

A New Structural Principle in Anion-Excess Fluorite-Related Superlattices

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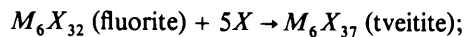
Abstract

A preliminary report on the rhombohedral structure of the ordered yttrifluorite mineral, tveitite (possible formulae: $\text{Ca}_{13+\delta}\text{Y}_{6-\delta}\text{F}_{44-\delta}$, $\text{Ca}_{14}\text{Y}_5\text{F}_{43}$ or $\text{Ca}_{13}\text{Y}_6\text{F}_{42}\text{O}$), is given. In this structure discrete M_6X_{37} groups occur, which consist of an octahedral arrangement of cation-centred square antiprisms sharing corners around the threefold axis to enclose a filled cuboctahedron of anions. The same group is found in other known fluorite-related superlattices, which suggests that it is a basic structural unit. Its formal derivation from the analogous element of fluorite is described.

Most naturally-occurring yttrifluorite is a disordered, fluorite-type solid solution containing <20% (Y,RE) F_3 . Recently, however, Bergstøl, Jensen & Neumann (1977) reported an ordered yttrifluorite from Norway (tveitite) with about 30% (Y,RE) F_3 , and an analogous mineral has been found independently by Crook (1978), occurring as small inclusions in normal yttrifluorite from the Barringer Hill district of Texas, USA.

A small sample of the Norwegian tveitite was kindly made available to us, and further studies by powder X-ray and single-crystal electron diffraction (Greis, 1978) have revealed its unit-cell geometry and place as the member $n = 19$ of the homologous series of fluorite-related compounds, M_nX_{2n+5} , in the system $\text{CaF}_2\text{-YF}_3$ (Gettmann & Greis, 1978). A structure determination on tveitite has now been carried out. The full details will be reported subsequently, but we present here the result and, emerging from it, a new structural principle which explains the existence of the series M_nX_{2n+5} .

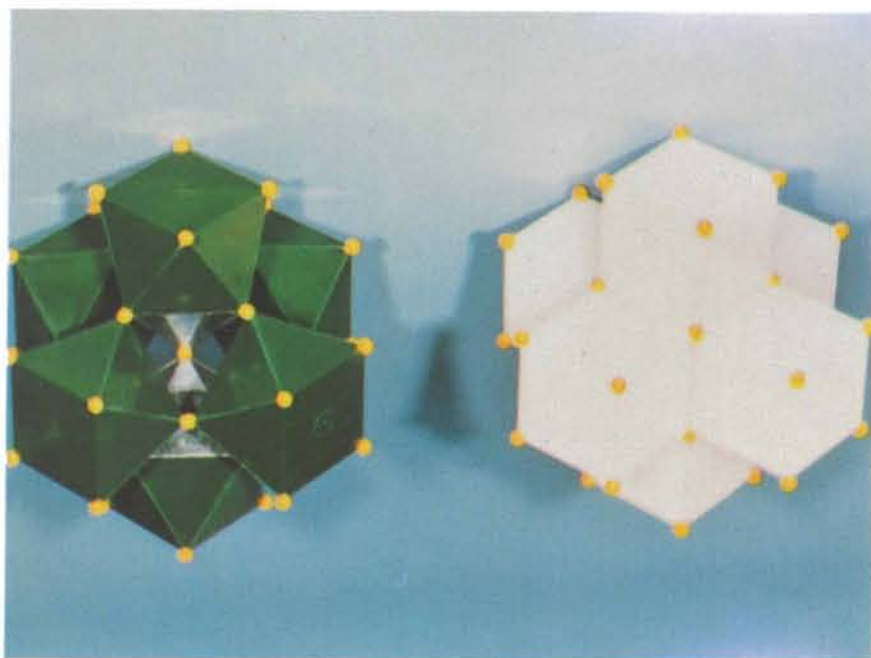
The tveitite unit cell is rhombohedral, with hexagonal parameters $a = 16.9620$ (9), $c = 9.6664$ (8) Å, $Z = 57$, and the space group is either $R\bar{3}$ or $R3$. The cations are displaced very little from their sites in the ideal fluorite structure, as is the case for most known fluorite-related superlattices, but the anion sublattice has undergone a major rearrangement with respect to that of fluorite. In order to describe this, and to emphasize the structural relationship between tveitite and its fluorite-type parent structure, we dissect from the latter and focus attention on an element which is an octahedron of six cations grouped around a threefold axis. In fluorite, each cation is coordinated by a cube of eight anions, and these MX_8 cubes share edges, so the relevant group, shown in Fig. 1(a), consists of six MX_8 cubes sharing edges to generate an empty X_8 cube in its centre. Such groups then further edge-share to fill space: this description is of course not new. In the tveitite structure, modified units, based on the same grouping of six cations around the now unique threefold axis, appear as discrete entities, and the modification is simply that the cation (yttrium) coordination polyhedra have transformed to square antiprisms which, by incorporation of additional anions, now share corners, as shown in Fig. 1(b), to enclose a cuboctahedron of anions. The centre of this cuboctahedron, as it happens, contains an anion also, which can be thought of as the common cap to all six square antiprisms. The transformation from the fluorite to the tveitite grouping can then be formulated as



the origin of the series M_nX_{2n+5} is thus immediately apparent. This same grouping of six square antiprisms around a filled cuboctahedron has been described by Nyman & Andersson (1979) in the alloy Cr_{23}C_6 .

The juxtaposition of these entities in the tveitite structure is illustrated in Fig. 2, and Fig. 3 shows an

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(a) (b)
Fig. 1. (a) Fluorite M_6X_{32} unit; (b) M_6X_{37} unit.

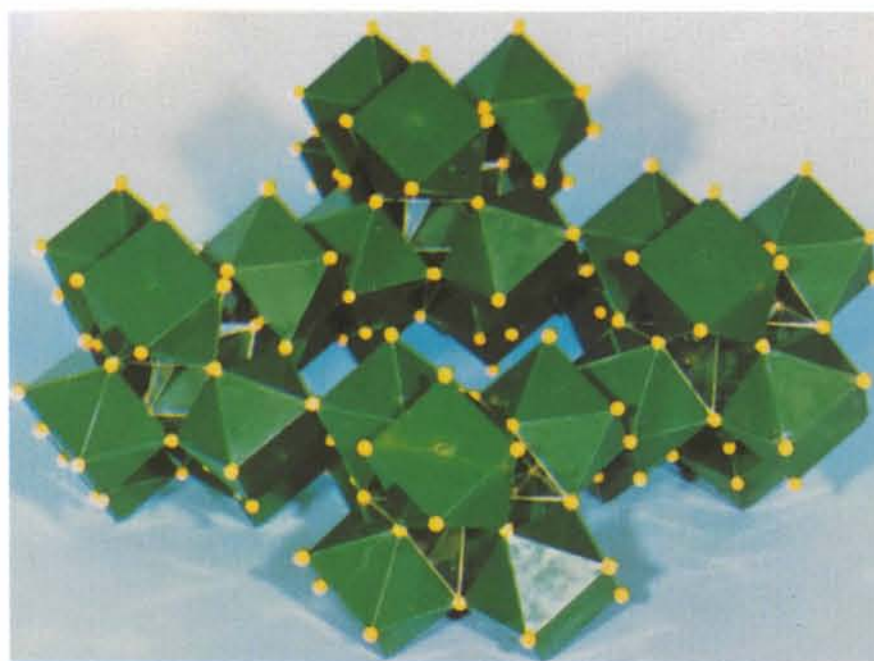


Fig. 4. Model showing the linking of M_6X_{37} units in $\text{Na}_7\text{Zr}_6\text{F}_{31}$; the Na atoms are not shown.

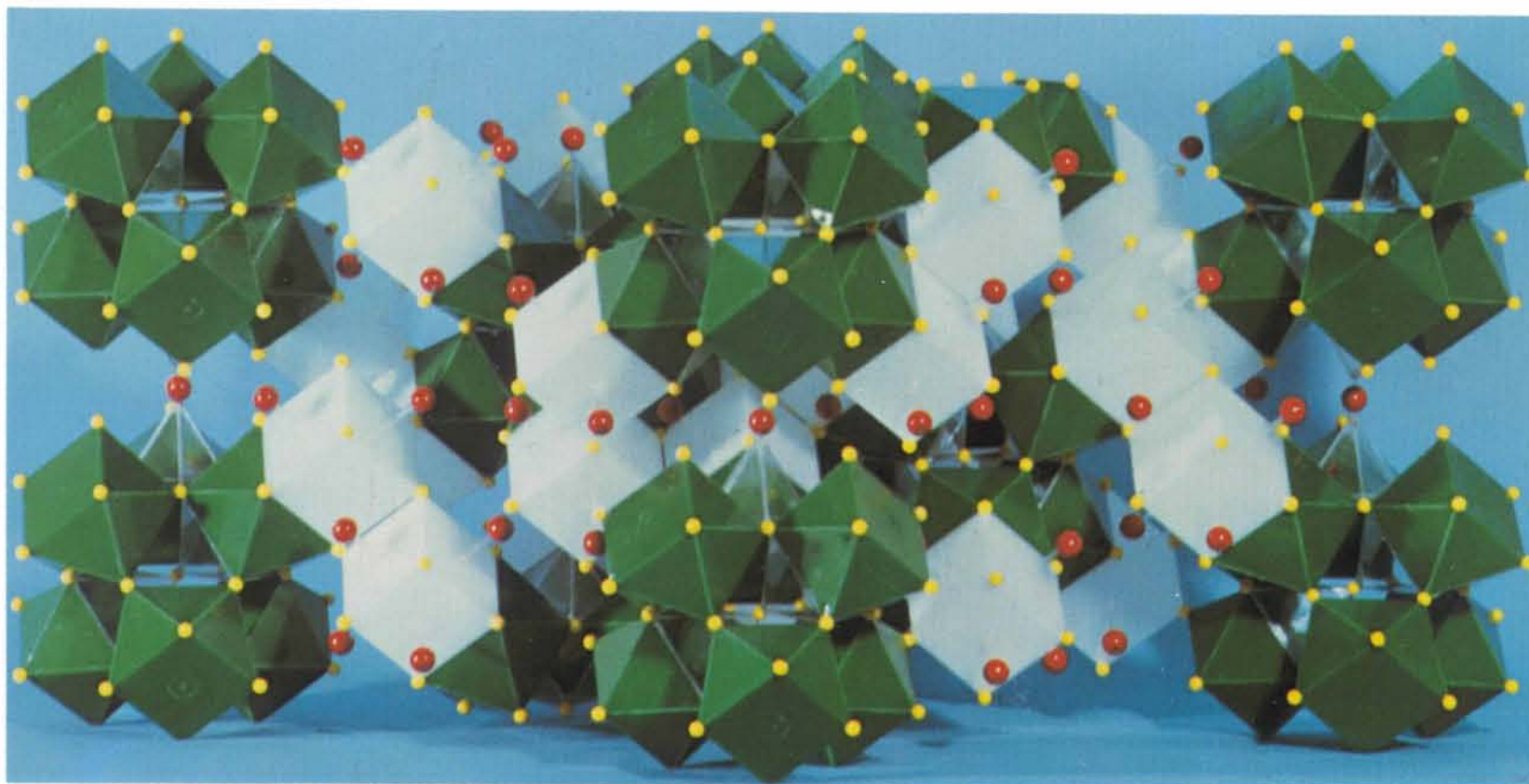


Fig. 3. Model of the tveitite structure. M_6X_{37} units are green, and Ca atoms are shown as red beads; the white cubes are empty.

idealized polyhedral model of the unit cell. Of those cations (Ca) not in the M_6X_{37} units, half are in almost undistorted cubic coordination, and the other half occur as more complex MX_{10} polyhedra. However, we will postpone further discussion of structural detail to the full report.

The significance of the M_6X_{37} grouping as a structural unit is revealed as a result of its discrete occurrence in tveitite, but its existence has been noted previously by Burns, Ellison & Levy (1968) in $\text{Na}_7\text{Zr}_6\text{F}_{31}$, the member $n = 13$ of the series M_nX_{2n+5} . In this structure, however, these groups are not discrete. Fig. 4 shows an idealized polyhedral model illustrating the way in which they are linked in $\text{Na}_7\text{Zr}_6\text{F}_{31}$, and the rhombohedral β phase of the $\text{CaF}_2\text{-YF}_3$ system (Gettmann & Greis, 1978) appears to have the same structure.

A very similar entity, M_6X_{36} (identical with M_6X_{37} except that the X anion at the centre of the cuboctahedron is missing), is only implied by Podbereskaya, Potapova, Borisov & Gatilov (1976) in describing the structure of cubic $\text{KTb}_3\text{F}_{10}$, which is isostructural with KY_3F_{10} (Pierce & Hong, 1973) and both α - and γ - $\text{KYb}_3\text{F}_{10}$ (Labeau, Aléonard, Védérine, Boutonnet & Cousseins, 1974). These authors have chosen instead to focus attention on the existence of $[\text{Tb}_6\text{F}_{32}]^{14-}$ polyanions, which consist of six octahedrally disposed cations (of a fluorite-type cation sublattice) each coordinated by eight anions in the form of a square antiprism; these share edges to enclose an unoccupied X_8 cube. This unit is derived very simply from the fluorite element of Fig. 1(a) by a 45° rotation of the outer faces of each cube, whereas the M_6X_{36} unit derives from the same rotation of the inner faces. Aléonard, Le Fur, Pontonnier, Gorius & Roux (1979) have further proposed that the M_6X_{32} unit, recognized independently by them in β - $\text{KYb}_3\text{F}_{10}$ (Aléonard, Guitel, Le Fur & Roux, 1976), is the unit common to a number of structures which they state as deriving from fluorite. We believe, however, that this M_6X_{32} grouping is not a

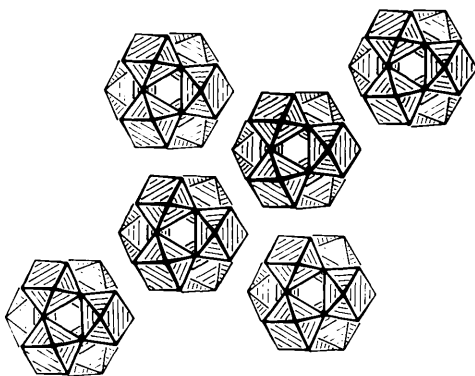


Fig. 2. M_6X_{37} units centred on equipoints of the hexagonal cell of tveitite in projection down $[001]$. Light, intermediate, and dark lines represent the levels $z = 0, \frac{1}{4}$ and $\frac{3}{4}$ respectively.

fundamental structural unit of truly fluorite-related (in the sense that the fluorite cation sublattice is retained in essence) superlattices, but rather the M_6X_{36} (or 37) unit. We have now shown that the cubic structures of KY_3F_{10} (Pierce & Hong, 1973), and its isotypes $\text{KTb}_3\text{F}_{10}$ (Podbereskaya *et al.*, 1976), α - and γ - $\text{KYb}_3\text{F}_{10}$ (Labeau *et al.*, 1974), all strictly fluorite-related, contain M_6X_{36} units connected in such a way as to generate M_6X_{32} groups. Moreover, as previously stated, both tveitite and $\text{Na}_7\text{Zr}_6\text{F}_{31}$ are known structures containing M_6X_{37} units, but not M_6X_{32} groups, and we have succeeded so far in building from M_6X_{37} units models of the as yet undetermined structures of $M_2^{\text{II}}(\text{RE})\text{F}_7$ and $M_9^{\text{II}}(\text{RE})_5\text{F}_{33}$ (Greis, 1979), which are consistent with the known unit-cell geometries and space groups: these do not contain M_6X_{32} groups either. It must be noted, however, that in β - $\text{KYb}_3\text{F}_{10}$ (Aléonard *et al.*, 1976), which is not fluorite related according to our definition, only M_6X_{32} groups occur: the M_6X_{36} units of α - and γ - $\text{KYb}_3\text{F}_{10}$ are destroyed in the transformation to β as a result of the change in the stacking of cation layers perpendicular to c_{hex} from $-ccc-$ (as in fluorite) to $-hchc-$.

Nevertheless, we agree with Aléonard *et al.* (1979) that the conversion of an MX_8 cube to a square antiprism is a fundamental first step in the formation of many anion-excess, fluorite-related compounds.

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References

- ALÉONARD, S., GUITEL, J. C., LE FUR, Y. & ROUX, M. T. (1976). *Acta Cryst.* B32, 3227–3235.
- ALÉONARD, S., LE FUR, Y., PONTONNIER, L., GORIUS, M. F. & ROUX, M. T. (1979). *Ann. Chim.* 3, 417–427.
- BERGSTØL, S., JENSEN, B. B. & NEUMANN, H. (1977). *Lithos*, 10, 81–87.
- BURNS, J. H., ELLISON, R. D. & LEVY, H. A. (1968). *Acta Cryst.* B24, 230–237.
- CROOK, W. W. (1978). *Mineral. Rec.* 9, 387.
- GETTMANN, W. & GREIS, O. (1978). *J. Solid State Chem.* 26, 255–263.
- GREIS, O. (1978). *Rev. Chim. Minér.* 15, 481–493.
- GREIS, O. (1979). *The Rare Earths in Modern Science and Technology*, Vol. II. New York: Plenum Press. In the press.
- LABEAU, M., ALÉONARD, S., VÉDRINE, A., BOUTONNET, R. & COUSSEINS, J. C. (1974). *Mater. Res. Bull.* 9, 615–624.
- NYMAN, H. & ANDERSSON, S. (1979). *Acta Cryst.* A35, 305–308.
- PIERCE, J. W. & HONG, H. Y. P. (1973). *Proc. Tenth Rare Earth Research Conference*, edited by C. J. KEVANE, pp. 527–537. US A.E.C. Tech. Inf. Centre.
- PODBEREZSKAYA, N. V., POTAPOVA, O. G., BORISOV, S. V. & GATILOV, YU. V. (1976). *J. Struct. Chem.* 17, 948–950.