



Elucidating non-classical nucleation of nanocrystals from an amorphous intermediate state

Alexis Freitas, Raj-Kumar Ramamoorthy, Marie-Alexandra Néouze, Eric Larquet, Fabienne Testard, Thierry Gacoin, David Carriere

► To cite this version:

Alexis Freitas, Raj-Kumar Ramamoorthy, Marie-Alexandra Néouze, Eric Larquet, Fabienne Testard, et al.. Elucidating non-classical nucleation of nanocrystals from an amorphous intermediate state. NANO 2018, Jun 2018, Hong Kong, China. cea-02340311

HAL Id: cea-02340311

<https://cea.hal.science/cea-02340311>

Submitted on 30 Oct 2019

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

Elucidating non-classical nucleation of nanocrystals from an amorphous intermediate state

A. Freitas^{1,2}, R-K. Ramamoorthy², M-A. Neouze¹, E. Larquet²,
F. Testard¹, T. Gacoin², D. Carrière¹

¹ LIONS, NIMBE, CEA, CNRS, Université Paris-Saclay, CEA Saclay, 91191 Gif-sur-Yvette Cedex

² LPMC (UMR 7643), CNRS-École polytechnique, Route de Saclay, 91128 Palaiseau, FRANCE

Keywords : oxides, non-classical nucleation, in-situ X-ray scattering, nucleation rate

While nanoparticles are attractive because of their peculiar properties, their production remains a challenge. Their attributes mostly depend on size and surface state, but also on their microstructure. However, this structure (size, shape, porosity, crystalline quality) is currently only controlled via trial-error experimentations and poorly described by the only tool available, the classical nucleation theory (CNT), especially for oxide nanoparticles synthesised in water [1].

Luminescent, europium-doped yttrium vanadate (YVO₄: Eu) illustrates nicely how important tuning the properties at the nanometric scale is. For light emission applications, a good crystalline quality and low surface to volume ratio is required, whereas porosity and high surface area will be key for chemical sensor applications [2,3]. This branching makes it crucial to understand the mechanisms of formation of these objects in order to have precise control on their structure and thus on their properties.

In this work, we focused on elucidating how crystalline YVO₄ is formed in water. A first striking result is that tuning the initial pH leads to two critical microstructures : (i) the “expected” [4], porous, one, with nanoparticles ~20nm wide composed of subunits of 2nm, (ii) a new, monocrystalline-like one, with particles 30nm large and no primary unit detected. To understand this difference, we conducted luminescence, pH, ICP-MS, and SAXS/WAXS/XRD studies during the reaction from reaction times as short as 5ms. In particular, we could show the existence of an amorphous intermediate state in both cases and its impact on the particles’ size and microstructure, and measure nucleation rates within the disordered network to improve nucleation theories.

REFERENCES

- [1] J. J. D. Yoreo *et al.*, Crystallization by particle attachment in synthetic, biogenic, and geologic environments. *Science*. **349**, aaa6760 (2015).
- [2] G. Mialon, S. Türkcan, A. Alexandrou, T. Gacoin, and J.-P. Boilot, New Insights into Size Effects in Luminescent Oxide Nanocrystals, *The Journal of Physical Chemistry C* 2009 **113** (43), 18699-18706.
- [3] Cedric Bouzigues, Thierry Gacoin, and Antigoni Alexandrou, Biological Applications of Rare-Earth Based Nanoparticles, *ACS Nano* 2011 **5** (11), 8488-8505.
- [4] B. Fleury *et al.*, Amorphous to Crystal Conversion as a Mechanism Governing the Structure of Luminescent YVO₄:Eu Nanoparticles. *ACS Nano*. **8**, 2602–2608 (2014).