In a search for new fluorescent materials, we have recently prepared and reported the structures of several rare earth halogen complexes such as the Na₃MnF₅·H₂O. The crystal structures were determined using 4-circle diffractometer X-ray data. In the form of a trigonal prism, the Mn atom is coordinated to four fluorine atoms and one oxygen atom. The crystal structure of Na₃MnF₅·H₂O is compared with those of other rare earth halogen complexes.

The crystal structure of Sr₂P₂O₇ is reported to be isostructural with thortveitite, (Ca,Na)₂SiO₃. Crystals of Sr₂P₂O₇ grow in air at 1550°C from aqueous hydrofluoric acid solutions of SrF₂ crystallisation from a three-dimensional network of hydrogen bonds. The unirradiated samples were prepared by heating SrF₂ at 1550°C in air at 1550°C. Powder photographs were obtained of these oxides using the Debye Scherrer method.

The irradiated specimen was a pellet which had been wrapped in aluminium foil and sealed into a helium filled stainless steel capsule before irradiation in DFR at 10 22 n cm⁻² giving an estimated burn-up of 0.03%.

Measurements were made on all the unambiguously indexed Bragg reflections which could be observed. The lattice parameters were determined with the program FIRESTAR (Astle G and Ferguson I F, UKAEA TRG Report 1812) and compared with those of other thortveitite-like phases.
The measured parameters and the two sigma errors in Å are

\[
\begin{align*}
\text{SiO}_3 & = 14.1757 \pm 0.0057 \\
b & = 3.6262 \pm 0.0014 \\
c & = 8.8502 \pm 0.0033 \\
\beta & = 100.056 \pm 0.034^\circ \\
X_{\text{SiO}} & = 7.958 \pm 0.005 \text{ g cm}^{-3} \\
\end{align*}
\]

\[
\begin{align*}
\text{O}_2 & = 14.1088 \pm 0.0058 \\
b & = 3.6020 \pm 0.0013 \\
c & = 8.8051 \pm 0.0027 \\
\beta & = 100.063 \pm 0.0031 \\
X_{\text{O}_2} & = 7.498 \pm 0.005 \text{ g cm}^{-3} \\
\end{align*}
\]

\[
\begin{align*}
\text{SiO}_3 \text{ irradiated } & = 9.9975 \pm 0.0028 \\
b & = 3.5740 \pm 0.0006 \\
c & = 8.7642 \pm 0.0021 \\
\beta & = 100.041 \pm 0.0025 \\
X_{\text{SiO}} & = 8.306 \pm 0.003 \text{ g cm}^{-3} \\
\end{align*}
\]

Now monoclinic europia swells when it is irradiated under these conditions by ∼ 5%. Since the crystal lattice parameters do not change it is clear that the swelling owes its origin entirely to vacancy clustering as already observed (Pearse J H, in UKAEA AERE Report 10116 pp 42–43).

The lattice parameters for the unirradiated oxides should be compared with other determinations for the samaria-gadolinia binary system (Ferguson I F, Acta Cryst. A 31 (2) 1975 569). It is also interesting to compare these results with those obtained for NaO₂-stabilised face centred cubic europia irradiated under the same conditions. There the lattice parameter expanded from 3.5704 ± 0.0008 to 3.5743 ± 0.0010 corresponding to an increase in length of 0.075% (Rayton A, in UKAEA AERE Report 10116 p 44).

The final model (R=0.048 for 5 free parameters) contains a tetrahedral framework [Al₆₄Si₄2O₁₂] with cristobalite topology and random distribution of Al and Si. The oxygen atoms lie statistically on one of six sites at 41.2 pm off the T-T line, which corresponds to a tetrahedral rotation of ±17.0°/2 and leads to a distance (Al₁₁₁)-0 =107.7(2) pm and an angle T=0-T=T=152.0(5)°. Potassium ions occupy statistically 2/3 of the framework cavities, most of them at 32e, slightly off the cavity’s center at 8b. This position is discussed in terms of electrostatic repulsion between potassium ions in neighbouring cavities, since it permits non-bonding distances K-K(trans)=564 pm and K-K(clis)=598 pm, which are considerably longer than for the ideal 8b site with K=333.3 pm. An ordered model based on all-trans configuration between neighbouring potassium pairs is proposed. It gives an interesting explanation for the observed stoichiometry and provides a possible twin mechanism which might account for a domain structure.

Clear octahedral crystals with composition close to \(\text{O}_2 \text{O}_{1.5} \text{Si}_{1.5} \text{Al}_{1.5} \text{K}_1 \text{Na}_1 \text{A}_1\text{Si}_3 \text{O}_{12} \cdot \text{H}_2\text{O} \) were grown at 850-1000°C from a mixture of the oxides in fused KF.

Powder diagrams including back-reflections and internal Si standard, as well as Weissenberg photographs (CuKα, spot and integrated reflections) for 11 crystals from 4 different syntheses led invariably to the cubic diffraction symmetry mm3m21, corresponding to space group Fm3m with \(\omega=765(2)\) pm and \(\delta=4.4\), the observed density being 2.603(5) g/cm³. A very small deviation from cubic symmetry (\(\text{La}^2=0.1\%\)), as suggested from the optical behaviour and peak widths in 2θ with occasional splitting of back-reflections, occurs possibly within twin domains and was not resolved in the present study.

For three samples, about 350 X-ray intensities were collected on an automatic single crystal diffractometer, using MoKα radiation and up to \(2\theta=93°\). After LP correction and data reduction, a total of 87 unique structure amplitudes was obtained, with internal consistency errors of \(\text{R}_1=0.0060(0.010,0.010)\) for the assumed symmetry and without appreciable differences for the three samples.

Symbolic addition gave the positional parameters for all atoms, with T=1, S1 at 8d, E statistically at 8h, and 0 near to 16c, plus a further peak at 32e with \(x=0.41\), which accounts for the existence of 4n,4n,4n,2 reflections and has been interpreted as an additional site for potassium. During refinement, several constraints have been applied concerning the repartition of potassium and the representation of oxygen either by anisotropic thermal motion or processing about the T-T line.