

08.2-9 STRUCTURAL STUDIES OF SOME NEW RARE EARTH METALLATES. By J. C. Calabrese and L. Brixner, Central Research and Development Dept., Experimental Station, E.I. du Pont de Nemours and Co., Wilmington, DE 19898, U.S.A.

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  $\text{La}_3\text{WO}_8\text{Cl}_3$ , the tungsten is coordinated to six oxygens in a trigonal prismatic arrangement, while in  $\text{LaWO}_4\text{Cl}$  it is five coordinated in the form of a trigonal bipyramid, and in  $\text{GdWO}_4\text{Cl}$  it is tetrahedral. Although similar compounds exist for molybdenum compositions containing niobium are relatively rare. The structure of  $\text{Pr}_2\text{NbO}_7\text{Cl}_2$  will be compared with that of the recently reported  $\text{LaNb}_2\text{O}_7\text{Cl}$ , where the chloride is part of the coordination sphere of the rare earth element.

08.2-11 STRUCTURAL STUDIES OF THORTVEITITE-LIKE



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The crystal structure of  $\text{Mn}_2\text{P}_2\text{O}_7$  is reported to be isomorphous with thortveitite,  $(\text{Sc},\text{Y})_2\text{Si}_2\text{O}_7$  (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  $\text{PO}_4$  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  $\text{M}_2\text{X}_2\text{O}_7$  compounds ( $\text{M}=\text{Mg},\text{Mn},\text{Co},\text{Cu},\text{Zn}$  and  $\text{X}=\text{Si},\text{P},\text{V},\text{As}$ ). We now report on some crystallographic studies of  $\text{Mn}_2\text{P}_2\text{O}_7$  by use of X-ray single-crystal data as well as X-ray and neutron powder diffraction data and  $^{57}\text{Fe}$  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  $166^\circ$ . The corner-sharing  $\text{PO}_4$  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  $\text{Mn}_2\text{P}_2\text{O}_7$  are compared with results of other thortveitite-like phases.

08.2-10 JAHN-TELLER-EFFECT AND CRYSTAL STRUCTURE IN THE SODIUM FLUOROMANGANATES (III):  $\text{Na}_2\text{MnF}_5$  AND  $\text{Na}[\text{MnF}_4(\text{H}_2\text{O})_2]\cdot\text{H}_2\text{O}$ . By W. Massa and R.E. Schmidt, Sonderforschungsbereich 127 (Kristallstruktur und Chemische Bindung) und Fachbereich Chemie der Universität Marburg, Hans-Meerwein-Str., D-3550 Marburg, Germany

Single crystals of  $\text{Na}_2\text{MnF}_5$  and the novel hydrate  $\text{Na}[\text{MnF}_4(\text{H}_2\text{O})_2]\cdot\text{H}_2\text{O}$  have been grown from aqueous hydrofluoric acid solutions of  $\text{Mn}^{3+}$  and  $\text{Na}^+$ . The crystal structures were determined from 4-circle diffractometer X-ray data.

$\text{Na}_2\text{MnF}_5$ . Space group  $P2_1/c$ ,  $Z = 4$ ,  $a = 7.719$ ,  $b = 5.236$ ,  $c = 10.862$  Å,  $\beta = 108.99^\circ$ ,  $R_w = 2.3\%$  for 1679 reflections. The structure consists of kinked trans-chains of  $[\text{MnF}_4\text{F}_2/2]^{2-}$  octahedra interconnected by 7-coordinated Na-ions. The pronounced lengthening of the axial Mn-F bonds ( $\bar{d}(\text{Mn}-\text{F})_{\text{ax}} = 2.109(1)$  Å,  $\bar{d}(\text{Mn}-\text{F})_{\text{eq}} = 1.849(1)$  Å) is partly due to the Jahn-Teller-effect of the  $d^4$ -high-spin configuration of  $\text{Mn}^{3+}$ .

$\text{Na}[\text{MnF}_4(\text{H}_2\text{O})_2]\cdot\text{H}_2\text{O}$ . Space group  $C2/c$ ,  $Z = 8$ ,  $a = 16.381$ ,  $b = 6.676$ ,  $c = 11.303$  Å,  $\beta = 103.78^\circ$ ,  $R_w = 3.2\%$  for 1696 reflections. Here, isolated trans- $[\text{MnF}_4(\text{H}_2\text{O})_2]^-$  octahedra and the water of crystallisation form a three-dimensional network of hydrogen bonds. The  $\text{H}_2\text{O}$  ligands at one of the two crystallographically different anions participate in three H-bonds: Two as H-donor ( $d(\text{O}-\text{H}\dots\text{F})$  2.637 Å and 2.690 Å) as usual and, in addition, a third one as H-acceptor ( $d(\text{O}\dots\text{H}-\text{O})$  2.832 Å). In contrast to the common planar M-OH<sub>2</sub> geometry in aquo complexes the O surrounding is distorted tetrahedral. This peculiarity is attributed to the severe weakening of the Mn-OH<sub>2</sub> bond by the J.-T. effect ( $\bar{d}(\text{Mn}-\text{O})$  2.246,  $\bar{d}(\text{Mn}-\text{F})$  1.837 Å).

08.2-12 LATTICE PARAMETERS OF MONOCLINIC  $\text{Sm}_2\text{O}_3$ ,  $\text{Eu}_2\text{O}_3$ ,  $\text{Gd}_2\text{O}_3$ , AND FAST NEUTRON IRRADIATED  $\text{Eu}_2\text{O}_3$ . By I. F. Ferguson, UKAEA Springfields, Preston, PR4 ORR, UK and A. Huyton, attached from BNFL, Springfields, Preston PR4 ORR UK.

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 fluorescence 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<sup>-3</sup>. 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  $\sim 3 \times 10^{22}$  n cm<sup>-2</sup> 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 K $\alpha$  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 (Aistle G and Ferguson I F, UKAEA TRG Report 1812).