Poster Presentation

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Formation of γ-Fe2O3 in hydrothermal synthesis: In situ total scattering studies

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The properties of metal oxide nanoparticles are highly dependent on particle characteristics such as size, crystallinity, and structural defects. To obtain particles with tailormade properties, it is crucial to understand the mechanisms that govern these characteristics during material synthesis. For this purpose, in situ studies of particle synthesis have proven powerful.[1] Here, in situ Total Scattering (TS) combined with in situ PXRD studies of the hydrothermal synthesis of γ-Fe2O3 (maghemite) from ammonium iron citrate will be presented. In situ TS with Pair Distribution Function (PDF) analysis has recently shown to be an efficient tool for understanding the fundamental chemical processes in particle crystallization.[2,3] The full γ-Fe2O3 crystallization process from ionic complexes over nanoclusters to crystalline particles is followed and material formation mechanisms are suggested. The study shows that the local atomic structure of the precursor solution is similar to that of the crystalline coordination polymer [Fe(H2citrate)(H2O)]n where corner sharing [FeO6] octahedra are linked by citrate. As hydrothermal treatment of the solution is initiated, clusters of edge sharing [FeO6] units form. Tetrahedrally coordinated iron subsequently appears in the structure and as the synthesis continues, the clusters slowly assemble into nanocrystalline maghemite. The primary transformation from amorphous clusters to nanocrystallites takes place by condensation of the large clusters along corner sharing tetrahedral iron units. The crystallization process is related to large changes in the local structure as the interatomic distances in the clusters change dramatically with cluster growth. The local atomic structure is size dependent, and particles below 6 nm are highly disordered. Whole Powder Pattern Modelling of the PXRD data shows that the final crystallite size (<10 nm) is dependent on synthesis temperature and that the size distribution of the particles broadens with synthesis time.

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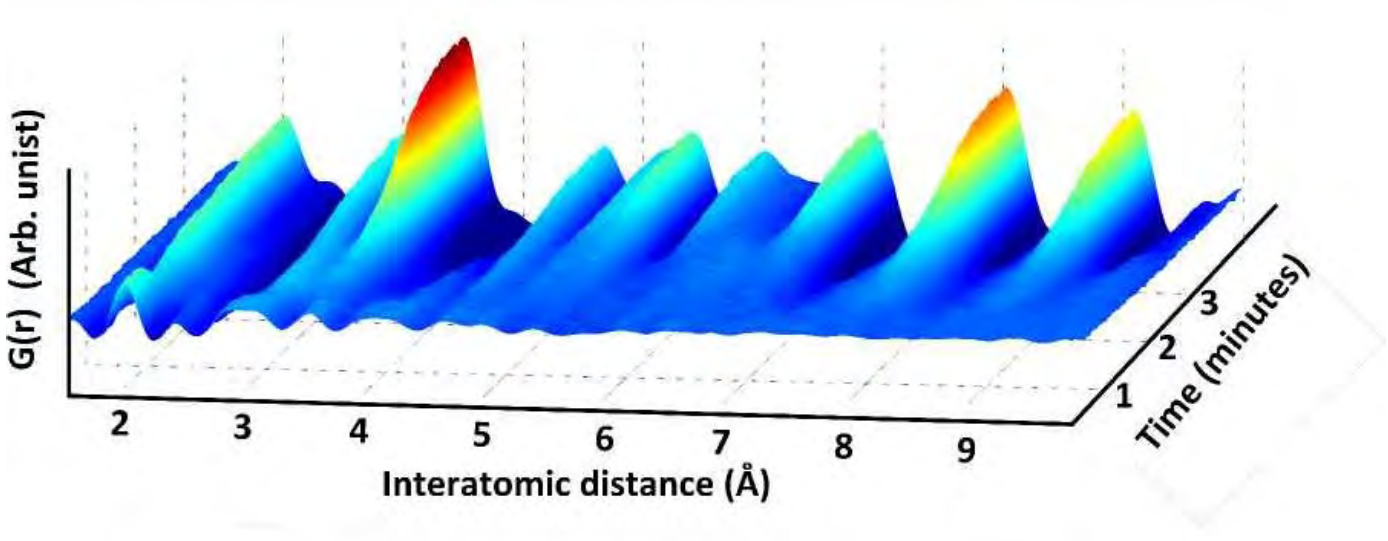

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