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The structure of cdse and au nanoparticle ensembles on carbon substrates

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Metal-containing nanoparticles is one of the most studied classes of nanoparticles nowadays. CdSe and Au nanoparticles attract much attention from scientific and practical point of view due to their properties. CdSe nanoparticles form optical active quantum dots materials displaying high brightness with a narrow emitting spectrum, which is perspective for application in optoelectronics, photocatalysis and biology as markers and sensors. Au nanoparticles are of interest for creation of fuel cells, nanosensors, catalysts etc.

New techniques of synthesis of CdSe and Au nanoparticles have been developed in this study. Ordered ensembles of nanoparticles formed via self-organization process have been fabricated and characterized as well. CdSe nanoparticles were synthesized by interaction of cadmium stearate with triphenylphosphine in heptadecan medium in the presence of oleamin and triphenylphosphine oxide as surface active agents (SAA). Au nanoparticles were synthesized by reduction of H₂AuCl₄ in hexane through boron hydride at the presence of SAA. A new preparation technique for electron-microscopic studies of nanoparticles has been developed. The technique provides a minimal substrate influence and high stability of image observation.

X-ray and electron diffraction patterns indicate that prepared samples of CdSe and Au nanoparticles are single-phase. CdSe nanoparticles have a wurzite structure (the P6₃mc space group). Crystal structure of Au nanoparticles is described in terms of face centered cubic lattice (the Fm3m space group). High resolution electron microscopy and X-ray small angle scattering evidence that the prepared samples contain nanoparticles of spherical form with a narrow size distribution. The average size of CdSe nanoparticles is 12 nm, and that of Au nanoparticles is 10 nm.

Self-assembly of CdSe nanoparticles into close-packed two-dimensional (2D) ensembles with the 6-order symmetry was observed on carbon substrate in the regions of high density of nanoparticles. The pronounced texture was present in CdSe ensembles when all nanoparticles were orientated with the [001] direction perpendicular to carbon substrate. A new type of ordered ensembles formed of associates of CdSe nanoparticles (several joined nanoparticles) has been found.

No texture in the form of preferred crystallographic orientation of nanoparticles in relation to each other or to the substrate has been found in close packed 2D ensembles of Au nanoparticles. The three-dimensional (3D) structures of Au nanoparticles have been found, where the second layer of nanoparticles resided in voids of the first layer forming a close-packed bulk.

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Accurate structure factors of skutterudites: electron diffraction techniques

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The utility of the precession technique in electron diffraction has been demonstrated by a number of applications to structure solution [1]. A basic advantage is the suppression of dynamic diffraction, allowing kinematical interpretation of intensity data. Next task should be to develop procedures whereby the remaining dynamical scattering effect can be included in practical way in structure solution and refinement. Extensive dynamical computations along the precession circle, based on either multislice or Bloch wave theory may be cumbersome. We propose therefore to develop methods based on approximate, two-beam-like expressions for intensity profiles pertaining to multiple beam situations, along the precession circle. These profiles can then be integrated according to the Blackman formula [2], [3]:

$$\int_{-\infty}^{\infty} I_g(s_g, t) ds_g = U_g \int_0^{U_g t} J_0(x) dx$$

This implies that an *effective potential*, U_g^{eff} can be inserted. Various alternatives for calculation of effective potentials will be presented and compared with complete Bloch wave computations.

Applications are to modified binary skutterudites with interesting thermoelectric properties. Voids in the basic TX₃ structure (Co₈P₂₄) have been filled with different "rattle" atoms (La, Ce). Skutterudites and "filled skutterudites", Co:P:Sn and Ce(La):Fe:P:Sn, have been prepared by mixing and melting the starting materials in the atomic ratios 1:3:25 and 1:4:20:50 respectively in evacuated silica tube and heat treated. HCl was used to dissolve away the tin from skutterudites. Phase identification and characterization of the material has been done by powder XRD and TEM.

The structural aim is to determine accurate Debye-Waller factors over a range of s-values. Intensity data collected by precession electron diffraction and rotation electron diffraction techniques will be used in conjunction with X-ray and neutron powder diffraction.

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Large-angle rocking-beam electron diffraction (LARBED)

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Large-angle rocking-beam electron diffraction (LARBED) [1], [2] is an alternative approach to diffraction tomography for recording 3D electron diffraction data [3], [4] which does not require the sample to be tilted or moved. An implementation of this technique which tilts the beam but keeps the illuminating spot on the same position on the sample by compensating for all 42 aberration coefficients of the illumination system up to 7th order is commercially available as a plug-in to DigitalMicrograph™ (Gatan Inc., Pleasanton, CA). Since the orientation of the sample is kept fixed, the tilt range available by this technique is determined by the quality of the electron optical setup of the microscope and is commonly less than ±10° in both θ_x - and θ_y -

direction. However, a tilt range of 10° would cover 17.4 % of reciprocal space, and if it is possible to collect high quality diffraction data up to 1 \AA resolution, this would still be much more than 1 independent reflection per non-hydrogen atom.

In contrast to precession electron diffraction (PED) [5] LARBED includes all tilt angles within the limits of the tilt range and thus records diffraction intensities at the Bragg condition for a large range of diffraction conditions. Averaging over all these different Umweg excitations allows one to reconstruct quasi-kinematic diffraction intensities for part of 3D reciprocal space, as shown in Figure 1 for the example of $\text{K}_2\text{O}\cdot 7\text{Nb}_2\text{O}_5$ [6], in a random $[\text{hk}0]$ orientation. $\text{K}_2\text{O}\cdot 7\text{Nb}_2\text{O}_5$ has space group $P4/\text{mbm}$ (No. 127) and unit cell vectors of length $a = b = 27.5\text{ \AA}$ and $c = 3.94\text{ \AA}$. The data was automatically acquired using the QED DM-PlugIn by HREM Research [7].

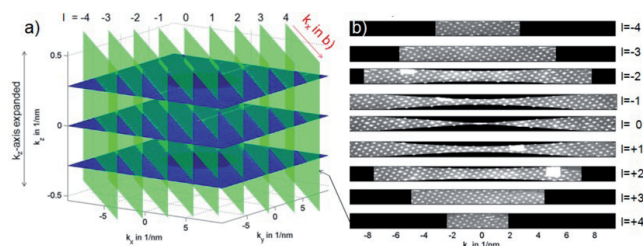


Figure 1: a) 3D reciprocal space reconstructed from the data shown in Fig. 2. Because of the tilt range of only $\pm 4^\circ$ the missing wedge is rather large. The vertical component spans a range of $-0.5\text{ nm}^{-1} \leq k_z \leq 0.5\text{ nm}^{-1}$. The green slices correspond to the vertical cuts through this 3D space shown in b). b) Positions of diffraction spots in 3D reciprocal space at different parallel planes. The intensities are the mean intensities averaged over a large number of diffraction patterns for which the Ewald sphere cut through that voxel in k -space. The contrast has been adjusted to reveal all reflections, not just the very bright ones. (White areas are due to the CCD read-out streak of very intense peaks.)

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Keywords: 3D electron diffraction, precession electron diffraction, aberration correction

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Structure analysis of charge-orbital ordered phases in A -site ordered $\text{SmBaMn}_2\text{O}_6$ using CBED

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A structure analysis method using convergent-beam electron diffraction (CBED) developed by Tsuda and Tanaka [1] enables us to directly determine crystal structures and electrostatic potential distributions from nanometer-scale specimen areas. Using the method, sp^3 bonding electrons of silicon [2] and an ordered state of $\text{Fe } 3d\ 3z^2-r^2$ orbitals of spinel oxide FeCr_2O_4 [3] were successfully observed. In the present study, the CBED method has been applied to an A -site ordered perovskite-type oxide $\text{SmBaMn}_2\text{O}_6$. The A -site ordered $\text{SmBaMn}_2\text{O}_6$

contains the alternate stack of SmO and BaO sheets along the c -axis with intervening MnO_2 sheets. This material undergoes a structural phase transformation at 190 K from a room temperature (RT) phase with charge- and orbital-ordering (COO) to a low-temperature (LT) COO phase [4]. Some different COO models have been proposed for the RT and LT phases. We aim to determine the crystal structures and COO patterns of the RT and LT phases and examine the relations between microscopic crystal structures and macroscopic physical properties. It is noted that the influence of the A -site randomness on CBED patterns can be excluded unlike the A -site disordered phase.

CBED patterns of $\text{SmBaMn}_2\text{O}_6$ were obtained at 293 K and 90 K using an energy-filter transmission electron microscope JEM-2010FEF operated at an accelerating voltage of 100 kV. The space groups of the RT and LT phases were determined by the CBED method. Based on the determined space groups, atom positions, atomic displacement parameters and low-order structure factors were refined by nonlinear least square fitting between the CBED patterns and dynamical diffraction calculations using our analysis software MBFIT [1].

From the symmetries of CBED patterns taken with five different incidences, the point group of the RT phase was determined to be mmm . The lattice type was determined to be primitive because no extinction by lattice type was observed. Dynamical extinction lines (DELs) were seen in the $h00$ ($h=\text{odd}$) zeroth-order Laue zone (ZOLZ) reflections and $0kl$ ($k+l=2n+1$) higher-order Laue zone (HOLZ) reflections, which indicate the existence of an a -glide symmetry perpendicular to the b -axis and an n -glide symmetry perpendicular to the a -axis, respectively. Thus, the space group of the RT phase of $\text{SmBaMn}_2\text{O}_6$ was uniquely determined to be $Pnam$ (No. 62). There are two different models were reported for the RT-COO phase. From the space group, an allowed COO model was selected.

Similarly, the space group of the LT phase was also determined to be $Pmam$ (No. 51) and a possible COO model was also selected.

The result of the refinement of crystal structural parameters will be presented.

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Keywords: convergent beam electron diffraction, TEM, charge orbital ordering

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Electric field induced deformation in piezoelectric LiH_2PO_4 and LiH_2PO_3 crystals

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LiH_2PO_4 and LiH_2PO_3 crystallize in space group symmetry $\text{Pna}2_1$ and show piezoelectric properties. Single crystalline plates have been investigated under external high-electric field to study structural changes due to the internal deformation. The experiments have been performed using a four-circle diffractometer at D3 beamline @ DESY in ω scan mode combined with an open X-ray point detector. Diffraction curves of LiH_2PO_4 crystal ($a_1=6.253$, $a_2=7.656$, $a_3=6.881$, $Z=4$)[1] with orientations $[011]$ and $[201]$ were under an external electric field ($\pm 3\text{ kV mm}^{-1}$). The measured peaks shifts reproduce the piezoelectric constants d_{ijk} of the material, the internal changes of atomic positions are deduced from changes of integrated intensities. The internal deformation was calculated to be larger for the Li-O bond compared to that of the P-O bonds. Normalized to an applied electric