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RAPID COMMUNICATION

Rapid microwave assisted synthesis of hydroxyapatite†

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Abstract. A fast, efficient and novel method of preparation of hydroxyapatite using microwaves has been described.

Keywords. Hydroxyapatite; microwave assisted synthesis; bioceramics.

Hydroxyapatite (HAp), $Ca_{10}(PO_4)_6(OH)_2$ is the principal inorganic constituent of bones and teeth and consequently has become a topic of extensive biological and physico-chemical investigations (Jarcho *et al* 1977; Monma and Kamiya 1987; Narasaraju and Phebe 1996). For prosthetics requiring bone repair and replacement, hydroxyapatites and related calcium phosphates are a natural choice, since they would be expected to possess the best biocompatibility for healthy and rapid tissue growth (Jarcho *et al* 1976). Our earlier studies also revealed that composites made starting from HAp and monoclinic ZrO_2 possess an agreeable combination of biocompatibility, microstructure and mechanical strength (Nagarajan and Rao 1993). Recently HAp has been plasma sprayed as a coating on titanium prostheses to improve the long-term rooting of the prosthesis to the bone. HAp powders are also used in the chromatographic separation of bio-macromolecules. However, the conventional methods (wet, dry and hydrothermal routes) of preparation of this important bioceramic material are tedious and time consuming. For example, in one process HAp was precipitated from aqueous solutions using appropriate amounts of calcium nitrate and di-ammonium hydrogen phosphate using NH_4OH to maintain high pH value (Hayek and Stadlmann 1955) and the mixture was kept stirred for about 2 h, later centrifuged and the product was allowed to ripen. In another method solid state mixture of tri- and tetracalcium phosphates had to be heated for several hours at 1283 K in a current of moist air to produce HAp (Narasaraju *et al* 1975). In yet another process Perloff and Posner (1956) described a hydrothermal route for the synthesis of HAp in which dicalcium phosphate was heated with water at 573 K for 10 days in a platinum lined hydrothermal bomb. There is thus great need to develop an efficient route to synthesize HAp.

Recently novel microwave irradiation routes (Lerner *et al* 1991; Mingos and Baghurst 1991; Vaidhyanathan *et al* 1996) have been developed for the synthesis of inorganic materials. Products with good structural uniformity and crystallinity have been obtained (Ramesh *et al* 1994; Vaidhyanathan *et al* 1995) in these microwave methods. In this communication a simple and fast precipitation method is described for the preparation of hydroxyapatite in which microwave irradiation has been used.

In the present procedure, equivolumes of 0·24 M $(NH_4)_2HPO_4$ solution and 0·4 M aqueous suspension of $Ca(OH)_2$ are mixed together (total volume of 150–250 cc), taken

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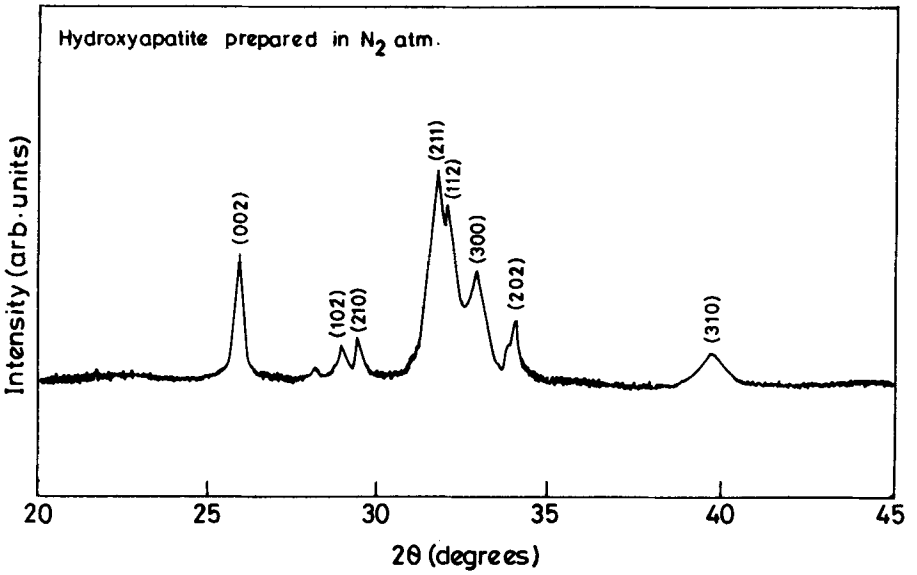

Figure 1. X-ray diffractogram of the microwave prepared hydroxyapatite.

in a flat bottomed glass flask and kept inside the domestic microwave oven (Batliboy, Eddy: Operating at 2·45 GHz and with a variable power up to a maximum of 980 W). The solution mixture was microwave irradiated for about 20–25 min, keeping the rate of boiling from going beyond control. Since the ambient in the oven was considered a factor in the course of the reaction, the irradiation was performed both in air and in ultra pure nitrogen (to avoid contact with atmospheric CO_2).

Water was boiled out in about 20 min and a dry looking product remained in the flask. The powdery product was scraped out of the container and characterized using X-ray diffraction (XRD), infrared spectroscopy (IR) and energy dispersive X-ray analysis (EDAX).

Figure 1 shows the X-ray diffractogram of the microwave prepared sample under N_2 atmosphere. All the peaks correspond to all those of hydroxyapatite (JCPDS card No. 9–432). The relative intensities of the various reflections designated in the figure are also in the correct order compared to solution prepared HAp before any further heat treatment. The peak widths confirm that the product has good crystallinity. The Ca/P ratio of the microwave prepared HAp was measured by EDAX and found to be 1·65 which is very close to the theoretical value of 1·67.

Figure 2 gives the infrared spectra of the same microwave prepared product. Appearance of broad vibrational bands at 1020 and 1080 cm^{-1} and the presence of clear triplet peak at 550, 590 and 625 cm^{-1} confirm the formation of good quality HAp by the above procedure. When the microwave assisted preparation was carried out in ambient air, carbonacious impurity was found in the product and was evidenced as a small peak at 1430 cm^{-1} in the infrared spectrum. This peak was completely removed when the product was washed in NH_4Cl solution and dried.

Thus, HAp is formed in quantitative yields in under 25 min in this microwave assisted procedure. It is not clear at this stage as to how crystalline stoichiometric HAp is formed, as if in a single step, in the above reaction. We tentatively suggest that under microwave irradiation formation of HAp occurs via truely ionic reaction with

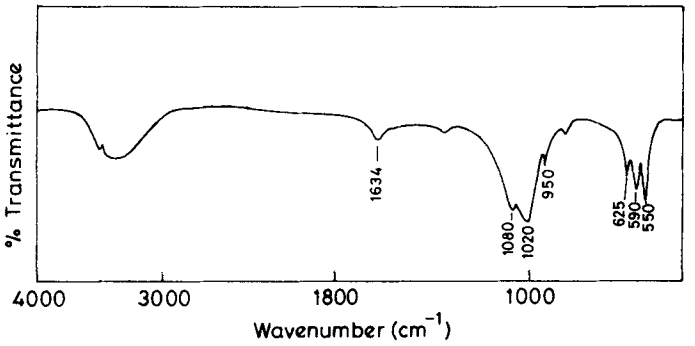

Figure 2. Infrared spectrum of hydroxyapatite.

effectively reduced kinetic barriers. The suspended $Ca(OH)_2$ particles are likely to be surrounded by $[HPO_4]^{2-}$ ions. Elements of H_2O in such a molecular complex interact with microwaves like bound water (Lerner *et al* 1991). As a result of intense absorption of energy from microwave field, H_2O is eliminated and Ca^{2+} ions are locally 'bared'. This triggers a fast ionic interaction resulting in the precipitation of HAp through a presumably complex reaction involving Ca^{2+}, $[OH]^-$ and $[PO_4]^{3-}$ ions. The presence of ammonium ions will ensure high alkalinity of the medium while HAp is being precipitated out. Although microwaves may be involved in transferring energy and activate many other complex ions like $[NH_4]^+$, $[HPO_4]^{2-}$ etc. through excitation of various rotational modes, the key step which enables the formation of HAp appears to us to be the process of 'readying' Ca^{2+} ions for the reaction by loosening out the surrounding H_2O molecules present in their 'aquo' complexes. However quantitative characterization of the various transient species is essential to understand the kinetics and mechanism of this reaction.

Thus a novel, microwave assisted synthetic route has been found for the preparation of hydroxyapatite. The process is very rapid (takes under 25 min) and the resulting HAp possess good crystallinity and phase purity.

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