The crystallization process of gel-derived SiO2-TiO2 amorphous nanobeads followed by an in situ high-temperature study

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Abstract

Crystallization phenomena include a set of reactions, leading to the appearance of a long-distance organization in an initially amorphous material. The mastery of the nucleation and crystal growth processes allows the control of the final microstructure and therefore of the properties of the materials.1-2 Lately, in-situ experimental investigation of crystallization processes from disordered precursors by Transmission Electron Microscopy (TEM) offers unprecedented possibilities to elucidate crystal nucleation and growth down to the nanoscale.3-4 Due to the challenges of in situ TEM experiments, few authors attempted to elucidate nucleation processes in oxide glasses. In this work, the structural ordering and compositional reorganization of spray-dried amorphous nanobeads of composition 50 SiO2 – 50 TiO2 is studied in situ at high temperature by TEM.
The nucleation and growth of TiO2 crystals in a single amorphous nanobead (diameter _˜50 nm) were first observed in the range 30-600 ºC, by continuously acquiring TEM micrographs while heating. In parallel, the evolution of local nanoscale enrichments was observed in STEM-ADF mode and characterized by EELS Spectrum-Imaging maps at various stages of heat treatment. Combined to in situ Raman spectroscopy and XRD, the results provide an overview of the mechanism of crystallization in these materials: the nanobeads initially contain TiO2-enriched nanodomains, which evolve in size and composition with increasing temperature, and which eventually can become TiO2 crystals. More generally, our study highlights potential, challenges and limitations of in situ high-temperature (S)TEM experiments for the elucidation of crystallization processes in oxide materials.

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