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Zinc- and strontium-doped hydroxyapatite: A comparative review of synthesis, characterization, and biomedical applications

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ABSTRACT

Hydroxyapatite (HA) is a ceramic material similar to the inorganic part of bone and can be synthesized in a laboratory environment using various methods. The structure of HA allows for ionic substitutions that modify its characteristics, particularly in terms of biological, antibacterial, and mechanical properties. In this review, the effects of doping HA with zinc (Zn) and strontium (Sr) ions are comprehensively discussed. Zn-doped HA has been extensively studied as a coating material, as a constituent of composites, and in tissue engineering scaffolds. This review summarizes the synthesis methods, sintering parameters, and crystal morphology of Zn-doped HAs. The lattice parameters, crystal size, phase composition, and specific Fourier-transform infrared spectroscopy (FTIR) bands detected for Zn-doped HA were collected. Sr-doped HA has also been widely used in various biological applications. The effects of Sr doping on the chemical composition, crystallinity, lattice parameters, morphology, and formation energies of HA were investigated. Overall, ionic doping is an effective strategy for modifying the properties of HA for biomedical applications. The selection of the doping ion and the synthesis method plays a crucial role in determining the properties and performance of HA.

Keywords: Crystallization; doping; hydroxyapatite; strontium; zinc

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INTRODUCTION

Synthetic hydroxyapatite (HA), which closely resembles the inorganic component of bone structure, has attracted extensive research attention due to its simple synthesis process in laboratory environments. The ionic compensation mechanism in biological apatite has inspired researchers to investigate the doping of synthetic HA with various ions. HA plays an essential role in bone and dental regeneration due to its superior biocompatibility and bone affinity [1].

Hydroxyapatite ($Ca_{10}(PO_4)_6(OH)_2$) is a calcium phosphate–based biomaterial with a composition similar to that of human bone and teeth minerals. Its bioactive, biocompatible, and osteoconductive properties make it an ideal candidate for numerous biomedical applications, including bone tissue engineering, bone fillers, and implant coatings [2]. Hydroxyapatite (HAp) is a ceramic biomaterial widely applied in biomedical fields due to its high calcium and phosphate content, serving as a major mineral component in bone and teeth formation [3]. Consequently, HAp possesses high biocompatibility and is frequently utilized in orthopedic nanomedicine [4].

The hexagonal structure of HAp (space group P63/m) has lattice parameters a = 9.32 Å and c = 6.881 Å, with an angle of 120°, while the P21/m group exhibits parameters a = 9.225 Å, b = 2a, and c = 6.881 Å, and a density of about 3.19 g/cm^3, corresponding to the chemical formula $Ca_{10}(PO_4)_6(OH)_2$ [5]. Hydroxyapatite materials derived from natural rock are often combined with functional apatite powders containing hydroxyl groups. Hydroxyapatite (HA) is composed of phosphate (PO_4^{3-}) and hydroxyl (OH^-) groups bound to a calcium ion crystal structure, which may be partially substituted with ions such as Sr^{2+} [6].

Modification of HAp composition through ionic substitution has become a major research focus to enhance its properties for specific biomedical applications. Strontium (Sr) and

zinc (Zn) are naturally present in bone and play significant roles in bone metabolism. The substitution of calcium ions (Ca^{2+}) in the HAp structure with Sr^{2+} or Zn^{2+} alters its physicochemical, mechanical, and biological properties [7]. Strontium, with the chemical symbol Sr and atomic number 38, is an alkaline earth metal found in minerals [8]. Owing to its chemical similarity to calcium, strontium can replace it in several biological processes. In medicine, strontium is used to treat osteoporosis due to its dual effect of promoting bone formation and inhibiting bone resorption [8].

The incorporation of strontium enhances bone density and reduces fracture risk. As a trace element in bone, Sr^{2+} has the ability to stimulate osteoblast activity while suppressing osteoclast-mediated bone resorption [9]. Therefore, Sr substitution into hydroxyapatite structures not only improves biocompatibility and osteoconductivity but also provides additional therapeutic benefits—particularly for treating bone-related disorders such as osteoporosis. Current research on Sr-doped HA continues to advance, exploring synthesis and characterization techniques to optimize material performance for clinical applications [10].

The addition of strontium ions is expected to enhance bone metabolism. Apatite exhibits pharmacological effects by suppressing osteoclast differentiation through ion-exchange mechanisms with calcium ions. Moreover, apatite serves as a bone filler and a drug delivery system, in which therapeutic agents are encapsulated and gradually released via osteoclastic phagocytosis [11]. Incorporating Sr ions into apatite crystals enables sustained drug release. In summary, this synthesis pathway supports the development of novel Sr-based drug-release systems [12].

Synthetic hydroxyapatite (HA), closely mimicking the inorganic component of bone, remains a central topic in research due to its ease of synthesis under laboratory conditions [10]. The ion-compensation mechanism in biological apatite continues to inspire the doping of HA with different ions. HA plays an essential role in bone and dental regeneration because of its superior biocompatibility and excellent bone-bonding capability [13]. Ionic doping represents an efficient and practical approach to modify the solubility and degradation rate of HA while introducing additional biological and antibacterial functionalities [14].

Zinc (Zn), with atomic number 30, is an essential micronutrient involved in various physiological processes. In orthopedics, Zn contributes to ideal bone healing and regeneration. Studies have demonstrated that Zn positively influences bone matrix formation and mineralization through osteoblast stimulation [15]. Zinc also helps prevent osteoporosis by maintaining bone density and enhancing osseointegration in orthopedic implants—an essential process where bone tissue structurally bonds to implant surfaces such as pins, screws, or joint replacements. Zinc doping, achieved by substituting calcium ions (Ca^{2+}) with Zn^{2+}, represents an innovative strategy to enhance the bioactivity and biocompatibility of implant materials [16].

Calcium, as the main component of hydroxyapatite, is widely used as an implant coating due to its similarity to natural bone minerals. However, partial substitution of Ca^{2+} with Zn^{2+} ions offers several advantages. Zn doping is an innovative approach to engineering more bioactive and biocompatible implant surfaces, aiming to develop materials that not only integrate effectively with the body but also actively promote faster and more sustainable bone healing—surpassing the capabilities of pure calcium-based materials [17].

RESEARCH METHODS

The synthesis methods used to produce zinc- (Zn) and strontium- (Sr) doped hydroxyapatite (HA) involve a variety of techniques that significantly influence the physical and chemical properties of the material. In the synthesis of Zn-doped HA, the most commonly employed techniques include the sol–gel, wet precipitation, and hydrothermal methods. The sol–gel method involves the formation of a sol

and subsequent gel through controlled chemical reactions, the wet precipitation method relies on the precipitation of solid particles from a solution, while the hydrothermal method utilizes high temperature and pressure to regulate reaction kinetics. These methods yield Zn-doped HA particles with diverse sizes and morphologies, most of which are nanosized and spherical. Particle size and morphology directly affect properties such as surface area, reactivity, and mechanical strength of HA.

The hydrothermal method is particularly used for preparing Sr-doped HA and HA nanoparticles, offering excellent control over composition, crystallinity, lattice parameters, and formation energy [10]. The choice of synthesis method plays a crucial role in determining the characteristics of Zn- and Sr-doped HA. The sol–gel method provides advantages such as high purity, good homogeneity, and relatively easy control over particle size and porosity. However, it involves higher cost, longer processing, and potential hazardous waste generation.

The wet precipitation method is more economical and suitable for large-scale production but often presents challenges in controlling particle size and achieving homogeneity, with products tending to exhibit higher levels of agglomeration [18]. The hydrothermal method, on the other hand, produces highly crystalline materials with controlled particle sizes—especially nanoparticles—through reactions conducted under closed systems at elevated temperature and pressure. Nevertheless, this technique requires specialized equipment, increasing production costs and extending reaction times [5]. Ultimately, the selection of an appropriate synthesis method depends not only on the specific application and the desired physicochemical properties of the material, but also on critical factors such as scalability, cost efficiency, reproducibility, environmental impact, availability of precursors, and the ability to precisely control particle size, morphology, and crystallinity during fabrication.

RESULTS AND DISCUSSION

This chapter presents a comparative discussion of Zn-doped and Sr-doped hydroxyapatite (HA) as coating materials. Zinc (Zn) doping enhances the bioactivity, dissolution behavior, and adsorption capacity of HA, all of which are essential for cell adhesion and proliferation. Meanwhile, strontium (Sr)-doped HA has been widely applied in various biological contexts, particularly in bone and dental regeneration. Sr doping improves the biocompatibility and bioactivity of HA, accelerates osteoblast differentiation, and suppresses osteoclast proliferation.

Hydroxyapatite (HA), with the chemical formula $Ca_{10}(PO_4)_6(OH)_2$, is a ceramic material structurally similar to the inorganic component of bone and teeth, making it highly attractive for biomedical applications. The ability of HA to undergo ionic substitution allows for modification of its properties to meet specific functional requirements. In this context, doping with zinc (Zn) and strontium (Sr) ions has become a key strategy.

Zn doping, achieved by substituting calcium (Ca^{2+}) with zinc ions (Zn^{2+}), affects the microstructure and properties of HA. The synthesis methods used to produce Zn-doped HA—such as sol–gel, wet precipitation, and hydrothermal—yield materials with varying particle sizes, morphologies, and crystallinities. Zn incorporation generally reduces HA crystal size and may transform particle morphology from rod-like to nanospheres or nanorods. Furthermore, Zn doping distorts the crystal lattice, alters the lattice parameters (a and c), and may lead to secondary phase formation such as β-tricalcium phosphate (β-TCP).

At the chemical level, FTIR spectroscopy reveals interactions between Zn ions and hydroxyl (OH^-) and phosphate (PO_4^{3-}) groups within the HA structure. Zn doping also affects mechanical properties, enabling modification of hardness and elastic modulus. Biologically, it enhances the bioactivity and adsorption capacity of HA, which are crucial for cellular interaction and drug delivery performance.

In contrast, Sr doping—through substitution of Ca^{2+} with Sr^{2+}—induces significant changes in HA's structural and biological behavior. The hydrothermal method is commonly used to synthesize Sr-doped HA, leading to increased crystal size and lattice parameters. DFT simulations have validated experimental findings regarding lattice parameter variations and provided insights into formation energy and substitution preferences (Ca(1) or Ca(2) sites). Although Sr doping does not markedly alter HA crystallinity, it affects phase stability and bone cell interactions, making it particularly relevant for bone regeneration applications.

Table 1. Comparison between Zn-doped HA and Sr-doped HA.

Aspect	Zn-doped HA	Sr-doped HA	References
Research objective	Synthesis, characterization, and biomedical applications of Zn-doped HA	Hydrothermal synthesis, characterization, and simulation of Sr-doped HA	[19, 20]
Method	Sol-gel, wet precipitation, hydrothermal	Hydrothermal	[21]
Ion	Zinc (Zn)	Strontium (Sr)	[22]
Structural effects	Alters crystal size and morphology, affects lattice parameters and phase composition	Increases lattice parameters and nanoparticle crystal size, with no significant change in crystallinity	[23]
Physical effects	Enhances cell proliferation, differentiation, and antibacterial activity	Promotes osteoblast differentiation and inhibits osteoclast proliferation	[24]
Biomedical applications	Implant coatings, tissue-engineering scaffolds, drug carriers	Bone and dental regeneration	[25]
Characterization techniques	XRD, FTIR, TEM, Raman spectroscopy, SEM–EDX	XRD, FTIR, TEM, DFT simulations	[26, 27]
Research highlights	Comprehensive review of Zn effects on HA properties and synthesis–application relationship	Deeper understanding of Sr doping mechanisms and DFT validation of experimental	[19, 20]

Table 2. Comparison of physical and chemical properties of Zn-doped HA and Sr-doped HA [19, 20].

Property	Zn-doped HA	Sr-doped HA
Chemical composition	Substitution of Zn^{2+} for Ca^{2+}; interaction between Zn^{2+} and OH^-/PO_4^{3-} groups	Substitution of Sr^{2+} for Ca^{2+}; stoichiometric variation of HA due to Sr substitution
Lattice parameters	Variation in a and c parameters; Zn ions cause lattice distortion	Increase in lattice parameters; DFT results consistent with experiments
Phase and crystallinity	Decrease in crystallinity with higher Zn content; formation of secondary β-TCP phase	Crystallinity remains largely unchanged with Sr doping
Morphology	Nanospheres, nanorods, platelets	Nanoparticles

In summary, Zn and Sr doping offer distinct yet complementary pathways for tailoring the physical, chemical, and biological characteristics of hydroxyapatite. Zn primarily affects crystal size, surface morphology, and antibacterial functionality, enhancing cellular response and corrosion resistance, while Sr improves lattice parameters, phase stability, and osteogenic activity, promoting better bone integration and regeneration performance. The combination of experimental studies and DFT simulations provides a comprehensive and synergistic understanding of the intricate relationships among composition, structure, and properties in doped HA—serving as a crucial scientific foundation for the rational design and optimization of next-generation biomaterials with enhanced performance and functionality.

The XRD patterns of Sr-doped HA with different Sr concentrations (0% – 100%) show that diffraction peaks (002) and (300) shift toward lower 2θ values with increasing Sr content. This shift indicates an expansion in lattice parameters (a and c) and interplanar spacing (d), attributed to the larger ionic radius of Sr^{2+} (0.118 nm) compared to Ca^{2+} (0.099 nm). Narrower diffraction peaks suggest increased crystallinity in Sr-doped HA. As shown in Table 3, crystallinity varies with Sr content—10% and 50% Sr-HA show lower crystallinity than 100% Sr-HA. The reduction in crystallinity at lower Sr concentrations may result from irregular Sr distribution, limited ion substitution, and lattice distortions that disrupt atomic periodicity, thereby hindering uniform crystal growth and compromising structural stability during the synthesis process. This suggests that insufficient Sr incorporation causes non-uniform lattice sites and localized strain, which disturb atomic order and hinder the formation of well-organized crystalline domains, ultimately reducing the crystallinity, phase stability, and integrity of the Sr-doped HA, affecting its mechanical, chemical, and biological performance [28].

The c parameter decreases with Zn incorporation into the HA structure when Zn content exceeds 5 mol%, whereas the a parameter increases, likely due to the incorporation of H_2O molecules into OH^- sites within the lattice. As Zn substitution increases up to Zn/(Zn + Ca) = 10 mol%, the c parameter decreases and then rises again beyond that level. Studies with Zn concentrations of 5–20 mol% suggest that Zn^{2+} occupies Ca(I) sites, with saturation at around 15 mol%. The trends of increasing a and decreasing c indicate Zn^{2+} preference for Ca(I) sites, accompanied by water and carbonate incorporation (Table 4).

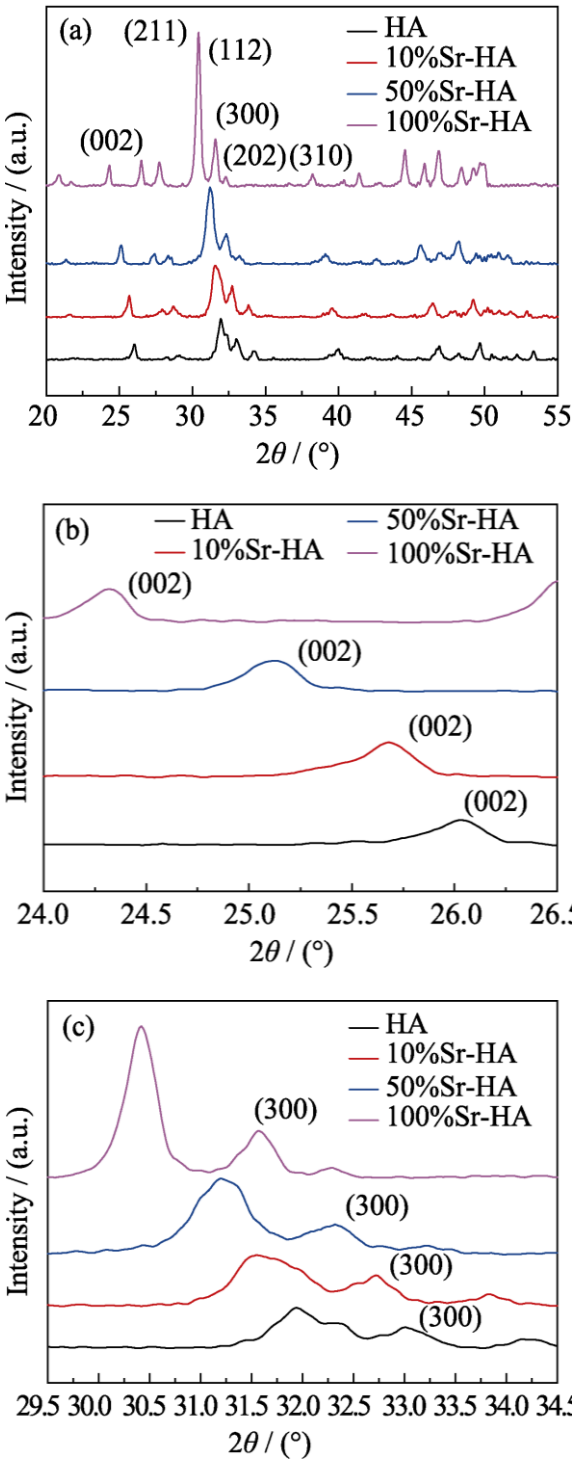

Figure 1. XRD patterns of HA and Sr-doped HA nanoparticles showing (b) the enlarged (200) peak and (c) the enlarged (300) peak.

Table 3. Lattice parameters and crystallinity of Sr-doped HA nanoparticles (XRD results) [19].

Sample	Crystallinity (%)	2θ (002) (°)	2θ (300) (°)	a (nm)	c (nm)
HA	53.3	26.07	33.09	0.93679	0.68286
10% Sr-HA	51.1	25.68	32.76	0.94625	0.69326
50% Sr-HA	49.4	25.12	32.34	0.95814	0.71056
100% Sr-HA	73.7	24.34	31.58	0.98058	0.73071

Table 4. Lattice parameters and volume of Zn-doped HA [20].

Amount of Zn doping	Synthesis method	Ca/P ratio	Lattice parameter a (Å)	Lattice parameter c (Å)	V ($Å^3$)
1 mol%	Hydrothermal		9.430; 9.428; 9.422; 9.424	6.879; 6.878; 6.874	529.7; 529.4; 528.5
2 mol%			9.426	6.871; 6.866	528.4; 528.2
3 mol%					
4 mol%					
5 mol%					
2 mol%			9.417; 9.438; 9.442	6.864; 6.880; 6.883	
5 mol%					
8 mol%					
0.05 mol%			9.427	6.903	
0.1 mol%	Constant additional		9.425; 9.413; 9.407	6.884; 6.889; 6.885;	529.6; 528.4; 527.6
0.5 mol%	precipitation method				
1 mol%					
10 mol%	Cathodic deposition		9.395	6.870	
5 mol%	Chemical co-precipitation		9.422; 9.387; 9.397; 9.509;	6.855; 6.829; 6.854;	525.0; 519.0; 522.0
10 mol% 15 mol%				6.836	533.3
20 mol%					
5 mol%	Chemical co-precipitation		9.393; 9.409; 9.411; 9.415;	6.861; 6.855; 6.854	522.3; 523.7; 524.3
10 mol% 15 mol%	Sintered at 1000 °C			6.852	524.3
20 mol%					
0.043 mol%	Modified neutralization	1.63 1.61	9.424; 9.433	6.897; 6.876	530.5; 529.9
0.42 mol%	Method				
5 mol%	Mechanical alloying		9.469	6.868	533.3
1 wt.%	Wet precipitation method	1.86	8.897	6.843	469.1
2 mol%		1.63	9.431	6.901	529.7
2 wt.%			9.212; 9.062; 8.841	7.065; 7.281; 8.404	1038.4; 1019.0; 925.3
5 wt.%					
10 wt.%					
1 mol%			9.432; 9.435; 9.436	6.883; 6.882; 6.881	
3 mol%					
5 mol%					
0.7 mol%	Sol-gel method		9.436; 9.439	6.881; 6.874	
2 mol%					

CONCLUSION

Hydroxyapatite (HA) for biomedical applications through ionic doping involves distinct approaches. Zn-doped HA exhibits different synthesis methods, material properties, and promising biomedical applications. The influence of Zn doping can modify the mechanical, antibacterial, and bioactive properties of HA, depending on factors such as synthesis method and sintering conditions. Meanwhile, Sr-doped HA, investigated through a combination of experimental techniques and DFT simulations, provides insights into the effects of Sr incorporation on structure, stability, and material properties. This integrated approach offers strong computational validation of experimental findings and a deeper understanding of Sr doping mechanisms. Although the focus is narrower on Sr-doped HA, such studies elucidate how ionic substitution can be used to tailor HA properties for bone regeneration. Comparatively, both studies complement each other by offering distinct yet relevant perspectives on HA modification, collectively addressing the complex challenges of designing more effective biomaterials for biomedical applications.

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