Alkaline earth fluoride apatites can be divided into two groups according to their structural behaviour when substituted by rare earth and sodium ions. Symmetry conditions found for the substituted Ca and Sr compounds show that the P6/m space group, characteristic for the apatites, persists also after substitution (I. Mayer, R. S. Roth and W.S. Kron, J. Solid State Chem. 11, 33 (1974)), while the substituted Ba compounds crystallize in the P6 and P5 space groups (M. Mathes, I. Mayer, B. Dickens and L.W. Schroeder, J. Solid State Chem. 28, 79 (1979)).

The present paper reports the structure of Ca$_2$Eu$_2$Na$_2$(PO$_4$)$_6$F$_2$ by single crystal X-ray determination using a Philips four circle automatic diffractometer.

The unit cell was found to be hexagonal, a = 9.384 and c = 6.902 A. The structure was refined by the full matrix least squares technique. The final value of R is 0.072 for 421 observed reflections.

The three different ions in the column positions are occupied by all the Na ions of the composition, Ca$^{2+}$ ions and a small amount of Eu$^{3+}$. The triangle sites contain only two different ions: most of the Eu (~80% of the composition) and Ca.

The different ions in the column position are non-commensurate to oxygen on the average. Ca$^{2+}$ and Eu$^{3+}$ in the triangle positions are six-coordinate.

Results thus show that the distribution of ions is different in the Ca than in the Ba compounds. The most significant difference observed is the preference of the triangle sites by the rare earth ions in case of a Ca compound, while in rare-earth substituted Ba compounds the rare earth ions are found to occupy column positions.


A detailed phase study of the system Y$_2$O$_3$-YF$_3$ (Mann and Bevan, J. Solid State Chem. (1972) 5, 410) showed that in the composition region X$Y_2$O$_3$ and X$Y_2$F$_3$ (X = Y) each and every phase prepared had its own unique structure, these individual structures, however, being closely related to each other and to the parent fluoro-type. A subsequent single-crystal structure analysis of the phase Y$_2$O$_3$F$_3$ (Bevan and Mann, Acta Cryst. (1975) B31, 1406) revealed the underlying structural principle, now known as the "vernier principle" (Hyde, Bagshaw, Andersson and O'Keeffe, Ann. Rev. Mater. Sci. (1974) 4, 43). In this structure (see Fig. 1) the Y$^{3+}$ cations are little displaced from the ideal fluoride sites, and the same is true for the other 15 anions - these constitute a 4-net at c = h. By contrast, the remaining anions (at h = 0) constitute a denser 3-net. Fig. 1 shows clearly the vernier effect resulting from the coincidences along [001] of these two non (semi)-commensurate nets (Makovicky and Hyde, Structure and Bonding, in press), which repeat after 8 "sub-lattice" vectors in this direction of the 3$^*_n$ and 7 such vectors of the 4$^*_n$ net.

This paper describes the structures, similar in kind and also based on a unit-vernier principle, of the compounds Y$_2$O$_3$F$_3$ and Y$_2$O$_3$F$_7$, which, like the compound Y$_2$O$_3$F$_3$, are members of the homologous series Y$_2$O$_3$-YF$_3$. The structure of the intermediate phase Y$_2$O$_3$F$_7$ has also been described, following Makovicky and Hyde, in terms of a multiple vernier (near coincidences of the non-commensurate 3$^*_n$ and 4$^*_n$ nets occur at intervals corresponding to those in both Y$_2$O$_3$F$_3$ and Y$_2$O$_3$F$_7$), or, alternatively, in terms of "intergrowth" of these two primary phases: Y$_2$O$_3$F$_3$ + Y$_2$O$_3$F$_7$.


Small single crystals of phases in the systems Na$_2$O:TiO$_2$, Ba$_2$:Nd$_2$:Ti$_2$O$_7$, Ba$_2$O:Al$_2$:TiO$_2$ and Ba$_2$O:Al$_2$:Ti$_2$O$_7$ were synthesized by melting and very slow cooling of various compositions in the ternary systems.

The compound Na$_2$Ti$_4$O$_9$ was found to be orthorhombic, space group Pnma a=28.156±.001, b=13.991±.001, c=10.072±.001. X-ray diffraction patterns indicated that Ba$_2$Nd$_2$:TiO$_7$ is orthorhombic, space group Pnma or Cmc2, a=35.289±.003, b=13.991±.001, c=7.666±.007 but electron diffraction revealed that the a-axis is really doubled (a=7.722) and the true space group is monoclinic, Ba$_2$Nd$_2$:TiO$_7$ is orthorhombic, space group Phm or Pba$_2$, a=22.346±.002, b=12.201±.001, c=3.840±.000. Ba$_2$:Al$_2$:Ti$_2$O$_7$ is orthorhombic, space group Phm or Pn2$_1$, a=7.138±.0006, b=28.156±.001, c=13.991±.0004 and preliminary results indicate that Ba$_2$:Al$_2$:Ti$_2$O$_7$ is monoclinic, space group C2/m, C22, or C2, a=15.713, b=11.341, c=8.985, β=109.5°.

Ideal structures of Ba$_2$:Nd$_2$:Ti$_2$O$_7$ and Ba$_2$:Al$_2$:Ti$_2$O$_7$ were deduced from high resolution electron microscope lattice images. The Ba$_2$:Nd$_2$:Ti$_2$O$_7$ phase consists of neodymium titanate perovskite-like blocks three octahedra wide, with similar distortions to those found in GdTiO$_3$, separated by barium ions. The compound Ba$_2$:Al$_2$:Ti$_2$O$_7$, on the other hand, consists of chains of 7-titanium-oxygen octahedra, edge shared as in rutile, separated by alternate rows of 8-coordinated neodymium and 6-coordinated titanium. These rows are inclined, to form a cavity occupied by 10-coordinated Ba ions.