

Keywords: Cobalt compounds, X-ray diffraction, magnetic properties.

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Kinetic and magnetic studies of the phase behaviour in LiFePO₄-FePO₄ mixed crystals. J. Davaasambu^a, N. Tuvjargal^b, F. Güthoff^a, P. Axmann^c, S. Demeshko^d, G. Eckold^a. ^a*Institute of Physical Chemistry, University of Göttingen, Germany.* ^b*Department of Physics, National University of Mongolia, Mongolia.* ^c*Zentrum für Sonnenenergie- und Wasserstoff-Forschung Baden-Württemberg, Ulm, Germany.* ^d*Institute of Inorganic Chemistry, University of Göttingen, Germany.*
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In the last years, the development of novel materials for battery applications on lithium-basis has achieved great progress. Among them, LiFePO₄ is one of the most prominent and promising compounds[1]. The phase behaviour of the mixed system LiFePO₄ - FePO₄ is controversially discussed in the literature. There are different phase diagrams reported by Delacourt et al.[2] and Dodd et al.[3].

Time-resolved X-ray diffraction was used to investigate the kinetics of phase separation in polycrystalline Li_xFePO₄ samples which were quenched from the homogeneous phase to lower temperatures. LiFePO₄ was synthesized via solid-state reactions according to Lee et al.[4]. For the preparation of mixed crystals with different concentrations of lithium we used the chemical delithiation route proposed by Dodd et al.[3]. On quenching from 380°C (homogeneous phase) to ageing temperatures around 100°C, we observed that the structural features of the formation of the two product phases LiFePO₄ and orthorhombic FePO₄, i.e. the splitting of selected Bragg reflections, appear on a time-scale of hours. But the demixing process does not complete within 24h. The kinetic behaviour seems to vary strongly with the ageing temperatures. In the case of quenching to temperatures lower than 50°C, no significant splitting of Bragg reflections is observed. Hence, the homogeneous phase may be stabilised by quenching to sufficiently low temperatures.

We have studied the magnetic properties of the samples by SQUID-magnetometry. The partially delithiated samples show the known temperature dependence of the magnetic susceptibility with ordering temperatures of about 122K (FePO₄) and 50K (LiFePO₄). In order to create a single phase, the samples were quenched from the homogeneous phase to room temperature. Obviously, Néel temperatures of these samples were observed in between the values of pure compounds and depend on the overall composition.

[1] Padhi A.K., Nanjundaswamy K.S., Goodenough J.B., *J. Electrochem. Soc.*, 1997, 144, 1188. [2] Delacourt C., Poizot P., Tarascon J.-M., Masquelier C., *Nature Materials*, 2005, 4, 254. [3] Dodd J.L., Yazami R., Fultz B., *Electrochemical & Solid-State Letters*, 2006, 9, A151. [4] Lee J., Teja A.S., *Materials Letters*, 2006, 60, 2105.

Keywords: battery materials, phase behaviour, magnetic properties

FA2-MS14-P12

Magnetic and Electrical Properties of InSe_{1-x}Fe_x(Co_x) in Relation to Nano- Structure. Karimat El-Sayed^a, Z.K. Heiba^a, K. Sedeek^b, Z.K. Heiba^a, H.H. Hantour^b.

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Introducing few magnetic elements such as (Fe,Co) into the non-magnetic semiconductor InSe changes the materials to ferromagnetic with very low coercivity and very low remanance magnetization in case of Fe and antiferromagnetic in case of Co. From the (magnetic susceptibility - Temperature relation) the Curie temperature and the Blocking temperature were calculated for InSe_{0.9}Fe_{0.1} to be 873K and 733K respectively, a property that will allow this system to be used in spintronic devices operated at room temperature and above. The cluster model was applied to explain the origin of ferromagnetism in the nanosize diluted magnetic semiconducting (DMS) sample InSe_{0.9}Fe_{0.1}. On the other hand InSe_{0.9}Co_{0.1} sample indicated that more than one antiferromagnetic transition states takes place with paramagnetic state in between and with two different Neel temperatures. The XRD indicates the presence of a non-magnetic second minor phase In₄Se₃ in InSe and confirm the presence of nano size particle of different ranges. Transmission electron microscope (TEM) confirms that the particle size ranges between the quantum dot and the bigger nano size. The scanning electron microscope (SEM) images demonstrate the presence of stacking faults in all samples. For InSe_{0.9}Fe_{0.1} sample, the relation between logσ and 1/T is a straight line which argues the exhaustion of the center of the forbidden gap of the InSe of localized states. Only one band of localized states situated at the top of the extended states was suggested (ΔE=0.43eV). The conductivity data argue that the incorporation of Fe or Co creates new band configuration and hence modification of the electronic density of states of InSe. The increase in σ_{RT} of InSe_{0.9}Fe_{0.1} was nearly hundred times that of the InSe. Correlation with the ferromagnetic and antiferromagnetic character of InSe_{0.9}Fe_{0.1} and InSe_{0.9}Co_{0.1} with each other and with nano structure was considered in discussing the magnetic and conductivity data.

Keywords: Diluted Simiconductor, Spintronic semiconductor, Nano materials

FA2-MS14-P13

The Thermoresponsive Phase Behaviour of CuSICON: CuM₂P₃O₁₂ [M = Ti, Zr, Sn & Hf]. Roy P. Forbes^a, David G. Billing^a. ^a*National Research Foundation Centre of Excellence in Strong Materials. School of Chemistry University of the Witwatersrand Johannesburg, South Africa.*
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The NaSICON (Na Super Ionic Conductor) structural family with formula A_xM_yP₃O₁₂ [0≤x≤1; 1≤y≤3] crystallize with rhombohedral symmetry [space group R-3c (No. 167)] and are composed of a three dimensional corner sharing framework of PO₄ tetrahedra and MO₆ octahedra connected to form a chain like structure with two dimensional channels extending throughout the structure [1]. Owing to the flexibility of this structure towards ionic substitutions at various lattice sites, these materials have enjoyed consistent scientific interest due to the various useful physical properties that they possess. CuSICON (Cu super ionic conductor), with general formula CuZr₂P₃O₁₂ is an example of a material that is isostructural with the NaSICON parent structure [2]. TGA and EPR studies

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.

[1] Hong, H.; *Mat. Res. Bull.*, 1976, 11, 173. [2] Yao, P.C.; and Fray, D.J. *Solid State Ionics*, 1983, 8, 35. [3] Schaffer, R.J.; Kumar, R.V. *et al*; *Mat. Res. Bull.*, 1999, 34, 1153.

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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.

[1] Grasselli, R. K. *Catal. Today* 2003, 99, 23. [2] Botella, P., Solsona, B., Martínez-Arias, A., López Nieto, J. M. *Catal. Lett.* 2001, 74, 149. [3] DeSanto Jr., P., Buttrey, D. J., Grasselli, R. K., Lugmair, C. G., Volpe Jr., A. F., Toby, B. H., Vogt, T. Z. *Kristallogr.* 2004, 219, 152. [4] García-González, E., López Nieto, J. M., Botella, P., González-Calbet, J. M. *Chem. Mater.* 2002, 14, 4416.

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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