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Understanding local structure in amorphous precursors using electron nano diffraction

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A deeper understanding of the mechanisms governing crystal nucleation is constantly being pursued. Total X-ray scattering combined with pair distribution function (PDF) analysis has been extremely successful in highlighting the role of amorphous pre-nucleation and intermediate structures during nanoparticle synthesis [1]. Information on the local and extended structure of a large ensemble average may reliably be extracted using this technique. However, in certain systems, e.g. solvothermally synthesized ZrO_2, the PDFs of different precursor mixtures are practically indistinguishable. Interestingly, the reaction outcomes, i.e., the ZrO_2 polymorphs produced upon heating, are significantly different [1]. Thus it is reasonable to assume that two samples showing similar PDFs may consist of different populations of local atomic configurations with a distinct structure and symmetry [2].

Here, we present how scanning electron nanodiffraction (END) may enable a differentiation between seemingly similar amorphous materials [2]. Electrons diffract more strongly than X-rays and neutrons and can be electromagnetically focused to probe sizes comparable to inter-atomic distances. By using a focused electron probe (FIG1A), the lateral size of the diffracting volume can be restricted to "regions of correlated structure". The spatial reduction in probe size brings about a break-up of the otherwise isotropic diffuse amorphous rings into statistically characteristic patterns comprising angular correlations related to the local symmetry (FIG1B). An ensemble of nano diffraction patterns may be collected from a scanned array to statistically sample many local configurations. A representative sampling of the vast amount of possible configurations and arrangements of clusters within the samples is achieved by collecting thousands of diffraction patterns. The advances within the field of modern scanning transmission electron microscopes and developments in computer hard- and software facilitates the acquisition and analysis of such large amounts of data.

The angular correlations in the END patterns can be quantified by calculating a set of Fourier coefficients for the periodic intensity around a specified diffraction ring. These Fourier coefficients probe three-body correlations and more strongly reflect local symmetry than the PDF function. The extracted Fourier coefficients can then be mapped to reveal extended structure within the sample. They may also be compared to theoretical calculations (FIG1C) of ideal nearest neighbor clusters with a well-defined point symmetry [2].

These measurements may provide an efficient and direct link between local structures, geometry and crystallization pathways. Novel techniques like this are a step on the way to understanding disorder and non-equilibrium materials, thereby broadening the scope of crystallography "beyond crystals" [3].

Figure Caption: A) Schematic of END B) END pattern from a ZrO_2 amorphous precursor, C) Three ideal units with distinct local symmetry and their calculated Fourier Coefficients.

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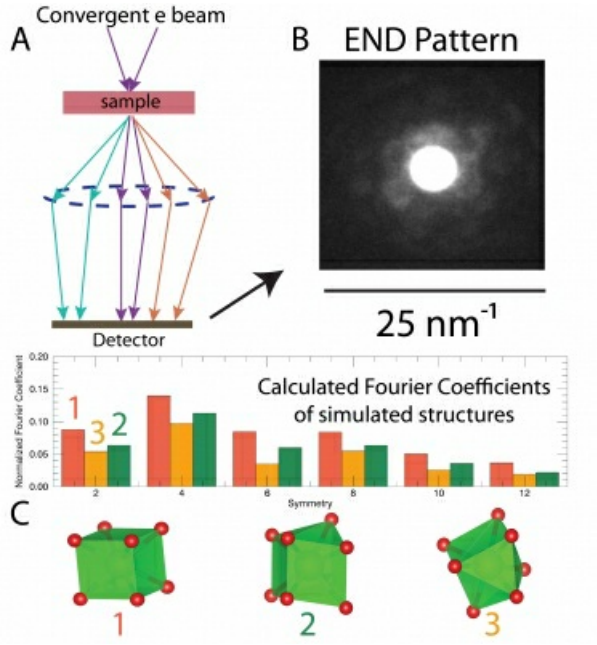

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