

have previously indicated the presence of a reversible oxidation-reduction reaction in which Cu(I) is oxidized to Cu(II) along with the formation of CuO [3]. This reaction is followed by the partial auto-reduction of Cu(II) to Cu(I). As a result of these observations, this study is directed towards gaining further understanding of the structural characteristics of members of the CuSICON family with general formula $\text{CuM}_2\text{P}_3\text{O}_{12}$ ($M = \text{Ti, Zr, Hf, Sn}$). Thus far *in situ* laboratory XRPD studies have shown that the oxidation-reduction reaction in question is the cause of a reversible 2nd order phase transformation. For example, the heating of $\text{CuSn}_2\text{P}_3\text{O}_{12}$ (S.G.:167 R-3cH) results in the oxidation of the material to $\text{Cu}_{0.5}\text{Sn}_2\text{P}_3\text{O}_{12}$ (S.G.:148 R-3), a Cu(II) compound, which then through continued heating is reduced back to $\text{CuSn}_2\text{P}_3\text{O}_{12}$ (S.G.:167 R-3cH) (figure 1). In each case small quantities of CuO was observed indicating that the reduction reaction does not continue to completion. Furthermore, it was found that quenching experiments conducted on the Cu(II) phase isolated this stable material which is distinct from the parent phase. This result has implications on any future applications that may be envisaged for this material and indeed similar results were obtained with all of the members that have been studied. Selected results will be presented.



Figure 1. Topographical view of XRPD data: $\text{CuSn}_2\text{P}_3\text{O}_{12}$ indicating the presence of a reversible phase transformation.

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FA2-MS14-P14

Structure investigations in the V-Mo-Te-O system.

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Oxides with the elemental composition V-Mo-Te-O (MoVTe) are well known for high catalytic activity and selectivity in the heterogeneous ammoxidation of propane to acrylonitrile [1]. For the direct oxidation of propane to acrylic acid, MoVTe systems also provide promising catalytic activity [2]. In literature actually three MoVTe structures are characterized and discussed for their effect on catalysis [3-4]. First two structures are orthorhombic with space groups *Pba2* ($a = 21.334(2) \text{ \AA}$, $b = 26.658(2) \text{ \AA}$, $c = 4.0146(3) \text{ \AA}$, *M1* structure) and *Pmm2* ($a = 12.6294(6) \text{ \AA}$, $b = 7.29156(30) \text{ \AA}$, $c = 4.02010(7) \text{ \AA}$, *M2* structure) [3]. The third, bronze-like structure is indexed with a hexagonal cell and lattice constants $a = 7.27(3) \text{ \AA}$ and $c = 4.012(2) \text{ \AA}$ [4]. We present a new structure

in the MoVTe system which could be highly interesting for catalysis but synthesized by a classical solid state method.

The crystals were obtained by a chemical transport of a pre-calced, stoichiometric mixture of V_2O_5 and MoO_3 . The reaction was carried out at 10^{-2} mbar and a temperature gradient T_2 ($560 \text{ }^\circ\text{C}$) $\rightarrow T_1$ ($450 \text{ }^\circ\text{C}$) for six days with TeCl_4 as transporting agent in a quartz tube. Black prismatic crystals were deposited in two different zones. The first zone provides nicely shaped but irregular prisms and the second zone at the end of the tube (T_1) exhibits a mixture of needle-like crystals and highly-twinned prisms.

First indexing was tried with a hexagonal cell which failed. After TEM investigations a reticular merohedrally twinned crystal is described consisting of three domains rotated through 120° about the pseudo-hexagonal axis. The unwrapping of individual layers in reciprocal space revealed unusual extinction rules. The observed reflections can all be explained by the overlap of three orthorhombic domains. These are indexed by an orthorhombic cell with the space group *Pca2*₁ and $a = 14.543(1) \text{ \AA}$, $b = 4.0066(3) \text{ \AA}$, $c = 12.604(1) \text{ \AA}$ (*R* indices all data 0.0774). The structure was solved and refined and the results are in full agreement with electron and X-ray powder diffraction experiments.

The presented structure has to be discussed in context with the existing catalytically relevant pseudo-hexagonal [3] and the hexagonal [4] structures. The *M2* structure seems to be closely related to the structure described here. Both structures exhibit similar building units like corner-sharing metal-oxygen octahedra and a Te-O chain of TeO_4E units (E = lone electron pair) shifted from the center of the hexagonal channels. Linked to catalysis, this new structure may also have an interesting activity towards selective oxidation or ammoxidation of alkanes and olefins comparable to the existing structures.

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Modulation of properties in a series of porous hybrid metal oxides.

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Hybrid metal oxides are porous materials that show promising applications in the field of heterogeneous catalysis, gas adsorption, nonlinear optical devices and magnetic materials. This class of compounds is built up from 3-D inorganic skeleton which topology is modulated by the presence of linked carboxylates. In spite of their potential applications, very few of these compounds have been described. In this domain, we have developed a family of compounds based on the 3-D connection of metal octahedra helices (see Fig. 1), generating 20 metal atoms windows and large crossing tunnels [(10,3) cubic network]. The first of the series named MIL-77, was obtained with nickel and glutaric acid [1]. It is a pure ferromagnet and it reveals a breathing effect of its 3D oxide