

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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FA2-MS14-P15

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

framework upon dehydration/ rehydration processes, due to reversible movements of some organic moieties and hopping of some nickel atoms. The ability of MIL-77 inorganic network to accommodate glutarate derivatives was demonstrated by the use of 3-methylglutaric acid (3-MG) and 2-methylglutaric acid (2-MG). Moreover, we have shown that the handedness of the inorganic helices could be imposed by the configuration of the enantiopur 2-MG ligand. With cobalt ion, the synthesis of bulk homochiral solid has been confirmed by optical circular dichroism [2]. Here, we will summarize the structural features and the properties of this unique family of materials.

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Keywords: porous solids, chiral compounds, thermal transformation

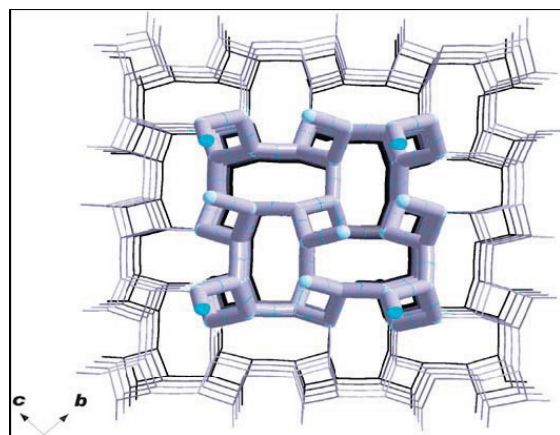


Fig. 1: View of the cubic (10, 3) chiral network

FA2-MS14-P16

Impact of pyroelectric LiNbO₃ and LiTaO₃ on water, organic dyes and *E. coli*. Emanuel Gutmann^a, Annegret Benke^b, Katharina Gerth^b, Erik Mehner^a, Christin Klein^a, Udo Krause-Buchholz^c, Wolfgang Pompe^b, Dirk C. Meyer^{a,d}. ^aInstitut für Strukturphysik, TU Dresden, Germany. ^bInstitut für Werkstoffwissenschaft, TU Dresden, Germany. ^cInstitut für Genetik, TU Dresden, Germany. ^dInstitut für Experimentelle Physik, TU Bergakademie Freiberg, Germany.
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LiNbO₃ and LiTaO₃ materials of polar crystal structure exhibit a spontaneous polarization that can be changed by temperature (pyroelectric effect). This leads to the generation of surface charges which are neutralized preferentially by external screening charges attracted from surrounding media [1]. In this context, we have investigated the impact of thermally excited pyroelectric LiNbO₃ and LiTaO₃ on the redox behavior of noble metal salts, and organic dyes in aqueous solutions. Based on various experimental results such as gold salt reduction, methylene blue degradation and conversion of dichlorofluorescein diacetate, a reaction mechanism including electron transfer and subsequent hydroxyl radical and hydrogen generation is proposed. Reaction rates strongly depend on the total surface of the pyroelectric particulate material in direct contact with the medium. As hydroxyl

radicals are highly reactive oxidants used for disinfection purposes, also successful bactericidal tests with *Escherichia coli* have been performed.

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Keywords: polar crystal, pyroelectric effect, hydroxyl radical

FA2-MS14-P17

Synthesis of new stoichiometric barium bismuth borates BaBi₂B₂O₇, BaBi₁₀B₆O₂₅, BaBi₈B₂O₁₆. Martun Hovhannisyan^a, Rafael Hovhannisyan^a, Hovakim Alexanyan^a, Nikolay Knyazyan^b. ^aScientific-Production Enterprise of Material Science, Yerevan, Armenia. ^bInstitute of General and Inorganic Chemistry of NAS RA, Yerevan, Armenia.
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Interest to ternary alkali free bismuth borate systems M₂O_y-Bi₂O₃-B₂O₃ (M=Zn,Sr,Ca,Ba) studies has amplified recently. Various research groups worked in this area and revealed a number of ternary compounds, determined their structure, optical and nonlinear optical properties. Well known research groups paid special attention to BaO-Bi₂O₃-B₂O₃ system studies and have revealed four ternary stoichiometric BaBiBO₄ [1], BaBiB₁₁O₁₉, BaBi₂B₄O₁₀ and Ba₃BiB₃O₉[2,3] compounds in it.

Using methodology based on glass samples investigation was more effective at BaO-Bi₂O₃-B₂O₃ system phase diagram construction, than a traditional technique based on solid phase sintered samples studies. Because DTA curves of glasses, to the contrary DTA curves of solid state sintered samples, indicates their all characteristics temperatures, includes exothermal effects of glass crystallizations and endothermic effects of formed crystalline phases melting. Using different melts cooling rates we at first have determined large glass-forming field in the BaO-Bi₂O₃-B₂O₃ system, which includes all eutectics in the binary Bi₂O₃-B₂O₃, BaO-B₂O₃ and BaO-Bi₂O₃ systems and covers majority of the concentration triangles, reaching up to 90 mol% Bi₂O₃. Ba₄O₇, Ba₂B₁₀O₁₇, Ba₈O₁₃, Bi₄B₂O₉, BiBO₃, Bi₃B₅O₁₂, BiB₃O₆ and Bi₂B₈O₁₅ binary compounds formed stable glasses. Ba₂O₄, Ba₂B₂O₅ and Bi₂₄B₂O₃₉ compounds are in the area of glasses formed by high cooling rates (10³-10⁴)K/c.

Phase diagrams construction have allowed us to reveal three new BaBi₂B₂O₇ and BaBi₁₀B₆O₂₅ congruent melted at 725 and 690°C respectively and BaBi₈B₂O₁₆ incongruent melted at 725 compounds in the BaO-Bi₂O₃-B₂O₃ system through same compositions glass crystallization, because all ternary compounds have enough glass forming ability.

Single crystals of BaBi₁₀B₆O₂₅ were grown by cooling of a melt with the stoichiometric composition. Preliminary melted glass powder of the stoichiometric 11.11BaO·55.55Bi₂O₃·33.33B₂O₃ (mol%) composition was heated in an uncovered quartz glass ampoule up to 750°C at a rate 10K/min. After 2h exposition at this temperature, the melt was cooled at a rate 0.5 K/h. Single crystals with size up to 1.66×0.38×0.19 mm³ were grown.

The X-ray characteristics of new compounds were determined. X-ray powder diffraction patterns of BaBi₂B₂O₇ and BaBi₁₀B₆O₂₅ could be indexed on an orthorhombic cell with lattice parameters as follows: for BaBi₂B₂O₇ a=11.818Å, b=8.753 Å, c=7.146Å, cell volume V= 739.203 Å³, Z=4; and