

08.2-13 THE CRYSTAL STRUCTURE OF $\text{Ca}_6\text{Eu}_2\text{Na}_2(\text{PO}_4)_6\text{F}_2$ By I. Mayer and S. Cohen, Department of Inorganic and Analytical Chemistry, Hebrew University, Jerusalem, Israel.

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 $\text{P6}_3/\text{m}$ space group, characteristic for the apatites, persists also after substitution (I. Mayer, R. S. Roth and W.E. Brown, *J. Solid State Chem.* **11**, 33 (1974)), while the substituted Ba compounds crystallize in the P6 and P3 space groups (M. Mathew, I. Mayer, B. Dickens and L.W. Schroeder, *J. Solid State Chem.* **28**, 79 (1979)).

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

The unit cell was found to be hexagonal, $\text{P6}_3/\text{m}$, with $a = 9.384$ and $c = 6.902$ Å. The structure was refined by the full matrix least squares technique. The final value of R is 0.072 for 421 observed reflections.

The structure contains disordered cations in the column as well as in the triangle positions. The column cation sites 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 three different ions in the column position are nine-coordinated to oxygens on the average. Ca^{2+} and Eu^{3+} in the triangle positions are six-coordinated.

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.

and 4^4 nets occur at intervals corresponding to those in both $\text{Y}_6\text{O}_5\text{F}_8$ and $\text{Y}_5\text{O}_4\text{F}_7$, or, alternatively, in terms of "intergrowth" of these two primary phases: $\text{Y}_{17}\text{O}_{14}\text{F}_{23} = 2(\text{Y}_6\text{O}_5\text{F}_8) + \text{Y}_5\text{O}_4\text{F}_7$.

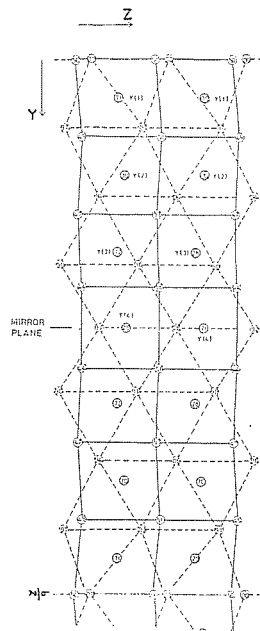


Figure 1

08.2-14 THE NON-COMMENSURATE STRUCTURES OF SOME YTTRIUM OXIDE FLUORIDES. By J. Mohyla, D.J.M. Bevan and M.R. Taylor, The Flinders University of South Australia, Bedford Park, South Australia, and B.F. Hoskins and R.J. Myers, Department of Inorganic Chemistry, University of Melbourne, Vic. Australia.

A detailed phase study of the system $\text{Y}_2\text{O}_3\text{-YF}_3$ (Mann and Bevan, *J. Solid State Chem.* (1972) **5**, 410) showed that in the composition region $\text{XY}_{2.12}$ to $\text{YX}_{2.22}$ ($X = \text{O}+\text{F}$) each and every phase prepared had its own unique structure, these individual structures, however, being closely related to each other and to the parent fluorite-type. A subsequent single-crystal structure analysis of the phase $\text{Y}_7\text{O}_6\text{F}_9$ (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 cations are little displaced from the ideal fluorite sites, and the same is true for 7 of the 15 anions - these constitute a 4^4 net at $x \approx \frac{1}{2}$. By contrast, the remaining anions (at $x \approx 0$) constitute a denser 3^6 net. Fig. 1 shows clearly the vernier effect resulting from the coincidences along $[010]$ 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 3^6 net and 7 such vectors of the 4^4 net.

This paper describes the structures, similar in kind and also based on a unit-vernier principle, of the compounds $\text{Y}_6\text{O}_5\text{F}_8$ and $\text{Y}_5\text{O}_4\text{F}_7$, which, like the compound $\text{Y}_7\text{O}_6\text{F}_9$, are members of the homologous series $\text{Y}_n\text{O}_{n-1}\text{F}_{n+2}$. The structure of the intermediate phase $\text{Y}_{17}\text{O}_{14}\text{F}_{23}$ has also been determined, and is described, following Makovicky and Hyde, in terms of a multiple vernier (near coincidences of the non-commensurate 3^6

08.2-15 SYNTHESIS, SYMMETRY AND STRUCTURE OF TITANATE SINGLE CRYSTALS. By R. S. Roth, H. S. Parker, and M. M. Koob, National Bureau of Standards, Washington, D.C. 20234 and A. Olsen, University of Oslo, Oslo, Norway.

Small single crystals of phases in the systems $\text{Nd}_2\text{O}_3:\text{TiO}_2$, $\text{BaO}:\text{Nd}_2\text{O}_3:\text{TiO}_2$, $\text{BaO}:\text{Al}_2\text{O}_3:\text{TiO}_2$ and $\text{BaO}:\text{MgO}:\text{TiO}_2$ were synthesized by melting and very slow cooling of various compositions in the ternary systems.

The compound $\text{Nd}_4\text{Ti}_9\text{O}_{24}$ was found to be orthorhombic, space group Fddd $a=35.289 \pm 0.003$, $b=13.991 \pm 0.001$, $c=14.479 \pm 0.001$ Å. X-ray diffraction patterns indicated that $\text{BaNd}_2\text{Ti}_3\text{O}_{10}$ is orthorhombic, space group Cmcm or $\text{Cmc}2$, $a=3.8655 \pm 0.0003$, $b=28.156 \pm 0.003$, $c=7.6661 \pm 0.0007$ Å but electron diffraction revealed that the a -axis is really doubled ($a=7.772$) and the true unit cell is monoclinic. $\text{BaNd}_2\text{Ti}_5\text{O}_{14}$ is orthorhombic, space group Pbam or $\text{Pba}2$, $a=22.346 \pm 0.002$, $b=12.201 \pm 0.001$, $c=3.8404 \pm 0.0003$ Å. $\text{BaAl}_6\text{TiO}_{12}$ is orthorhombic, space group Pnmm or $\text{Pnn}2$, $a=7.1385 \pm 0.0006$, $b=4.8648 \pm 0.0004$, $c=13.597 \pm 0.002$ Å and preliminary results indicate that $\text{Ba}_3\text{Al}_{10}\text{TiO}_{20}$ is monoclinic, space group $\text{C}2/\text{m}$, Cm or $\text{C}2$, $a=15.754$, $b=11.341$, $c=4.985$ Å, $\beta=109.5^\circ$.

Ideal structures of $\text{BaNd}_2\text{Ti}_3\text{O}_{10}$ and $\text{BaNd}_2\text{Ti}_5\text{O}_{14}$ were deduced from high resolution electron microscope lattice images. The $\text{BaNd}_2\text{Ti}_3\text{O}_{10}$ 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 $\text{BaNd}_2\text{Ti}_5\text{O}_{14}$, 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.