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Dyes are key elements of dye sensitized solar cells (DSSC). Understanding their chemical properties at the molecular level and their adsorption mechanism on TiO₂ is of paramount importance for DSSC characterization and further developments. The crystal structure of a polyene aniline based dye, named D5 [1], was solved from synchrotron high resolution powder patterns, while that of its precursor without linking moiety was solved by standard single crystal XRD. The two molecules show remarkable differences in their intermolecular interactions and in crystal packing. In the precursor a T-like interaction is observed between pairs of molecules, while in D5 π - π interactions, together with intermolecular H-bonds between carboxyl groups, impose a planar stacking. However in both structures the packing is driven by the hydrophobic interactions between the phenyl moieties in adjacent molecules. This structural information sheds light on the features of D5 when bonded to TiO₂ (P25) in the working DSSC devices and can help explaining the limited (8%) conversion efficiency. Indeed the strong hydrophobic interactions can interfere with the dye grafting process. After grafting, intermolecular H bonds can not play a role, since the COO⁻ is involved in the bond with TiO₂, but strong lateral interactions between adjacently bonded D5 molecules may facilitate the charge recombination processes that lower the yield of electron injection into the P25 conduction band, with an overall smaller efficiency of DSSC cells.

The adsorption mechanism of D5 on the TiO₂ surface has been characterized by UV-Vis spectroscopy, Grazing Incidence-XRPD and Scanning Electron Microscopy together with elemental analysis by Energy Dispersive Spectrometry (EDS). UV-Vis spectra on the D5 solutions after contact with TiO₂ allowed to determine, by difference, the quantity of adsorbed dye. The experiments were carried out on both P25 powders and on commercial Dyesol glasses, and, using an optimized analytical procedure, the number of adsorbed molecules was determined under different conditions: D5 concentration, contact time and presence of CDCA anti-aggregation agent. Dyesol glasses were also analyzed by GI-XRPD to verify the size of TiO₂ crystallites, while the thickness of the TiO₂ layer was determined by SEM. The elemental analysis by EDS showed that the sulfur signal, only due to D5, is uniformly distributed along the TiO₂ thickness. The results of all these crystallographic and spectroscopic analyses and their relevance for the characterization of TiO₂-D5 interactions will be presented.

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The cation distribution in off stoichiometric CuInSe₂ and CuGaSe₂

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Chalcopyrite type compound semiconductors with Cu(In,Ga)Se₂ composition are successfully implemented as absorber layers in

thin film solar cells. The stoichiometric compound Cu(In,Ga)Se₂ crystallizes in the tetragonal chalcopyrite type crystal structure with space group *I42d*. Within this crystal structure the monovalent cations (Cu⁺) occupy the 4a site (0 0 0), the trivalent cations (In³⁺ and Ga³⁺) are situated on the 4b position (0 0 ½) and the selenium anions are on the 8d site ($x \frac{1}{4} \frac{1}{8}$). The cations are tetrahedrally coordinated by the anions and vice versa.

In general Cu(In,Ga)Se₂ absorber layers exhibit a copper-poor composition (Cu/(In+Ga) < 1), whereby the chalcopyrite type crystal structure still persists but the occupation of the Wyckoff sites may change and various kinds of intrinsic point defects are present within the material. The kind and concentration of these defects strongly correlate with the electronic and optical properties of the final device and the knowledge about them is crucial to tailor high efficient photovoltaic devices made of such compounds.

Distinguishing between isoelectronic species like Cu⁺ and Ga³⁺ by conventional diffraction techniques, like laboratory X-ray powder diffraction, is almost impossible. Therefore, at first neutron powder diffraction with subsequent Rietveld refinement was applied to evaluate possible cation distribution models for copper – poor CuInSe₂ and CuGaSe₂, by the method of average neutron scattering length [1]. To decide if Cu⁺ and Ga³⁺ in Cu-poor CuGaSe₂ are ordered or partially disordered distributed within the structure, anomalous X-ray diffraction experiments were performed complementary to the neutron diffraction experiments.

For the anomalous diffraction experiments synchrotron X-rays with two different wavelengths, close to and far off the Ga-K-absorption edge (10367 eV), were used. This complementary diffraction technique made a differentiation between an ordered and a partially disordered distribution of the cations in copper-poor CuGaSe₂ possible.

The dominant native point defects in copper-poor CuInSe₂ were specified to be copper vacancies (V_{Cu}) and In_{Cu} anti-site defects. Moreover, the type and density of these isolated native defects is dependent on the Cu/In ratio [2]. The dominating native point defects in copper – poor CuGaSe₂ are copper vacancies and gallium on interstitial position (Ga_i).

The study presented here identified, by the use of advanced diffraction techniques, possible cationic point defects in off stoichiometric chalcopyrite type compound semiconductors. This knowledge leads to a further understanding of the complex electronic properties of Cu(In,Ga)Se₂ absorber layers in thin film solar cells, which is indispensable to aim in highly efficient photovoltaic devices based on such compounds.

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Pressure-induced phase transitions in Na-Au intermetallic compounds

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Sodium and gold are found to react at room temperature under high pressure. We have compressed a mixture of sodium and a fine powder of gold in a diamond anvil cell (DAC), and taken powder x-ray diffraction

patterns at high pressures and room temperature. We identified four Na-Au intermetallic phases (phases I ~ IV) in the pressure range up to 60 GPa.

The powder patterns taken at pressures lower than 3.5 GPa are complicated, showing phase mixture. Above about 3.5 GPa, we obtained clear diffraction patterns of single phase III. By decreasing pressure from phase III, we obtained single-phase patterns of phases II and I.

The first phase (phase I) exists below ~1.3 GPa. The critical pressure required for the solid-solid reaction of Na and Au is not well established, since some minimum pressure is necessary to seal the gasket of the DAC. Phase I is the known phase Na₂Au with the CuAl₂-type structure (*I4/mcm*, *Z*=4). It changes to phase II, which is stable between 0.7 and 3.6 GPa. Note that the pressure range includes the region of phase mixture with phase I or phase III. Phase II has the composition Na₃Au with the AsCu₃-type structure (*P-3c1*, *Z*=6). In this structure, a gold atom is coordinated by 11 sodium atoms. It should be noted that the compound Na₃Au is not known at atmospheric pressure. Phase II further transforms to phase III above about 2.0 GPa. Phase III has again the composition Na₃Au with the BiF₃-type structure (*Fm-3m*, *Z*=4). The same structure has been found for K₃Ag synthesized at high pressures [1]. Phase III is stable over a wide pressure range up to about 54 GPa, where it transforms to phase IV. Phase IV gives broad diffraction patterns, indicating large structural disorder. On decreasing pressure, phase IV is retained to at least 18 GPa. The powder pattern taken at 2.3 GPa shows the back-transformation to phase III. With further decrease of pressure, phase III changes to phase II and I, successively. Phase I seems to be stable at atmospheric pressure in agreement with the Au-Na binary alloy phase diagram [2].

The present finding suggests that the gold-alkali metal system may have a rich variety of intermetallic phases at high pressures.

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Making use of topological similarities in HP structures

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As soon as we introduce a sample into a high-pressure device we lose information and it becomes increasingly difficult to derive models for high pressure phases; especially after phase transitions – when a new structure has formed. The effects of strain, scattering contrast, absorption, limited real-space resolution, high background, multiphase patterns *etc* can all contribute to rendering solution or refinement more difficult. Here we present examples of the potential for use of models derived from topologically similar features that may allow one to more readily identify structures and refine high-pressure datasets from them. Examples will be drawn from a variety of systems: *AX*₂ to complex minerals; from *OD*, polytypic and isomorphous structures and from materials science and mineralogical investigations at high pressure. These will be complemented by real powder data, collected from samples held in diamond-anvil cells or large-volume devices. We will also demonstrate typical code (none of which is the author's) that can allow one to manipulate structural assemblages, derive symmetry and a standardised structural description and how this can then be refined to

extract a complementary set of information on the state of the sample under extreme conditions.

Keywords: pressure, transition, systematics

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The origin of memory glass effect in pressure amorphized rare earth molybdates

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A phenomenon called “memory glass effect” has been observed in AlPO₄, Zeolite Y(Na-Y), clathrasils and some other materials, which have been subjected to pressure-induced amorphization. This effect is that the single-crystal/polycrystalline samples brought to the amorphous state due to applied pressure further restore the initial crystalline phase after pressure release. Moreover in the case of AlPO₄ it is argued that the single-crystal sample returns to a single-crystal state with the original crystal orientation. However the nature and possible mechanisms of this phenomenon are still not clear. In this work we report on studies of the memory glass effect in β'-Eu₂(MoO₄)₃ single crystal samples.

Early it was established [1] that powder samples of some rare earth molybdates undergo phase transformation from initial metastable crystalline β'-phase to the amorphous state at relatively moderate pressures ~7-9 GPa. However high pressure treatments of Eu₂(MoO₄)₃ single crystal samples in the same pressure range resulted in more complex structural states[2]. Here we carried out detailed structural analysis of the HP treated single crystal samples and structural transformations at subsequent annealing using XRD, HRTEM and HAADF STEM techniques. It was found that the “treated” sample structural state is complex and inhomogeneous: the most part of the sample has amorphous-like structure and this amorphous medium contains nano-sized inclusions of a crystalline phase distributed evenly over the medium, total content of the inclusions being a few percents. These crystalline domains are highly correlated in orientation over the sample, due to what they produce single-crystal diffraction patterns, in both XRD and TEM methods, relatively weak, along with intensive diffuse-like diffraction pattern from the amorphous part. The crystal structure of the domains corresponds to a new high pressure phase (HPP) of Eu₂(MoO₄)₃ (*P* > 2.1 GPa). Thus the nano-sized inclusions in the amorphous medium of the sample are in fact the residual islands of HPP. In the talk we are presenting the detailed picture of the structure transformations under high pressure treatment and following annealing illustrated by both X-ray single diffraction patterns and TEM/HRTEM images. These studies reveal the origin of memory glass effect to be result of the retention of the residual inclusions of HPP in the amorphous medium of sample.

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