Progress in Crystal Growth and Characterization of Materials 60 (2014) 63–73

Contents lists available at ScienceDirect

Progress in Crystal Growth and Characterization of Materials

journal homepage: www.elsevier.com/locate/pcrysgrow

Review

Surface properties of biomimetic nanocrystalline apatites; applications in biomaterials

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Keywords:
Apatite nanocrystals
Biomimetism
Hydrated surface layer
Ion exchange
Adsorption
Biomaterials

1. Introduction

Several types of nanocrystalline apatites have been described, obtained in various ways. Among these, biomimetic nanocrystalline apatites (BNA), whose characteristics are close to those of biological apatites, have been shown to exhibit specific properties mainly related to their surface structure and composition. The aim of this paper is to review current knowledge of these compounds.

2. Biomimetic nanocrystalline apatites

The term biomimetic is used with different meanings; applied to materials it is often intended to denote preparative techniques and/or properties mimicking those of biological materials. BNA are

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http://dx.doi.org/10.1016/j.pcrysgrow.2014.09.005

defined as apatites exhibiting the main characteristics of biologically produced apatites found, for example, in calcified tissues of vertebrates or ectopic calcifications. Four main characteristics can be identified:

- Non-stoichiometric composition.
- Presence of CO_3^{2-} and HPO_4^{2-} ions.
- Nanometric platelet crystals.
- Hydrated layer on the crystal surface.

2.1. Non-stoichiometry

Several types of non-stoichiometric apatites can be distinguished depending on the substituents and vacancies present in these widespread structures. Stoichiometric apatites are ideally represented by the following formulae:

$$Me_{10}(XO_4)_6Y_2 \tag{1.1}$$

where Me represents a bivalent ion (Ca, Sr, Ba, Pb, Cd, Mn, …), XO_4 a trivalent anion (PO_4, AsO_4, VO_4, …) and Y a monovalent anion (F, Cl, Br, OH, …). A model compound of biomimetic apatite is the calcium phosphate hydroxyapatite:

$$Ca_{10}(PO_4)_6(OH)_2 \tag{1.2}$$

Solid solutions often exist between apatites with different compositions [24]. Non-stoichiometry is related to vacancies in Me sites and Y sites. Significant number of vacancies in XO_4 sites have never been reported and theoretical calculations have shown that the creation of PO_4 vacancies in calcium phosphate hydroxyapatite would be associated with strong destabilization of the structure [17]. In other terms, the creation of large defects like XO_4 vacancies in the apatite structure would produce a collapse of the structure and the formation of other phases, whereas small defects like those corresponding to Me and Y vacancies allow preservation of the structure, although they are associated with a loss of cohesion and stability. Full characterization of non-stoichiometry in apatites thus requires, in principle, determination of the two atomic ratios, Me/X and Y/X, assuming that the number of vacancies in X sites is negligible. In a number of cases, however, only the Me/X ratio is considered, for several reasons; more specifically, concerning biomimetic apatites, the difficulty in determining the OH content.

2.2. HPO_4^{2-} and CO_3^{2-} in biomimetic apatites

Non-stoichiometry in BNA is mainly related to the substitution of PO_4^{3-} ions by bivalent ions like CO_3^{2-} (leading to type B carbonated apatites) or HPO_4^{2-}. All biological apatites contain variable amounts of carbonate and hydrogen phosphate ions [23,4]. In bone the level of HPO_4^{2-} ions has been found to decrease with age and to be associated with an increase in the CO_3^{2-} content. These incorporations of bivalent ions, which are related to a loss of negative charge, are mainly compensated for by a complex defect associating calcium and OH^- vacancies, as represented in the following formulae:

$$Ca_{10-x}(PO_4)_{6-x}(HPO_4, CO_3)_x(OH)_{2-x} \tag{1.3}$$

Rietveld analyses of non-stoichiometric apatites have partially confirmed this compensation mechanism [29,30], initially based on composition considerations only [9]. Other compensation mechanisms involving Ca^{2+} substitution by Na^+ have also been shown, in the case of carbonated apatites, although such substitutions remain very limited in bone mineral. The existence of vacancies clustering in biomimetic apatites, once proposed on the basis of Pauling's rule relative to crystal constitutions, is still debated. More accurate chemical formulas taking into account slight deviations