

Role of intermediate amorphous phases in CeO₂ mesocrystal formation

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The growth of mesocrystals is an example of a non-classical crystallization (NCC) pathway. During NCC a sequence of metastable phases of increasing density is formed. Such a sequential process is often preferable since it requires to overcome smaller activation energy barriers as compared to the classical crystallization route, happening in one step. Although NCC theory describes the formation of mesocrystals generally well, a detailed understanding of particular stages of growth (e.g. the mechanism of three-dimensional mutual alignment of the nanoparticles and the role of intermediates) is still missing. Here we use the process of γ -radiation induced synthesis of CeO₂ mesocrystals as a model reaction. This reaction is performed in aqueous solution, without additives, at elevated temperatures and under constant dose-rate, thus giving precise control over the reaction and excluding many of the parameters which would otherwise complicate the separation of different stages of growth (e.g. additives, heating). In addition, the radiation-induced process allows a direct comparison of ex-situ time-dependent TEM characterization with the in-situ growth process inside the TEM liquid-cell.

Energy-filtered electron radial distribution functions and HRTEM data obtained at different reaction times together with detailed characterization of solution and analysis of radiolytic processes allowed us to identify several stages in CeO₂ mesocrystal formation: (1) the formation of hydrated Ce(IV)-hydroxides, which appear as a “gel” on HRTEM images and serve as an intermediate in the liquid-to-solid phase transformation. The composition of the intermediate is variable since the de-hydration of the earlier-formed hydroxides and the hydrolysis of the later-formed hydroxides occurs simultaneously; (2) CeO₂ primary particles nucleate and grow inside the intermediate; (3) the alignment of the primary particles into “pre-mesocrystals” and subsequently to mesocrystals. In the particular case of the studied reaction, we found that mutual alignment of particles to mesocrystals is complex and is controlled by different mechanisms, including (i) particle alignment inside the constrained environment of the intermediate phase based on simple geometric arguments and (ii) the formation of so-called “mineral bridges”.

In-situ liquid-phase investigation of the initial solutions in TEM was carried out in both transmission and scanning modes, which enables to vary not only the dose rates but also local electron current densities. The observed processes can be directly correlated to the stages of the mesocrystal formation found through ex-situ time-dependent TEM.

It is worth mentioning that upon drying, further alignment of the obtained mesocrystals into supracrystals occurs, making it possible to form complex hierarchical architectures.

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