08.2–9 STRUCTURAL STUDIES OF SOME NEW RARE EARTH METALLATES.

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In a search for new fluorescent materials, we have recently prepared and reported the structures of several rare earth halo tungstates where W is coordinated only to oxygen. In $La_3WO_6Cl_3$, the tungsten is coordinated to six oxygens in a trigonal prismatic arrangement, while in $LaWO_4Cl$ it is five coordinated in the form of a trigonal bipyramid, and in $GdWO_4Cl$ it is tetrahedral. Although similar compounds exist for molybdenum compositions containing niobium are relatively rare. The structure of $Pr_3NbO_4Cl_6$ will be compared with that of the recently reported $LaNb_2O_6Cl$, where the chloride is part of the coordination sphere of the rare earth element.

08.2–10 JAHN-TELLER-EFFECT AND CRYSTAL STRUCTURE IN THE SODIUM FLUOROMANGANATES(III): Na_2MnF_5 AND $Na[MnF_4(H_2O)_2]\cdot H_2O$.

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Single crystals of Na_2MnF_5 and the novel hydrate $Na[MnF_4(H_2O)_2]\cdot H_2O$ have been grown from aqueous hydrofluoric acid solutions of Mn^{3+} and Na^+. The crystal structures were determined from 4-circle diffractometer X-ray data.

Na_2MnF_5. Space group $P2_1/c$, $Z = 4$, $a = 7.719$ $b = 5.236$ $c = 10.862$ Å, $\beta = 108.99°$, $R_w = 2.3\%$ for 1679 reflections. The structure consists of kinked trans-chains of $[MnF_4F_{2/2}]^{2-}$ octahedra interconnected by 7-coordinated Na-ions. The pronounced lengthening of the axial Mn-F bonds ($\bar{d}(Mn\text{-}F)_{ax} = 2.109(1)$ Å, $\bar{d}(Mn\text{-}F)_{eq} = 1.849(1)$ Å) is partly due to the Jahn-Teller-effect of the d^4-high-spin configuration of Mn^{3+}.

$Na[MnF_4(H_2O)_2]\cdot H_2O$. Space group $C2/c$, $Z = 8$, $a = 16.381$ $b = 6.676$ $c = 11.303$ Å, $\beta = 103.78°$, $R_w = 3.2\%$ for 1696 reflections. Here, isolated trans-$[MnF_4(H_2O)_2]^-$ octahedra and the water of crystallisation form a three-dimensional network of hydrogen bonds. The H_2O ligands at one of the two crystallographically different anions participate in three H-bonds: Two as H - donator (d(O-H...F) 2.637 Å and 2.690 Å) as usual and, in addition, a third one as H - acceptor (d(O...H-O) 2.832 Å). In contrast to the common planar $M\text{-}OH_2$ geometry in aquo complexes the O surrounding is distorted tetrahedral. This peculiarity is attributed to the severe weakening of the $Mn\text{-}OH_2$ bond by the J.-T. effect (d(Mn-O) 2.246, $\bar{d}$(Mn-F) 1.837 Å).

08.2–11 STRUCTURAL STUDIES OF THORTVEITITE-LIKE $Mn_2P_2O_7$

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The crystal structure of $Mn_2P_2O_7$ is reported to be isomorphous with thortveitite, $(Sc,Y)_2Si_2O_7$ (Zachariasen, Z. Kristallogr. 73, 1, 1930). It has recently been refined in space group $C2/m$ (Tondon & Calvo, Ind. J. Pure Appl. Phys. 19, 107, 1981) although with a high R_F factor, 0.12. The results indicated a very high thermal motion of the bridging oxygen and PO_4 tetrahedra which were more regular than they should be according to theory (Cruickshank, J. Chem. Soc. 5486, 1961), a fact which has also been noted for many other thortveitite-like $M_2X_2O_7$ compounds (M=Mg,Mn,Co,Cu,Zn and X=Si,P,V,As). We now report on some crystallographic studies of $Mn_2P_2O_7$ by use of X-ray single-crystal data as well as X-ray and neutron powder diffraction data and ^{57}Fe Mössbauer spectroscopy of iron-doped manganese diphosphate. The experimental data indicate the centro-symmetrical space group $C2/m$, although with a disorder of the bridging oxygen so that P-O-P is no longer linear but 166°. The corner-sharing PO_4 tetrahedra are somewhat distorted, with P-O distances in the region 1.52-1.58 Å ; the mean value is 1.54 Å. The Mn-O distances are in the region 2.16-2.32 Å; mean 2.20 Å.

The structural results for $Mn_2P_2O_7$ are compared with results of other thortveitite-like phases.

08.2–12 LATTICE PARAMETERS OF MONOCLINIC Sm_2O_3, Eu_2O_3, Gd_2O_3, AND FAST NEUTRON IRRADIATED Eu_2O_3.

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Monoclinic europia is being assessed for use in fast reactor control rods. Therefore its physical properties are being determined before and after fast neutron irradiation. These properties include its crystal lattice parameters.

Since the measurements were difficult it was necessary to determine the lattice parameters of samaria and gadolinia as well as europia.

The unirradiated samples were prepared by heating Specpure oxides in air at 1500°C. Powder photographs were obtained of these oxides using the Debye Scherrer method. V filtered Cr X-radiation was used. The potential applied to the X-ray tube was chosen to be 44 kV to avoid bremsstrahlung induced fluoresence of the lanthanide atoms.

The irradiated specimen was a pellet which had initially been sintered at 1550°C and had then a measured density of 7.65 g cm^{-3}. It had been wrapped in molybdenum foil and sealed into a helium filled stainless steel capsule before irradiation in DFR at 650°C (nominal) to a total fast neutron dose of ~ 3 x 10^{22} n cm^{-2} giving an estimated burn-up of 0.03 captures per atom. Measurements were made on the freshly ground and polished surface of such a pellet using a specially designed diffractometer which employed monochromatised Cu Kα radiation (Wait E et al., Radiation Damage in Solids (IAEA) 1962 Vienna, Vol. II).

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).

The measured parameters and the two sigma errors in Å are

	Sm_2O_3		Eu_2O_3
a =	14.1767 ± 0.0057	a =	14.1088 ± 0.0058
b =	3.6262 ± 0.0014	b =	3.6020 ± 0.0013
c =	8.8502 ± 0.0033	c =	8.8051 ± 0.0027
β =	100.056 ± 0.034°	β =	100.063 ± 0.0031
Xaℓρ =	7.758 ± 0.005 g cm^{-3}	Xaℓρ =	7.958 ± 0.005 g cm^{-3}

	Gd_2O_3		irradiated Eu_2O_3
a =	14.0972 ± 0.0028	a =	14.1083 ± 0.0073
b =	3.5740 ± 0.0006	b =	3.6018 ± 0.0013
c =	8.7642 ± 0.0021	c =	8.7988 ± 0.0042
β =	100.041 ± 0.020	β =	100.042 ± 0.041
Xaℓρ =	8.306 ± 0.003 g cm^{-3}		

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 (Pearce 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. A31 (S.3) (1975) S.69.

It is also interesting to compare these results with those obtained for MoO_3-stabilised face centred cubic europia irradiated under the same conditions. There the lattice parameter expanded from 5.3704 ± 0.0008 to 5.3745 ± 0.0010 corresponding to an increase in length of 0.07% (Huyton A, in UKAEA AERE Report 10116 p 44).

08.2–13 THE AVERAGE STRUCTURE OF $\square_{0.7}K_{1.3}[Al_{1.3}Si_{0.7}O_4]$, AN ALKALI-DEFICIENT COMPOSITION BASED ON A FRAMEWORK WITH CRISTOBALITE TOPOLOGY.

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Clear octahedral crystals with composition close to $\square_{0.7}K_{1.3}[Al_{1.3}Si_{0.7}O_4]$ 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 m3mFd--, corresponding to space group Fd3m with a=765(2) pm and Z=4, the observed density being 2.603(5) g/cm³. A very small deviation from cubic symmetry ($\Delta a/a \approx 0.1\%$), 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 2θ=83°. After LP correction and data reduction, a total of 87 unique structure amplitudes was obtained, with internal consistency errors of R_i=0.006(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=Al,Si at 8a, K statistically at 8b, and O 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 precessing about the T-T line.

The final model (R=0.048 for 5 free parameters) contains a tetrahedral framework $[Al_{1.3}Si_{0.7}O_4]$ 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 ϕ=17.0°↻**a** and leads to a distance (Al,Si)-O =170.7(2) pm and an angle T-O-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)= =364 pm and K-K(cis)=359 pm, which are considerably longer than for the ideal 8b site with K-K=331.3 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.

08.2–14 K- AND Rb-EXCHANGED NEPHELINE HYDRATE I

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The crystal structures of the K^+- and Rb^+-exchanged forms of the microporous framework silicate nepheline hydrate I (NHI) were refined in space group $Pnm2_1$ to R = 0.032 and R = 0.048, respectively, using single crystal X-ray diffraction data. Lattice constants: a = 8.113(3), b = 15.223(2), c = 5.1817(7) Å for KNHI, and a = 8.0802(8), b = 15.259(2), c = 5.1584(5) Å for RbNHI (subcell). Compositions of $K_{1.1}Na_{1.9}Al_3Si_3O_{12}\cdot H_2O$ and $RbNa_2Al_3Si_3O_{12}\cdot H_2O$, Z = 2 were indicated by the least-squares refinements.

Both structures contained two Na^+ ions which were but little affected by the ion-exchange process, a behaviour that is also exhibited by CsNHI (Hansen and Fälth, Z. Kristallogr. (1983), *164*, 79). The two Na atoms coordinated by 7 framework O atoms were situated in a void built of 6-rings.

In the 8-ring channels the exchange was complete, K^+ and Rb^+ occupied similar sites in the vicinity of an elongated 8-ring. In KNHI the coordination sphere was completed by two symmetry-related water molecules, a situation which was probably paralleled in RbNHI.

The main difference between the two structures was that KNHI had a second cation in the 8-ring tunnel. This K^+ ion provided the necessary charge compensation for the 10 % vacancy in one of the Na sites.