>Pnma</i>	<i>Pnma</i>
<i>a</i> (pm)	1211.43(8)	1261.32(8)	1353.58(8)
<i>b</i> (pm)	395.56(3)	410.89(3)	438.47(3)
<i>c</i> (pm)	1427.81(9)	1487.74(9)	1593.62(9)
<i>V_m</i> (cm ³ /mol)/ <i>D_x</i> (g/cm ³)	103.007/5.975	116.081/6.918	142.394/7.006
Formula units (<i>Z</i>)	4	4	4
<i>F</i> (000)/ <i>θ</i> _{max}	1048/28.2	1336/28.2	1624/28.2
± <i>h</i> /± <i>k</i> /± <i>l</i>	16/5/18	16/5/19	17/5/21
Reflections (independent)	12319 (955)	10976 (1087)	17321 (1312)
(<i>μ</i> /mm ^{−1})	35.42	49.23	36.83
<i>R</i> _{int} / <i>R</i> _σ	0.078/0.047	0.062/0.036	0.094/0.061
<i>R</i> ₁ / <i>wR</i> ₂	0.074/0.136	0.030/0.058	0.090/0.103
<i>Goof</i>	1.186	1.053	1.181

All three water- and air-stable products exhibit the shape of needles with different colors (BaLu₂S₄: colorless, BaLu₂Se₄: dark red, BaLu₂Te₄: black) and were characterized by single crystal X-ray diffraction (κ-CCD, Bruker-Nonius, Mo-Kα radiation with graphite monochromator: λ = 71.01 pm) at room temperature. Essential information about the structure solutions and refinements for the BaLu₂Ch₄ series (Ch = S, Se, Te) by using the program package SHELXS-97 and SHELX-97 [36] as well as X-SHAPE for correction for absorption [37] and scattering factors from the International Tables, Vol. C [38], is available in Table 3. Further details may be obtained from the Fachinformationszentrum (FIZ) Karlsruhe, D-76344 Eggenstein-Leopoldshafen, Germany (Fax: (+49)7247-808-666, E-mail: crysdata@fizkarlsruhe.de), on quoting the depository numbers CSD-422891 (BaLu₂S₄), CSD-422892 (BaLu₂Se₄) and CSD-422893 (BaLu₂Te₄).

4. Conclusions

The crystal structures of all three barium lutetium chalcogenides BaLu₂Ch₄ (Ch = S, Se and Te) exhibit a CaFe₂O₄-type arrangement. As a particularity, the two crystallographically distinct trivalent lutetium cations can be found in two different types of $\frac{1}{\infty} \{[\text{LuCh}_{4/4}^e \text{Ch}_{2/2}^t]\}^{8-}$ chains. These first build double chains by edge-linkage, which are corner-connected further to form a three-dimensional $\frac{3}{\infty} \{[\text{Lu}_2\text{Ch}_4]^{2-}\}$ framework apt to embed divalent barium cations. It should be noted that these

compounds were obtained in order to produce lutetium nitride chalcogenides (Lu_3NCh_3 or $\text{Lu}_4\text{N}_2\text{Ch}_3$) by using barium azide chloride as flux and a nitrogen source, which leads to the assumption that this starting material is not suitable as a source of nitrogen for these kinds of synthetic experiments.

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