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The Crystal Structure of Tveitite, an Ordered Yttrofluorite Mineral*

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Tveitite is an ordered yttrofluorite mineral with an abnormally high yttrium plus rare-earth content. It has rhombohedral symmetry (space group $R\bar{3}$) with cell contents $M_{19}X_{43}$, and is the member $n = 19$ of an homologous series of phases M_nX_{2n+5}. The hexagonal unit cell parameters are $a = 1669.20 \pm 0.09$ pm; $c = 966.64 \pm 0.08$ pm; $Z = 3$, and the structure is strongly fluorite-related. Structure analysis shows the presence of discrete M_6X_{37} clusters which consist of an octahedral arrangement of six MX_8 square antiprisms sharing corners to enclose a cuboctahedron of anions with an additional anion at its center—a 13-member ccp anion cluster. The M_6X_{37} clusters are distributed in an ordered manner within a fluorite-type matrix. The composition of tveitite has not been defined unambiguously; ideally, it is probably $Ca_{14}Y_5F_{43}$.

Introduction

Particular interest in the yttrofluorite mineral, *tveitite,* first reported by Bergstøl *et al.* (*1*), has been occasioned by two facts. First, tveitite is considerably richer in yttrium plus rare-earth cations than any previously known natural yttrofluorite, and, second, it is an *ordered,* anion-excess, fluorite-related superlattice phase; other yttrofluorites are disordered, fluorite-type solid solutions.

A small sample of tveitite was kindly given to us by Professor Neumann and Dr. Jensen of the Geological Museum, Oslo, Norway. Initially, X-ray powder and single-crystal electron diffraction studies were carried out; the results (*2*) showed that the specimen was diphasic, consisting of the ordered phase which is tveitite, and a disordered cubic solid-solution (*cα*) from which it is supposed that tveitite was formed. Moreover, tveitite was shown to have a rhombohedral unit cell (rhγ) and to be the

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* Dedicated to Professor A. F. Wells on his 70th birthday.

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member $n = 19$ of the homologous series of fluorite-related compounds, M_nX_{2n+5}, which occur in the systems LnF_2–LnF_3 (*3–6*), CaF_2–YbF_3 (*7*), and CaF_2–YF_3 (*8*). Subsequently, its structure was determined from single-crystal X-ray diffraction data, and a preliminary report of certain geometrical features thus revealed has been presented already in describing a new structural principle in anion-excess, fluorite-related superlattices (*9*). In the present paper we now give a full description and discussion of this structure.

Crystal Data and Structure Determination

Tveitite has rhombohedral symmetry, and the space group is either $R3$ or $R\bar{3}$; lattice constants are $a = 1669.20 \pm 0.09$ pm, $c = 966.64 \pm 0.08$ pm in the hexagonal representation (*2*), and this unit cell contains 57 cations, none of which is far removed from a cation site of the ideal fluorite structure.

For intensity measurements an irregular but apparently untwinned single-crystal fragment, measuring approximately $0.1 \times 0.1 \times 0.15$ mm^3, was selected and mounted on an automatic, four-circle diffractometer (CAD-4: Enraf-Nonius). Initially, the fluorite-type subcell reflections were used in determining the crystal orientation, since the supercell reflections are relatively very much weaker, but after transformation to the known superlattice cell only superlattice reflections were used in determining an exact orientation matrix.

Diffracted intensities from this crystal were measured by an ω/θ scan in the range $\theta = 3$–$29°$, and over several equivalent regions of reciprocal space, with monochromatic Mo$K\alpha$ ($\lambda = 0.71069$ Å) radiation (graphite monochromator). To these measurements the normal Lorentz and polarization corrections were applied, but because of the very irregular form of the crystal, absorption corrections were not attempted. Furthermore, since the electron diffraction studies (*2*) had shown that, even within a "single crystal," both the ordered (tveitite) and disordered ($c\alpha$) phases were intergrown, it was necessary to remove from the data set all the subcell reflections to which both phases contributed. Finally, 1164 independent superstructure reflections with observable intensity were obtained and used in the determination and refinement of the tveitite structure.

The structure was solved by Fourier methods. First, a Patterson synthesis was calculated (*10*), from which a sensible model of the distribution of cations (assumed at this stage to be 13 Ca and 6 Y), and their shifts from the ideal fluorite positions, was obtained. The number (43) and positions of the F atoms were then obtained through a succession of difference syntheses. The structure was refined (*10*) in the space group $R\bar{3}$. Initially Ca(1) and F(8) were placed in the positions $3b$ and $3a$, respectively, of this space group, and all other atoms on the general site $18f$. Each atom was also assigned an isotropic temperature factor. Refinement then converged to a conventional R value of 0.129. At this stage a difference synthesis showed significant electron density along the $\bar{3}$ axis both above and below the atoms Ca(1) and F(8). The temperature factors of these two atoms were also about 50 times greater than those of their counterparts on other sites. For further refinement, then, these two atoms were placed in the $6c$ site ($00z$, $00\bar{z}$) with a statistical occupancy of 0.5, and given z coordinates of 0.555 and 0.061, respectively. The R value dropped only slightly to 0.125, but a difference synthesis no longer showed any electron density at the ideal site of Ca(1) (0,0,0.5) and only a density corresponding to about 1.7 electrons at 0,0,0. Moreover, the temperature factors of Ca(1) and F(8) now had sensible values. The refinement was based on a weighting scheme $w = 0.007/(\sigma^2(F) + 0.123F^2)$.

A calculation with anisotropic tempera-

TABLE I

POSITIONAL PARAMETERS AND ISOTROPIC TEMPERATURE FACTORS FOR THE ATOMS OF TVEITITE IN SPACE GROUP $R\bar{3}$[a]

Atom	x	y	z	B
Y	0.0169(1)	0.1489(1)	0.1786(2)	0.60(6)
Ca(1)	0.0	0.0	0.5353(6)	2.8(5)
Ca(2)	0.2654(3)	0.2348(3)	0.1557(4)	0.1(5)
Ca(3)	0.1749(3)	0.4059(3)	0.1672(4)	1.2(3)
F(1)	0.1958(7)	0.0831(7)	0.0040(11)	1.0(2)
F(2)	0.1102(8)	0.0975(8)	0.2349(12)	1.4(3)
F(3)	0.0190(6)	0.1495(6)	0.4146(10)	0.1(5)
F(4)	0.2702(6)	0.1024(6)	0.2573(11)	0.3(2)
F(5)	0.1576(6)	0.2686(6)	0.2515(11)	0.2(2)
F(6)	0.0324(6)	0.2842(6)	0.0971(11)	0.4(2)
F(7)	0.2955(6)	0.3838(6)	0.0744(11)	0.3(2)
F(8)	0.0	0.0	0.060(9)	1.4(8)

[a] The temperature parameters, B(pm^2), are multiplied by 10^{-4}, and relate to the expression $\exp(B.\sin^2\theta/\lambda^2)$. Standard deviations in the last significant figure are given in parentheses.

ture factors for the heavy atoms led only to a very small improvement of the R value to 0.122, and the temperature factor of Ca(2) was nonpositive definite. Again, based on the chemical analysis for cerium in the mineral, a refinement was carried out in which yttrium was substituted by cerium to the extent of 20%, but no improvement in R value was achieved.

The splitting of the sites of Ca(1) and F(8) suggested that refinement of the structure in the noncentrosymmetric space group $R3$ might be more appropriate, and after several cycles of such refinement the R value converged to 0.092. In comparison with the results of refinement in $R\bar{3}$ this new refinement indicated no significant shifts of atom positions, but the standard deviations of the new positional coordinates were now a factor of two greater than before. More significantly, however, difference syntheses always showed electron density at the alternative split positions of Ca(1) and F(8). It must be concluded, therefore, that the space group $R\bar{3}$ is correct, and that there is statistical occupancy by Ca(1) and F(8) of 6*c* sites of this space group. A similar phenomenon was observed by Burns *et al.* (*11*) in their analysis of the closely related structure of $Na_7Zr_6F_{31}$.

Table I gives the final positional parameters and temperature factors obtained in the $R\bar{3}$ refinement of the tveitite structure.

Description and Discussion of the Structure

The structure analysis shows that the cation to anion ratio in tveitite is 19 : 43, and that the cation sublattice, with an ordered distribution of Ca and Y atoms, is only very slightly distorted from that of fluorite. The anion sublattice of the $M_{19}X_{43}$ rhombohedron is, by contrast, anion-rich relative to fluorite, there being 5 "excess" anions. Nature's method of accommodating such anion-excess in fluorite-related phases appears to involve simply the conversion of some parts of the primitive cubic anion sublattice of the parent to a denser, close-packed array. Thus, in the vernier phases (*12*, *13*, and references cited therein) 4^4 and 3^6 anion nets alternate along one cubic subcell direction, and the transformed parts of the parent structure are two-dimensional anion sheets. In tveitite, however, the formation of three-dimensional clusters of 13 cubic close-packed anions is observed. These clusters have the form of a filled cuboctahedron (Fig. 1), and are ordered in the structure.

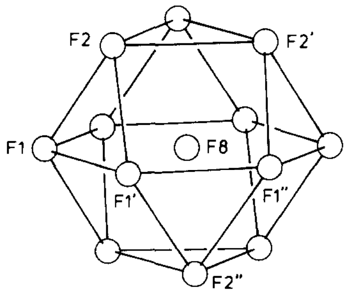

FIG. 1. Coordination polyhedron around F(8): a three-dimensional cluster of 13 cubic close-packed F^- ions.

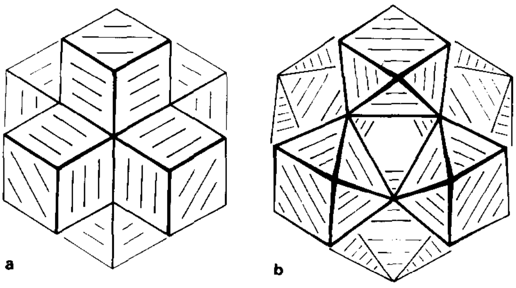

FIG. 2. Comparison of the two equivalent structural units: (a) M_6X_{32} in the fluorite structure; (b) M_6X_{37} in the structure of tveitite. The enclosed polyhedron in the M_6X_{37} unit is the cuboctahedron shown in Fig. 1.

Figure 2 illustrates an alternative and perhaps better description of the way in which the additional anions are incorporated in tveitite. In Fig. 2a an element of the fluorite-type structure is represented, which consists of six MX_8 cubes sharing edges to enclose an empty X_8 cube; such elements, of composition M_6X_{32}, then further edge-share to fill space. Figure 2b shows a new structural element, produced from the M_6X_{32} element by a simple rotation mechanism (*9*), which consists of six MX_8 square antiprisms sharing corners to enclose an empty cuboctahedron; its composition is now M_6X_{36}, which becomes M_6X_{37} when the center of the cuboctohedron is occupied by an anion, as it is in tveitite. The transformation can be written as

$$M_6X_{32}\ (\textit{fluorite}) + 5X \rightarrow M_6X_{37}\ (\textit{tveitite}).$$

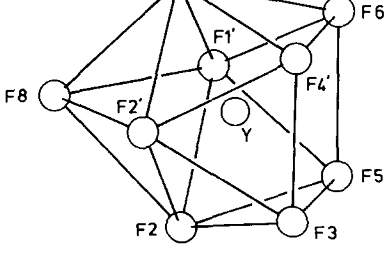

FIG. 3. The coordination polyhedron of the Y atom—a monocapped square antiprism.

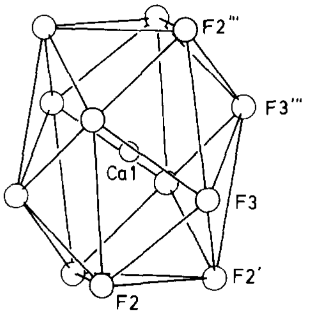

FIG. 4. Icosahedral coordination of the atom Ca(1).

The origin of the homologous series M_nX_{2n+5} is now clear. Tveitite, as already mentioned, is the member $n = 19$, and other members whose structures have been determined (e.g., $Na_7Zr_6F_{31}$ (*11*) and $Nd_{14}Cl_{32}O$ (*14*)—the members $n = 13$ and 14, respectively) contain this M_6X_{37} cluster. So does the alloy $Cr_{23}C_6$ (*15*). M_6X_{36} clusters are also known to be present in the fluorite-related structure of KY_3F_{10} (*16*).

The cations (Y) of the M_6X_{37} clusters in tveitite have an 8 + 1 coordination by anions in the form of a monocapped square antiprism (Fig. 3), the atom F(8) in the cuboctahedron being the common cap for all six square antiprisms of the cluster. These clusters are distributed along the threefold symmetry axes so that their centers occupy the positions 0,0,0; $\frac{1}{3}, \frac{2}{3}, \frac{2}{3}$ and $\frac{2}{3}, \frac{1}{3}, \frac{1}{3}$; with symmetry $\bar{3}$. Between each pair of clusters lying one above the other along $[001]_{hex}$ there is generated a somewhat distorted icosahedron of 12 F atoms, within which

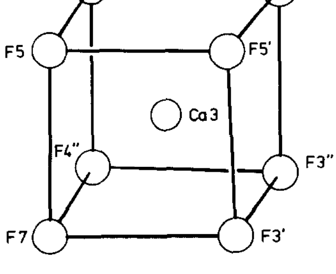

FIG. 5. Cubic coordination of the atom Ca(3).

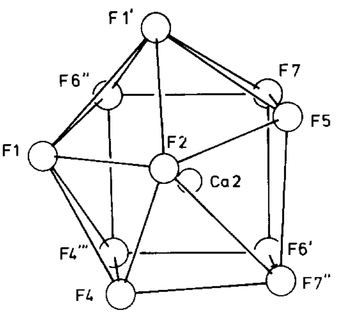

FIG. 6. The coordination polyhedron of the atom Ca(2).

the atom Ca(1) is found (Fig. 4), and these [001] columns of alternating M_6X_{37} clusters and CaF_{12} icosahedra, fused together, are embedded in a matrix of virtually unmodified fluorite-type structure, where the atom Ca(3), coordinated by eight F atoms in the form of an almost undistorted cube (Fig. 5), is found. The Ca(2) atoms occur in the boundary region between the fluorite-type matrix and the columns. These are 10-coordinated (Fig. 6), and the coordination polyhedron can be described as the combination of a half cube (on the side of the fluorite-type matrix) and a half icosahedron (on the side of the column). Alternatively, this polyhedron can be derived from a cube by substitution of the equilateral triangle F(1)–F(1')–F(2) for one corner. A similar polyhedron has been recognized by Edshammer in the structure of Pt_8Al_{21} (*17*).

Figure 7 shows drawings of these various polyhedra as they appear when viewed in planes perpendicular to the hexagonal *c* axis. Further explanation is given in the figure legend. Figure 8 then shows the polyhedra associated with a *single* cation plane parallel to [001] of the tveitite structure, and illustrates diagrammatically what the text has attempted to describe.

The most important interatomic distances are shown in Table II; these take account of the "split" character of Ca(1) and F(8). Within the square antiprisms of the M_6X_{37} cluster the Y–F distances range from 221.8 to 233.8 pm, and, as might be expected, are generally shorter than Ca–F distances. The common cap to the six square antiprisms, F(8), is significantly further away from the Y atoms (265.4 pm), so that the yttrium coordination is properly described as 8 + 1. The mean Ca–F distances vary somewhat, depending on the coordina-

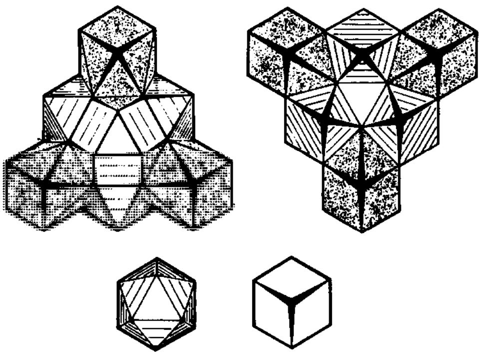

FIG. 7. Views down $[001]_{hex}$ of the various cation-centered polyhedra in the tveitite structure. Bottom left: the Ca(1) F_{12} icosahedron. Bottom right: the Ca(3) F_8 cube. Top left: the YF_8 square antiprisms (hatched) *in the bottom plane of* an M_6X_{37} cluster (see also Fig. 2b) together with the adjacent Ca(2) F_{10} polyhedra (dotted) *in the same plane*. Top right: as above, but the cations are now *in the top plane of an M_6X_{37} cluster* (see also Fig. 2b).

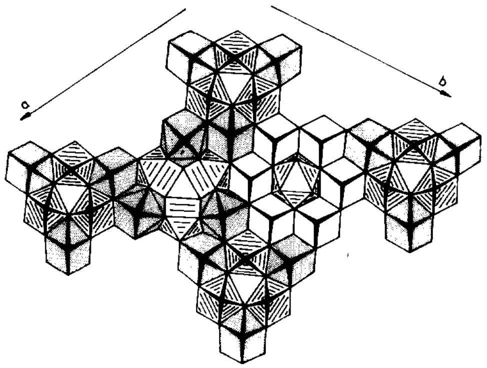

FIG. 8. A single cation plane of the tveitite structure showing the juxtaposition of the various cation-centered polyhedra. Stacking of such layers in accordance with the space group translations leads to the [001] columns of clusters and icosahedra embedded in a fluorite-type matrix, with boundary regions between (see text).

TABLE II

INTERATOMIC DISTANCES IN TVEITITE (pm)[a]

Y–F(2′)	221.8(8)	Ca(3)–F(3″)	229.3(8)
Y–F(2)	222.3(9)	Ca(3)–F(3′)	231.7(8)
Y–F(1″)	224.9(8)	Ca(3)–F(5)	234.3(8)
Y–F(1′)	225.7(9)	Ca(3)–F(4″)	235.6(8)
Y–F(3)	228.1(8)	Ca(3)–F(6)	236.0(9)
Y–F(6)	231.4(8)	Ca(3)–F(5′)	240.1(8)
Y–F(4′)	232.9(9)	Ca(3)–F(7′)	242.4(8)
Y–F(5)	233.8(7)	Ca(3)–F(7)	242.9(9)
Y–F(8)	265.4(29)	F(8)–F(2)	244.6(29)
Ca(1)–F(3‴)	244.0(8)	F(8)–F(1)	293.8(29)
Ca(1)–F(3)	266.1(8)	F(8)–F(1′)	295.3(29)
Ca(1)–F(2‴)	284.1(8)	F(8)–F(2″)	335.7(29)
Ca(1)–F(2)	340.2(9)		
Ca(2)–F(5)	236.1(8)		
Ca(2)–F(4‴)	238.6(8)		
Ca(2)–F(7)	244.4(8)		
Ca(2)–F(7″)	244.9(8)		
Ca(2)–F(6″)	246.3(9)		
Ca(2)–F(4)	248.9(8)		
Ca(2)–F(6′)	251.6(9)		
Ca(2)–F(2)	260.9(10)		
Ca(2)–F(1)	267.0(8)		
Ca(2)–F(1′)	279.6(9)		

[a] Standard deviations in the last significant figure are given in parentheses.

tion of Ca. The shortest (236.5 pm) is found for the Ca(3)F_8 cube, and this is identical, within experimental error, to the value of 236.6 pm reported for pure CaF_2 (*18*). The mean Ca(2)–F distance (251.8 pm) is somewhat longer, and longer still is the mean Ca(1)–F distance (283.6 pm). However, Ca(1) is a "split atom," so it is probably more sensible to think in terms of two groups of Ca(1)–F distances, one with six shorter (264.0 pm) and the other with six longer (303.2 pm) distances.

In spite of the denser packing of F atoms in the filled cuboctahedron, there are no unusually short F–F distances. The shortest calculated, 245 pm for F(2)–F(8), results from the shifting of F(8) from the center of the cuboctahedron. All other F–F distances are significantly longer, and compare with the value of 273.2 pm in CaF_2 (*18*).

We believe it is very significant that, in terms of both external shape and volume, the M_6X_{37} (or M_6X_{36}) cluster is virtually identical with the M_6X_{32} unit of fluorite, so that the former can be incorporated readily within a fluorite matrix. In tveitite, this occurs in an ordered manner, although the coexistence of both tveitite and *cα* in the mineral specimen shows that such ordering is still incomplete. Experiments have shown (*1, 2*) that tveitite disorders to a high-temperature cubic phase at 670°C, and that this transition cannot be reversed after weeks or months of annealing. However, we believe that the integrity of the M_6X_{37} clusters is retained in the disordered state on time average. The available evidence suggests that ease of ordering increases with increasing concentration of M_6X_{37} clusters in the fluorite matrix (*8*). In normal, disordered yttrofluorites, then, the concentration of these clusters, which contain the yttrium, is simply too low for ordering to occur, even in geological time.

One problem remaining concerns the true composition of tveitite. The careful chemical analyses carried out in the course of the Norwegian work (*1*) lead to an overall sample composition $MX_{2.252}$, with the Ca : (Y + *Ln*) ratio equal to 2.24, but the sample is not monophasic. In the tveitite structure, the three-valent cations are all in the M_6X_{37} clusters, and the *structural* formula appears as $Ca_{13}(Y + Ln)_6X_{43}$ ($MX_{2.263}$) with a Ca : (*Ln*) ratio of 2.17. The charge-balance condition then requires that the formula should be $Ca_{13}(Y + Ln)_6F_{42}O$, which is quite consistent with the analysis data. Moreover, an ordered distribution of these atoms in the $R\bar{3}$ space group is possible, the O atom being placed in the position 3*a* at the center of the cuboctahedron (F(8) in Table I). This same situation has also been assumed in the structure of the compound $Nd_{14}Cl_{32}O$ (*14*).

However, Greis (*2*) reported the appearance of a few, very weak, pseudofluorite reflections on a heavily exposed Guinier powder pattern of tveitite; these he attributed to the presence of some rare-earth oxide-fluoride. The approximate cell-edge, although not reported at the time, was measured as 5.75 Å, which is in fair agreement with the value of 5.70 Å reported by Roether (*19*) for cubic CeOF. If we now assume that tveitite *is* a pure calcium–yttrium fluoride, and that *all* the rare-earth elements present (mainly La–Sm, with Ce predominating) occur as the oxide-fluoride *Ln*OF, recalculation of the analysis data leads to the formula $Ca_{13.89}Y_{5.07}F_{43}$. For this, the M_6X_{37} clusters must contain approximately one Ca atom and five Y atoms (randomly distributed in space group $R\bar{3}$). Evidence that Ca atoms do coexist with rare-earth atoms in M_6X_{36} clusters is found in the structure of $Ba(CaLn_2)F_{10}$ (*20*); for *Ln* = Tm, Yb, Lu this compound is isostructural with KY_3F_{10}. The ideal formula for tveitite would now be written as $Ca_{14}Y_5F_{43}$, and our considered view is that this is the more probable of the two.

Acknowledgments

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