



# Sol–gel synthesis, phase composition, morphological and structural characterization of $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$ : XRD, FTIR, SEM, 3D SEM and solid-state NMR studies



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## ABSTRACT

Aqueous sol–gel chemistry route based on ammonium–hydrogen phosphate as the phosphorus precursor, calcium acetate monohydrate as source of calcium ions, and 1,2-ethylenediaminetetraacetic acid (EDTA), or 1,2-diaminocyclohexanetetraacetic acid (DCTA), or tartaric acid (TA), or ethylene glycol (EG), or glycerol (GL) as complexing agents have been used to prepare calcium hydroxyapatite ( $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$ , CHAp). The phase transformations, composition, and structural changes in the polycrystalline samples were studied by infrared spectroscopy (FTIR), X-ray powder diffraction analysis (XRD), and scanning electron microscopy (SEM). The local short-range (nano- and mezo-) scale effects in CHAp were studied using solid-state NMR spectroscopy. The spatial 3D data from the SEM images of CHAp samples obtained by TA, EG and GL sol–gel routes were recovered for the first time to our knowledge.

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## 1. Introduction

Development of a morphologically controllable synthesis of different functional materials is urgently important to answer the demand for exploring the potentials of these compounds. For example, well-controlled hierarchical nanostructures of manganese cobaltates or lanthanum manganates revealed that high specific capacitance and magnetic properties of these compounds depend on the morphological features and could be applied as supercapacitor electrode materials [1,2]. The connection between electrical and morphological properties of magnetocaloric nano zinc/nickel ferrites was also recently demonstrated by Hemedal et al. [3]. The importance of surface morphology of nanomaterials

to biological responses was revealed in Ref. [4]. The challenges and opportunities of controlling the morphological characteristics of phosphate materials were also put forward [5,6].

Calcium hydroxyapatite,  $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$ , commonly referred to as CHAp, is one of the calcium phosphate based material which makes up the majority of the inorganic components of human bones and teeth. The specific chemical structural and morphological properties of CHAp are highly sensitive to the changes in chemical composition and processing conditions [7–10]. The solid-state synthesis of CHAp from oxide or inorganic salt powders usually requires extensive mechanical mixing and lengthy heat treatments at high temperatures [11,12]. These processing conditions do not allow facile control over micro-structure, grain size and grain size distribution in the resulting powders. Several other techniques such as polymerized complex routes, hydrothermal synthesis, precipitation, microemulsions, spray-, and gel-pyrolysis and sonochemical methods have been used to produce CHAp phases [13–24]. Inhomogeneous CHAp having significant amount

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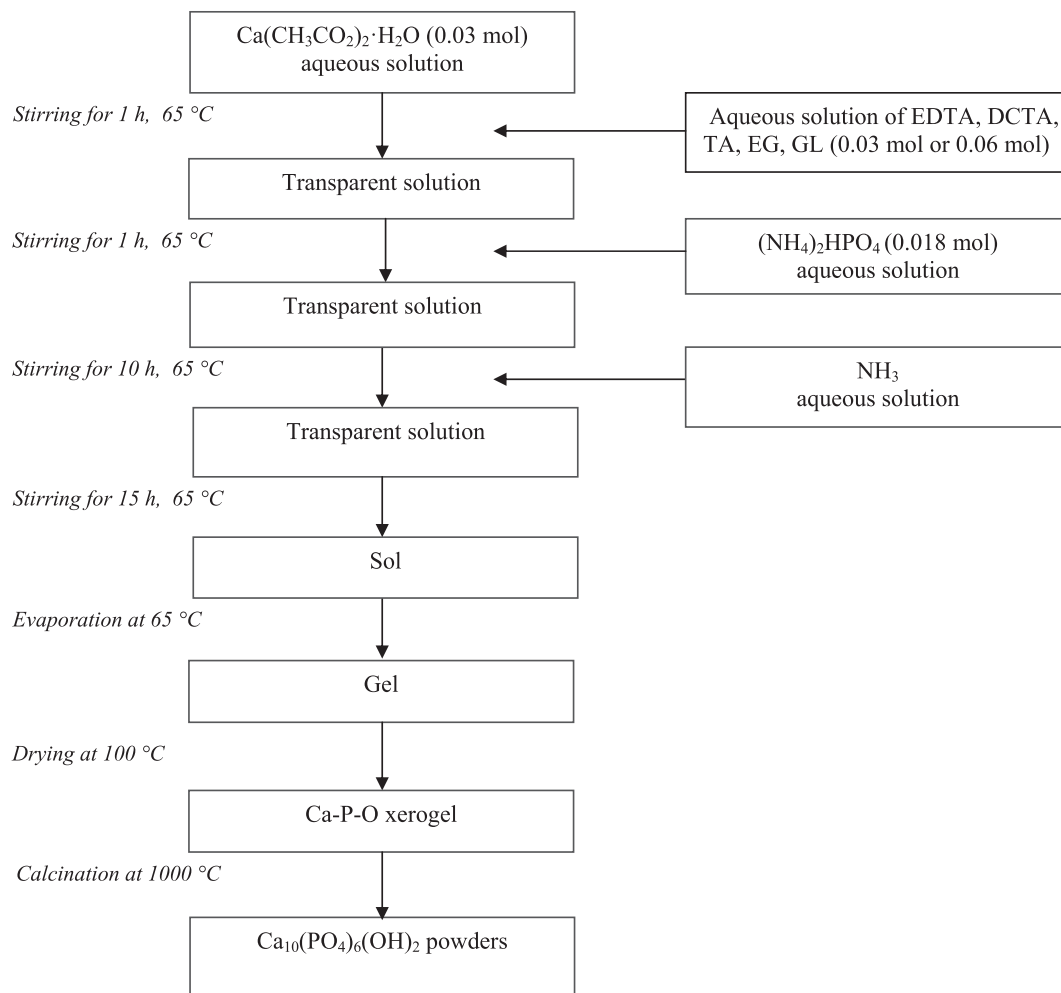


Fig. 1. A schematic diagram of the steps involved in the sol–gel processes used for the preparation of  $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$  samples.

of impurities was produced using most of these methods.

It has been well demonstrated that the sol–gel process offers considerable advantages of good mixing of the starting materials and excellent chemical homogeneity and stoichiometry of the CHAp. Several sol–gel approaches, starting from nonaqueous solutions of different precursors of calcium and phosphorus, have been used for the preparation of CHAp powders. The major limitation for its applications was found to be very low solubility of the calcium alkoxides in the organic solvents and their low reactivity which caused deviations from the stoichiometry of the final materials. The aqueous synthesis route of sol–gel preparation offers an effective and relatively simple way to produce CHAp [25–28].

Over the last few decades, the sol–gel techniques have been used to prepare a variety of mixed-metal oxides, nanomaterials and nanoscale architectures, nanoporous oxides, organic-inorganic hybrids [29–33]. The aqueous sol–gel synthesis technique for the preparation of  $\text{YBa}_2\text{Cu}_4\text{O}_8$  superconductor was studied using two different complexing agents with the same chemical composition, namely L-(+)-tartaric (natural) acid and DL-tartaric (synthetic) acid. The SEM micrographs of the Y–Ba–Cu–O acetate-tartrate gels indicated the formation of monolithic gels with slightly different morphological features [34]. The nature of complexing ligand used in the sol–gel preparation of yttrium aluminium (or gallium) garnets was found to be essential for the morphological properties of sol–gel derived compounds [35,36]. Besides, aqueous sol–gel chemistry routes using different complexing agents have been

developed to prepare calcium hydroxyapatite samples with different morphological properties [7,28,37].

NMR and FTIR spectroscopy techniques provide the unique information on the local short-range (nano- and mezo-) scale effects. Therefore these methods are most perspective to study structure and dynamical changes in complex solids, such as calcium hydroxyapatites having different morphological features among them [38–41]. These techniques have been applied in the present work studying very fine structural details, viz., the surface effects and the characteristic size profiles of sub-nano  $^{31}\text{P}$ – $^1\text{H}_n$  spin clusters. Since the NMR experiments sometimes are long-lasting and thus are hardly applied in technological routes, a hunt around correlations with FTIR data has a definite sense. It would allow to apply FTIR spectroscopy as a very rapid and powerful tool searching for the best complexing agents, controlling and optimizing fine surface and structural features as well as the perfectness (uniformity) of synthesized nano-structures in series of related materials.

These results have initiated the present work on the impact of the nature of the gelation agent used in the sol–gel process on the CHAp formation process and its morphological features. Five different complexing agents were selected to be used in the sol–gel processing experiments: EDTA, DCTA, tartaric acid, ethylene glycol and glycerol. The aim of this work was to elucidate the impact of the nature of the complexing agent on the calcium hydroxyapatite formation process, phase purity and morphological properties.

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