

## Controlling crystallization pathways and kinetics in multiferroic $\text{Bi}_2\text{Fe}_4\text{O}_9$

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Functional nanomaterials are frequently synthesized by the facile sol-gel method. In a broader sense, the process can be described as the conversion of molecular precursors in solution into inorganic solids via hydrolysis, condensation and aggregation [1]. It allows the targeted control of structural characteristics e.g. particle/crystallite size and polymorphism of a material. This is of particular importance for quantum materials, where the charge, spin, orbital and lattice are intrinsically coupled due to strong electronic interactions [1]. Since the sol-gel method is a non-equilibrium process, the synthesis of pure nanocrystalline samples is challenging if various stable and metastable phases exist, often leading to co-crystallization. Subtle changes in the synthesis parameters, such as temperature, pH and complexing agent, can strongly influence the resulting structural and physical properties of the materials. Despite this knowledge and the popularity of this synthesis method, studies on the parameters driving the crystallization process are rare and a deep understanding of the formation mechanisms is usually lacking.

The  $\text{Bi}_2\text{O}_3$ - $\text{Fe}_2\text{O}_3$  system is known to be challenging from a synthetic point of view, as sillenite-type  $\text{Bi}_{25}\text{FeO}_{39}$ , mullite-type  $\text{Bi}_2\text{Fe}_4\text{O}_9$  and perovskite-type  $\text{BiFeO}_3$  have a strong tendency to co-crystallize [3]. The target compound  $\text{Bi}_2\text{Fe}_4\text{O}_9$  shows multiferroic behaviour close to room-temperature [4] and a spin liquid state just above the transition [5]. Its exotic magnetism materialises due to five competing magnetic exchange interactions involving two distinct Fe-sites, which drive antiferromagnetic coupling in the  $ab$ -plane and non-collinear ferromagnetic ordering along the  $c$ -axis [6]. Below a critical size of  $\sim 120$  nm, size-dependent properties can be observed due to significant changes in the structural lattice [7].

In this study, we investigate how the synthesis parameters in a sol-gel approach affect the crystallization pathways and kinetics of  $\text{Bi}_2\text{Fe}_4\text{O}_9$ . We follow the transformation of molecular precursors into the fully crystalline structures using *in situ* total scattering and Pair Distribution Function (PDF) analysis with a second-scale time resolution. In total, five different precursors were synthesized using the respective metal nitrates and meso-erythritol as the complexing agent. The phases qualitatively appearing during crystallization as well as their transition and growth kinetics can be controlled by the synthesis medium and ratio of metal nitrate to complexing agent. More specifically, we observe multiple crystallization pathways including the initial formation of rhombohedral  $\text{BiFeO}_3$  and subsequent transition into orthorhombic  $\text{Bi}_2\text{Fe}_4\text{O}_9$ , co-crystallization of  $\text{BiFeO}_3$  and  $\text{Bi}_2\text{Fe}_4\text{O}_9$ , or the direct formation of  $\text{Bi}_2\text{Fe}_4\text{O}_9$  from the precursor. During crystal growth, the lattice parameter  $b$  decreases significantly, although  $\text{Bi}_2\text{Fe}_4\text{O}_9$  is known to exhibit positive thermal expansion [8] highlighting the influence of the crystallite size on the lattice. In addition, the overall crystallization process is predetermined very early in the synthesis process and mainly governed by the gel structures formed during evaporation of the solvent and organic components, as suggested by *ex situ* PDF analysis.

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