Chiolite-like $Ca_5Te_3O_{14}$: An X-ray and neutron diffraction study

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ABSTRACT

The crystal structure of $Ca_5Te_3O_{14}$ at room temperature was studied by the Rietveld method using combined X-ray and neutron powder diffraction data. The compound crystallizes in the space group *Cmca* with the lattice parameters $a = 10.4268(2)$ Å, $b = 10.3908(2)$ Å and $c = 10.4702(2)$ Å. The structure of $Ca_5Te_3O_{14}$ is chiolite-like and consists of a framework of corner-linked TeO_6 octahedral layers in which a linear TeO_2 group of every fourth octahedron is substituted by a Ca atom. This type of structure was previously observed in $BaSr_4U_3O_{14}$. The relationship between the chiolite-like structure and the fluorite structure is discussed.

1. Introduction

The chiolite structure is adopted by a small number of complex fluorides with the formula $Na_5M_3F_{14}$ (M = Al, Cr, Fe and Ga). The structure of chiolite $Na_5Al_3F_{14}$ was first determined by Brosset [1] about 70 years ago, and re-investigated using single crystals by Jacoboni et al. [2]. The parent chiolite structure $AA'_4M_3X_{14}$ consists of a framework of MX_6 octahedra linked by their corners to form layers. In every fourth octahedron a linear group MX_2 is replaced by an A atom: one-third of the MX_6 octahedra shares four corners with other octahedra and two-thirds share only two corners. The latter octahedra are free to rotate along the axis connecting the two corners to accommodate a better coordination around the A atom. The layer composition is thus M_3X_{14}. The A' atoms are located between the layers. The alternate layers are staggered by half the base diagonal of the unit cell, so that c-axis is twice the interlayer distance. In the absence of octahedral tilting, the parent chiolite structure has tetragonal symmetry, with the space group $I4/mmm$ and lattice constants $a_c \approx 4(r_M+r_X)$ and $c_c \approx \sqrt{2}a_c$. The atomic positions are: A in $2b$ $(0,0,1/2)$; A' in $8f$ $(1/4,1/4,1/4)$; $M(1)$ in $2a$ $(0,0,0)$; $M(2)$ in $4c$ $(0,1/2,0)$; $X(1)$ in $4e$ $(0,0,z)$ with $z \approx 0.18$; $X(2)$ in $8i$ $(x,0,0)$ with $x \approx 0.25$ and $X(3)$ in $16g$ in $(0,y,z)$ with $y \approx 0.32$ and $z \approx 0.38$, respectively. In the case that the voids are too large to accommodate the A and/or A' atoms, tilting of the octahedra MX_6 occurs that reduces the size of the voids. In fact, the chiolite $Na_5Al_3F_{14}$ crystallizes at room temperature in the subgroup $P4/mnc$. The octahedra are tilted about $15.4°$ around the axes parallel with [001] and the tilting in the next layer is anti-phase. The structure of $Na_5Al_3F_{14}$ at low temperature has been

described in the lower subgroup $P2_1/n$ where an additional tilting around [010] is present [3]. A similar phase transition has also been observed in $Na_5M_3F_{14}$ (M = Cr, Fe, Ga) [4]. On the other hand, γ-$Na_5Fe_3F_{14}$ is chiolite-like, at about $640°C$, crystallizing in the subgroup $P4_22_12$ with highly distorted FeF_6 octahedra. Between 622 and $640°C$ it is monoclinic [4] and below this temperature there exists a very complicated unknown monoclinic structure [5].

Ravez et al. [6] have prepared a large family of monoclinic oxy-fluorides, which are all ferroelectric at room temperature and have structures closely related to chiolite-like $Na_5W_3O_9F_5$. The structure of $Na_5W_3O_9F_5$ has been determined by Abrahams et al. [7] to have the space group $I2$, a subgroup of $I4/mmm$, with the lattice parameters: $a = 7.3597(7)$ Å, $b = 10.6342(10)$ Å, $c = 7.3618(10)$ Å and $\beta = 90.77(2)$.

Oxides that adopt the chiolite structure are also known. Burchard and Rüdorff [8] described $SrCa_4Te_3O_{14}$ to be a tetragonal chiolite with the lattice parameters $a = 7.403$ Å and $c = 10.471$ Å. $Ca_5Te_3O_{14}$ was depicted as a monoclinically distorted chiolite with $a = 7.384$ Å, $b = 7.384$ Å, $c = 10.388$ Å and $\beta = 90.15°$ [8]. For both compounds, however, no structural details have been reported. The compounds $Ca_2Ln_3M_3O_{14}$ (Ln = lanthanides and Y, M = Sb, Ta) were also suggested to adopt the chiolite structure [8]. On the other hand, it is reported that $BaSr_4U_3O_{14}$ crystallizes at room temperature in a modified structure of the parent chiolite [9]. In this compound, the octahedra are tilted around the twofold axes in the layer plane, and the rotations in the alternate layer are opposite, resulting in the space group *Cmca* with $a \approx b \approx \sqrt{2}a_c$ and $c \approx c_c$. In $Sr_5U_3O_{14}$ an additional tilt occurs around [001], leading to the space group *Pbca* [9].

In a recent study [10] we showed that the compounds $Ca_2Ln_3Sb_3O_{14}$ (Ln = lanthanides and Y) are not chiolite-like, but

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belong to an unknown monoclinic variant of the weberite structure. In continuation of our earlier research on chiolite-like structures [9] we have now investigated the structure of $Ca_5Te_3O_{14}$ using the combination of neutron powder diffraction and X-ray powder diffraction data. In this paper we show that $Ca_5Te_3O_{14}$ is indeed chiolite-like, but it crystallizes in the orthorhombic space group *Cmca*, which precludes ferroelectric behavior at room temperature.

2. Experimental

$Ca_5Te_3O_{14}$ was prepared from $CaCO_3$ and TeO_2 in alumina crucibles. The stoichiometric mixtures were heated in air gradually from 250 to 700 °C. It was observed that the very pure $Ca_5Te_3O_{14}$ was difficult to obtain; a trace of a double perovskite-like phase Ca_3TeO_6 appears as contamination. Therefore, the mixtures were kept at 700 °C for several weeks with repeated re-grindings. Finally, the samples were furnace cooled to room temperature.

X-ray powder diffraction data were recorded using a Philips X'Pert diffractometer, equipped with the X'Celerator, using $CuK\alpha$ radiation in steps of $0.02°$ (2θ) (the actual step size is 0.0167 (2θ)) and 8 s counting time between $10°$ and $140°$ (2θ). The neutron powder diffraction data were collected on a sample of approximately 20 g on the powder diffractometer of the high flux reactor of NRG in Petten, The Netherlands. A vanadium can was used as sample holder. The neutron wavelength is 1.4317 Å. The Rietveld refinements were carried out using the Rietica computer program [11]. A polynomial function with six parameters was employed to fit the background. The X-ray profiles have been fitted with a pseudo-Voigt function and the neutron profiles with a Gauss function.

3. Results

The X-ray diffraction pattern of $Ca_5Te_3O_{14}$ is shown in Fig. 1. It is easily recognized that the main diffraction lines resemble those of the parent chiolite. A closer inspection of the peak splitting shows, however, that the symmetry of $Ca_5Te_3O_{14}$ is neither tetragonal nor monoclinic as was previously suggested [8]. In Fig. 2 the enlarged sections are shown containing the (220)/(004),
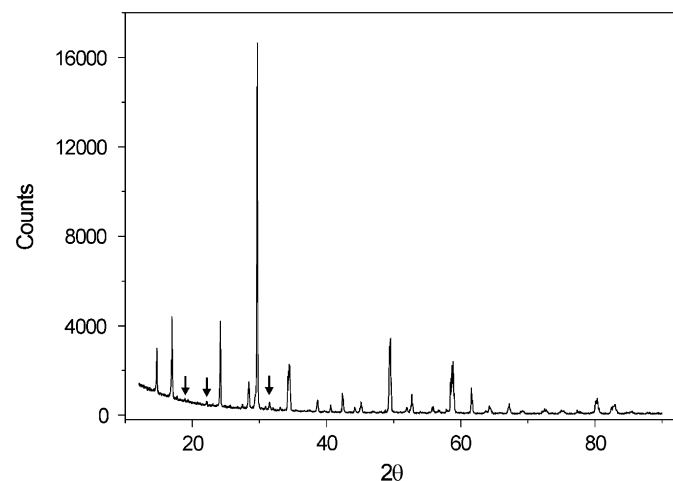

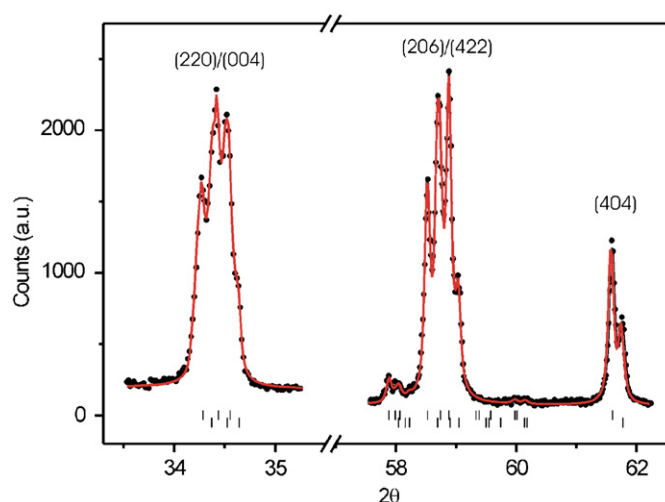**Fig. 2.** An enlarged section of the diffraction pattern of $Ca_5Te_3O_{14}$ showing the (220)/(004), (206)/(422) and (404) reflections as indexed with the parent chiolite. The continuous line is the Le Bail fit using the space group *Cmca*. The significance of the peak splitting is discussed in the text.

(206)/(422) and (404) reflections indexed with the parent chiolite unit cell. One sees that the first two groups are actually triplets which cannot be explained by a tetragonal cell of $a \approx 7.4$ Å and $c \approx 10.4$ Å. The monoclinic unit cell, i.e. $a = 7.384$ Å, $b = 7.384$ Å, $c = 10.388$ Å and $\beta = 90.15°$, reported by Burchard and Rüdorff [8] also fails to account for the observed profiles. For example, the (404) reflection should split up into a doublet, but it remains single instead. In fact, Le Bail fitting using the monoclinic unit cell indicates that the β-angle is just $90°$ within the standard deviation. Further, the appearance of some weak superlattice reflections, e.g. $2\theta \approx 40.6°$ and $44.3°$ (see Fig. 1), suggests that the cell dimension of $Ca_5Te_3O_{14}$ is larger than those of the tetragonal and monoclinic structures mentioned above.

On the other hand, the X-ray diffraction pattern can be readily explained by using an orthorhombic unit cell with $a \approx b \approx \sqrt{2}a_c$ and $c \approx c_c$ (Fig. 2), where a_c and c_c denote the lattice parameters of the parent chiolite. As this unit cell is an analog of that of $BaSr_4U_3O_{14}$ [9], the space group *Cmca* was used to model the structure of $Ca_5Te_3O_{14}$. Because our neutron diffraction data have poor resolution compared to the X-ray diffraction data, but is more sensitive to the oxygen positions, the refinements were carried out using combined neutron and X-ray diffraction data [12]. Further, as a trace of Ca_3TeO_6 was observed in both the X-ray and neutron powder diffraction data (Fig. 1), it was included as the second phase in the refinement [13].

The Rietveld refinement in the space group *Cmca* yielded a satisfactory fit. In convergence, the agreement factors were $R_{wp} = 3.94\%$ and 9.62% for the neutron and X-ray data, respectively. As was mentioned in Introduction, the chiolite-like $Sr_5U_3O_{14}$ adopts a different orthorhombic space group [9] due to an additional octahedral tilt around [001]. To investigate whether the space group *Pbca* describes the structure of $Ca_5Te_3O_{14}$ better, we carried out an additional refinement. However, the system of equations became unstable. Using only the neutron powder diffraction data, the Rietveld refinement did result in a lower R_{wp} (3.65%), but led to an unusually low χ^2-value (0.01). This indicates that the *Pbca* model may contain more parameters than can be justified by the quality of the data [14]. Therefore, in our opinion the space group *Cmca* is consistent with the powder neutron and X-ray diffraction data, and correctly describes the structure of $Ca_5Te_3O_{14}$.

Fig. 1. X-ray powder diffraction pattern of $Ca_5Te_3O_{14}$. A trace of contamination of the perovskite-like phase Ca_3TeO_6 can be seen as indicated by arrows.
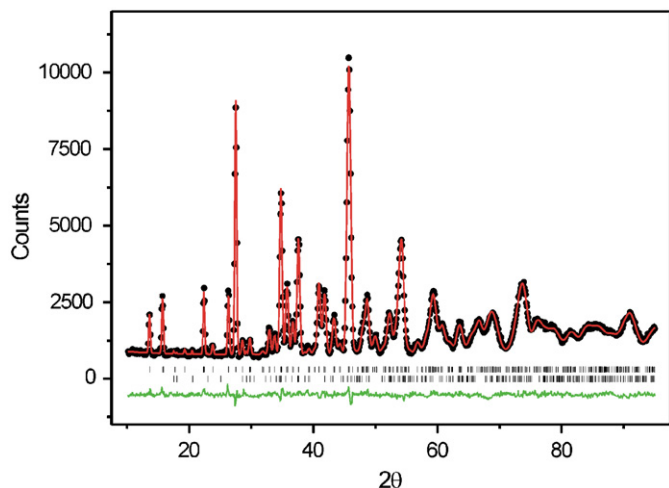
Fig. 3. Observed (crosses) and calculated (full line) profiles of the neutron powder diffraction. Tick marks below the profiles indicate the positions of the Bragg reflections of $Ca_5Te_3O_{14}$ (up row) and Ca_3TeO_6 (down row). A difference curve (observed-calculated) is shown at the bottom of the plots.

Table 1
Refined lattice parameters, atomic positions and thermal parameters of $Ca_5Te_3O_{14}$ in the space group $Cmca$ with $a = 10.4267(2)$ Å, $b = 10.3907(2)$ Å and $c = 10.4702(2)$ Å

Atom	Site	x	y	z	B (Å)^2
Ca1	4b	0	0	0.5	1.3(1)
Ca2	8e	0.25	0.0190(4)	0.25	0.23(4)
Ca3	8f	0.5	0.2575(4)	0.2736(3)	0.23
Te1	4a	0	0	0	0.20(2)
Te2	8c	0.25	0.25	0	0.20
O1	8f	0	−0.0538(5)	0.1732(5)	0.46(4)
O2	16g	0.1292(4)	0.1208(4)	0.0611(3)	0.46
O3	16g	0.1658(4)	0.3674(4)	0.1136(3)	0.46
O4	16g	0.1441(4)	0.3202(4)	−0.1305(3)	0.46

$R_{wp} = 3.94\%^a$ $(9.62\%)^b$, $R_p = 3.06\%^a$ $(6.94\%)^b$, $\chi^2 = 2.57^a$ $(2.59)^b$

[a] R-factor of neutron diffraction data.
[b] R-actor of X-ray diffraction data.

Table 2
Selected interatomic distances in $Ca_5Te_3O_{14}$

Ca1–O3	2.510(3) 4x	Te1–O1	1.898(4) 2x	O2–Ca3	2.612 (4) 1x
Ca1–O4	2.760(3) 4x	Te1–O2	1.949(5) 4x	O2–Te1	1.949(5) 1x
Ca2–O1	2.831(3) 2x	Te2–O2	1.949(4) 2x	O2–Te2	1.949(5) 1x
Ca2–O2	2.572(4) 2x	Te2–O3	1.917(3) 2x	O3–Ca1	2.510(4) 1x
Ca2–O3	2.300(4) 2x	Te2–O4	1.902(4) 2x	O3–Ca2	2.300(4) 1x
Ca2–O4	2.361(4) 2x			O3–Ca3	2.384(4) 1x
Ca3–O1	2.225(4) 1x	O1–Ca2	2.830(2) 2x	O3–Te2	1.917(3) 1x
Ca3–O2	2.612(4) 1x	O1–Ca3	2.225(4) 1x	O4–Ca1	2.760(3) 1x
Ca3–O3	2.384(4) 2x	O1–Te1	1.898(4) 1x	O4–Ca2	2.361(4) 1x
Ca3–O4	2.271(4) 2x	O2–Ca2	2.572(4) 1x	O4–Ca3	2.271(4) 1x
				O4–Te2	1.902(4) 1x

Fig. 3 shows the plots of the observed and calculated profiles. The refined structural parameters are given in Table 1. Table 2 lists some selected interatomic distances.

4. Discussion

The structure of $Ca_5Te_3O_{14}$ is chiolite-like and consists of a framework of TeO_6 octahedra linked by their corners to form

layers. In every fourth octahedron a linear TeO_2 group is substituted by a Ca atom. The $Te1O_6$ octahedra share four corners with $Te2O_6$ octahedra, while the $Te2O_6$ octahedra share only two axial corners with the $Te1O_6$ octahedra. The structure of $Ca_5Te_3O_{14}$ is easily derived from the parent chiolite structure (space group $I4/mmm$) by tilting the $Te1O_6$ octahedron at (0,0,0) about a two-fold axis parallel to [−110] with a tilting angle of about 17° (Fig. 4(a)). In the adjacent layer the octahedra tilt oppositely. The tilting destroys the four-fold axis as well as the first two symmetry planes being present in $I4/mmm$. This results in the space group $Cmca$ with the unit cell of $\sqrt{2}a_c$, $\sqrt{2}a_c$ and c_c. The Te1–O bond distances differ slightly, but their averaged value (1.932 Å) is close to the sum of the Shannon's ionic radii (1.95 Å) (Table 2) [13]. The tilting of the $Te1O_6$ octahedra also causes a rotation of the $Te2O_6$ octahedra around a two-fold axis in the layer. Again the change in the Te2–O bond lengths is relatively small with an averaged value (1.924 Å) almost equal to the sum of the ionic radii.

The Ca1 atoms are in the layer of corner-linked TeO_6 octahedra, and are coordinated to eight oxygen atoms arranged in a deformed cubic (Fig. 4(a)). The average Ca1–O distance (2.635 Å) is somewhat larger than that expected from the Shannon's ionic radii (2.50 Å) for the corresponding coordination of cation and anion [15]. This may be the reason for the observed high value of the isotropic thermal parameter of Ca1. Ca2 and Ca3 atoms are located between the TeO_6 layers. The Ca2 has six oxygen atoms near by, at distances ranging from 2.300 to 2.572 Å, and two additional oxygen atoms at a longer distance (2.831 Å). The Ca2–O polyhedron is, in fact, a deformed octahedron (Fig. 4(b)). Ca3 is in a mono-capped trigonal prism, where the Ca3–O distances range from 2.27 to 2.612 Å. There is also an O1 at a distance of 3.284 Å, which is too far to be considered as the coordination oxygen of Ca3. In $Ca_5Te_3O_{14}$ each oxygen atom has four cation neighbors: three Ca and one Te for O1, O3 and O4, but O2 has two Te and two Ca neighbors.

A different way of viewing the chiolite structure is based on the cubic fluorite structure with lattice constant a_0, which consists of the fcc close packing of cations with anions occupying the tetrahedral interstices. In $Ca_5Te_3O_{14}$, which is an anion-deficient derivative of the fluorite with $a \approx b \approx c \approx 2a_0$, the metal atoms are in fcc close packing with alternating Ca_3Te and Ca_2Te_2 layers. Three-fourths of the oxygen atoms are located in the tetrahedral interstices, and one-fourth oxygen atoms, originally at $16g$ ($\approx 1/8$, $\approx 1/8, \approx −1/8$) positions, is relocated in the octahedral interstices at $8f$ (0,0.054,−0.1735). This results in the octahedral coordination of Te. The z parameters of O3 and O4 are close to $z = \frac{1}{8}$, but the z parameter of O2 is smaller. It is interesting to compare the chiolite structure with the related weberite and pyrochlore structures; all three have the close packing of the metal atoms. The compositions of the alternating layers are, however, different. In $Ca_2Sb_2O_7$ with weberite structure, the compositions of the adjacent metal layers are Ca_3Sb and Sb_3Ca, respectively [10]. For $Pb_2Sb_2O_7$ with the pyrochlore structure, the metal layers are PbSb. Also the filling of the anions in the interstitials is different. In weberite and pyrochlore structures, all anions are located in the tetrahedral interstitials, but one-eighth of them remains unoccupied. In fact, both structures have a three-dimensional network of SbO_6 octahedra. In contrast, the chiolite $Ca_5Te_3O_{14}$ has a layered arrangement of TeO_6 octahedra. In the unit cell, the Te atoms are at $z = 0$ and $\frac{1}{2}$, and only in these planes the TeO_6 octahedra share corners with each other.

It should be pointed out that the monoclinic unit cell reported for $Ca_5Te_3O_{14}$ by Burchard and Rüdorff [8] is, in fact, a subcell of the orthorhombic cell with $a_m \approx b_m \approx ((1/2a)^2 + (1/2b)^2)^{1/2}$, $c_m \approx c$ and $\gamma = 90.20°$ (see Fig. 4(a)). Although this subcell does contain all the crystallographically distinct atoms, the tilting of the $Te1O_6$

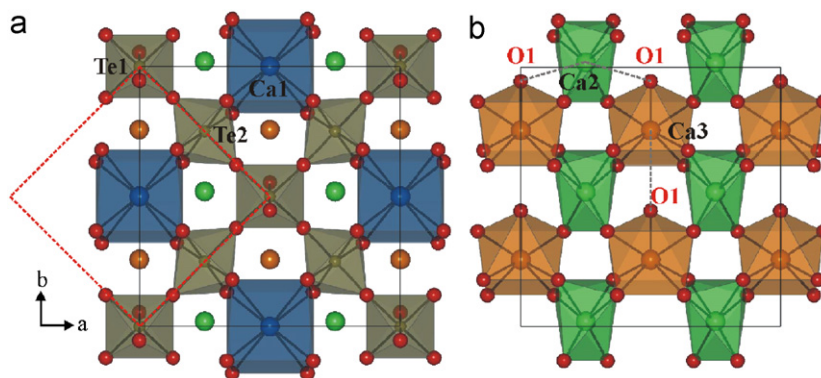**Fig. 4.** The structure of $Ca_5Te_3O_{14}$ around $z = 0$(a) and 0.25(b), respectively. The dimension of the unit cell is drawn in full line and that of the sub-cell in dashed line. In (b) the relatively too long Ca2–O1 and Ca3–O1 bond distances are also shown in dashed line.

octahedra does not allow the monoclinic subcell to be preserved. The true symmetry is orthorhombic instead.

Why can the ideal parent chiolite structure with the space group $I4/mmm$ not be realized in $Ca_5Te_3O_{14}$? In the simulated parent structure with $a = 7.64\,\text{Å}$ and $c = 10.47\,\text{Å}$ using $z_{(O1)} = 0.177$, $x_{(O2)} = 0.25$ and O3 at (0,0.32,0.38), the coordination of Ca2, with four short (Ca2–O1 = 2.42 Å) and two long (Ca2–O1 = 2.81 Å) bond distances, is clearly unfavorable. The coordinations of the O1 and O2 atoms are also disadvantageous. For example, O1 is surrounded by four Ca at 2.81 Å and one Te1 at 1.91 Å as a square pyramid, and O2 by two Te at 1.91 Å with Te–O2–Te 180° and four Ca at 3.25 Å. Clearly, the Ca–O distances are larger than the expected distances ($\sim$2.40–2.50 Å) [15]. Tilting of the Te1O$_6$ octahedron around [001] does not change the square pyramidal coordination of O1, but tilting around $[-110]_p$ does results in a (distorted) tetrahedron of cations around O1. The coordination of the other atoms also becomes more regular due to the tilting (Table 2).

Burchard and Rüdorff [8] reported the compounds $SrCa_4Te_3O_{14}$ to be a tetragonal chiolite with the lattice parameters $a = 7.403$ Å and $c = 10.471$ Å. In the light of the present investigation, such a description may be incorrect. Our $SrCa_4Te_3O_{14}$ sample has not yet been prepared sufficiently pure, but a preliminary study indicates that $SrCa_4Te_3O_{14}$ is likely to be an orthorhombic chiolite with the lattice constants $a = 10.5108(4)\,\text{Å}$, $b = 10.4451(4)\,\text{Å}$ and $c = 10.4755(4)\,\text{Å}$.

In conclusion, we have studied the crystal structure of $Ca_5Te_3O_{14}$ using the combined X-ray and neutron powder diffraction data. The compound adopts a chiolite-like structure with the space group $Cmca$. This type of structure has been previously observed in $BaSr_4U_3O_{14}$. The structure of $Ca_5Te_3O_{14}$ can be derived from the anion-deficient fluorite structure, but is different from that of the compounds $Ca_2Ln_3Sb_3O_{14}$, which crystallize in the related weberite-like structure.

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