Structural and morphological study of mechanochemically synthesized crystalline nanoneedles of Zr-doped carbonated chlorapatite

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1. Introduction

Bioceramics are an important subset of biomaterials with wide range in biocompatibility, from the ceramic oxides to the other extreme of resorbable materials [1]. There have been significant advances in this field in hard-tissue replacement and regeneration over the last decade or so [2]. Recently, it has been found that doping or modification of original hexagonal apatite crystal structure with various ions such as Ca²⁺, Mg²⁺, Sr²⁺, Ba²⁺, Mn²⁺, Fe²⁺, Zn²⁺, Cd²⁺, Pb²⁺, Na⁺, K⁺, Al³⁺, PO₄³⁻, AsO₄³⁻, VO₄³⁻, SO₄²⁻, CO₃²⁻, SiO₃²⁻, OH⁻, F⁻, Cl⁻, Br⁻, and O²⁻ can improve the phase stability, mechanical and electrical properties as well as biological responses [3,4]. Therefore, current biomedical applications of these modified bioceramics may include substitutions for hips, knees, teeth, tendons and ligaments, as well as restoration for periodontal disease, maxillofacial reconstruction, augmentation and stabilization of the jawbone, spinal fusion and bone fillers after tumor surgery [5]. Besides, these bioceramics have potential applications in drug-delivery systems [6] and tissue engineering applications [7].

The substitution of Zr ions in different ceramic lattices have shown improvements in optical transparency [8], mechanical flexibility [9], critical current density and upper critical field [10] as well as an increment of photocatalytic degradation of bisphenol A (BPA) [11]. In the field of bioceramics, this replacement can improve the mechanical properties and biological responses [12]. To the best of our knowledge, the role of Zr substitution in the apatite crystal growth orientation, however, remains unaddressed. Hence, in the present study, the structural and morphological features of mechanochemically synthesized n-ZCCA are explored for the first time.

2. Materials and methods

Ca(OH)₂ (≥ 96 wt%), H₃PO₄ (≥ 85 wt% in H₂O), and ZrCl₄ (99.99 wt%) (all from Sigma-Aldrich Co., USA) were used as reactants. The designed level of replacement of Ca by Zr is shown by the x value in the CA, where the x values are 0.0, 0.25, 0.50, and 1.0 and consequently the products were labeled as Z₀, Z₀.25, Z₀.51, and Z₁, respectively (see Supplementary data 1). Adequate amounts of reagents were first blended and the mixed powders were milled for 3 h in a high-energy planetary ball mill (Retsch, PM100) using zirconia vials and balls (see Supplementary data 2). The general form of the reaction is as follows (see Eq. 1 and Supplementary data 2). To study the influence of subsequent...
annealing on the structural evolutions, the milled specimens were annealed under atmospheric pressure at 800 °C for 1 h.

\[(10 - x - y)Ca(OH)_2 + (6 - y)H_3PO_4 + xZrCl_4 + yH_2CO_3 \text{ (from air)} \rightarrow Ca_{10-x-y}Zr_x(PO_4)_{6-y}(CO_3)_y(OH)_{2-y-2xCl_2+xCl_2+(18-y)H_2O} \text{ (1)}\]

The phase compositions were checked by powder X-ray diffraction (XRD) analysis with a PANalytical Empyrean X-ray diffractometer (Cu-Kα radiation) over a 2θ range from 10° to 70°. To identify the functional groups of nanopowders, attenuated total reflection (ATR) analysis was carried out on a Tensor 27 (Bruker FT-

Fig. 1. (a) XRD profiles, (b) phase volume fraction (PVF, %), (c) crystallite size (D, nm), (d) lattice strain (η, %), and (e) crystallinity degrees (Xc, %) of the 3 h milled specimens before and after annealing at 800 °C for 1 h.
IR spectrophotometer) with a frequency range of 4000–400 cm\(^{-1}\). The microstructure of the products was analyzed using FE-SEM/EDS (SU8000, Hitachi, Japan) and TEM (HT-7700, Hitachi, Japan).

3. Results and discussion

Fig. 1a shows the XRD profiles of 3 h milled specimens before and after annealing. In the absence of Zr, milling for 3 h resulted in the formation of CHA (Ca\(_{10}\)(PO\(_4\))\(_6\)(OH)\(_2\))(OH\(_2\))\(_y\) (JCPDS01-072-0072). With the x value of 0.25 (Z0.25), ZCCHA (Ca\(_{9.75}\)Zr\(_{0.25}\))(PO\(_4\))\(_6\)(OH\(_2\))(OH\(_2\))\(_y\) (CO\(_3\))(H\(_2\)O)\(_{1.5}\)-Cl\(_2\)) was formed with the same milling time. In addition, calcium carbonate (CaCO\(_3\), JCPDS01-072-1651) appeared as a secondary phase in the XRD profile. With the increase of Zr concentration in Z0.5, the intensity of the characteristic peaks of ZCCHA declined notably and new diffraction peaks attributed to calcium chlorophosphate (CCP, Ca\(_3\)PO\(_4\)Cl, JCPDS01-072-0010) emerged due to the incomplete reaction of the raw materials. Further increasing the Zr content to \(x=0.5\) (Z0.5), the intensity of the characteristic peaks of ZCCHA declined notably and new diffraction peaks attributed to calcium chlorophosphate (CCP, Ca\(_3\)PO\(_4\)Cl, JCPDS01-072-0010) emerged due to the incomplete reaction of the raw materials. Further increasing the Zr content to \(x=0.75\) (Z0.75), ZCCA crystallized to Zr-doped chlorapatite (ZCA, Ca\(_9\)Zr\(_0.25\))(PO\(_4\))\(_6\)(Cl\(_2\)) and consequently the phase compositions were ZCA and CCP. Before thermal treatment, the values of a-axis, c-axis, and unit cell volume of the apatite lattice were 9.55583 Å, 6.76548 Å and 535.02 Å\(^3\), respectively. The incorporation of Zr into the apatite structure resulted in the shrinkage of the lattice constants, as the radius of Zr\(^{4+}\) (0.82 Å) is smaller compared to Ca\(^{2+}\) (1.00 Å) [14]. After annealing, due to the recovery of the crystal lattice, the unit cell volume increased to 543.40 Å\(^3\).

From Fig. 1c–e, the structural features of the products are influenced significantly by the level of a substitution and subsequent annealing process. Here, crystallite size (\(D\)) and lattice strain (\(\eta\)) of the samples were calculated using the XRD data [15]. In Fig. 1c, there is a positive linear correlation between Zr content and crystallite size until \(x=0.5\). From this value on, the correlation is negative. It seems that the addition of Zr up to \(x=0.5\) can promote surface diffusion, densification and grain growth which resulted in an increase in the crystallite size [16]. As the Zr concentration increased further to \(x=1.0\), the crystallite size decreased to 44 ± 2 nm and lattice strain increased to 0.37 ± 0.02%. These opposite changes suggest that Zr content equal to \(x=1.0\) effectively inhibits grain growth probably by staying at grain boundaries which leads to a reduction in the crystallite size and an enhancement in lattice strain. After annealing, an apparent increase in the crystallite size (90 ± 4 nm) and a significant reduction in the lattice strain (0.19 ± 0.01%) was perceived, which are probably due to the completion of crystal recovery and further reduction in the internal energy (achieved by reducing the total area of grain boundary) [17]. Moreover, the crystallinity degree (\(X_c\)) was determined by taking the sum total of relative intensities of individual characteristic peaks [18]. Results show that the crystallinity degree of the heat treated Z0 is 89 ± 2% but increased to 97 ± 2% in the annealed Z1 (see Supplementary data 3).

The ATR spectra of the 3 h milled samples are shown in Fig. 2. The low intensity OH-derived band at 638 cm\(^{-1}\), the disappearance of OH stretching band at 3573 cm\(^{-1}\) and the broadening of PO\(_4\)-derived bands are due to the decrease of crystallinity from the carbonate substitution in the apatite lattice [19]. With the presence of Zr, the concentration in Z0.5, the intensity of the characteristic peaks of ZCCHA declined notably and new diffraction peaks attributed to calcium chlorophosphate (CCP, Ca\(_3\)PO\(_4\)Cl, JCPDS01-072-0010) emerged due to the incomplete reaction of the raw materials. Further increasing the Zr content to \(x=0.5\) (Z0.5), the intensity of the characteristic peaks of ZCCHA declined notably and new diffraction peaks attributed to calcium chlorophosphate (CCP, Ca\(_3\)PO\(_4\)Cl, JCPDS01-072-0010) emerged due to the incomplete reaction of the raw materials. Further increasing the Zr content to \(x=0.75\) (Z0.75), ZCCA crystallized to Zr-doped chlorapatite (ZCA, Ca\(_9\)Zr\(_0.25\))(PO\(_4\))\(_6\)(Cl\(_2\)) and consequently the phase compositions were ZCA and CCP. Before thermal treatment, the values of a-axis, c-axis, and unit cell volume of the apatite lattice were 9.55583 Å, 6.76548 Å and 535.02 Å\(^3\), respectively. The incorporation of Zr into the apatite structure resulted in the shrinkage of the lattice constants, as the radius of Zr\(^{4+}\) (0.82 Å) is smaller compared to Ca\(^{2+}\) (1.00 Å) [14]. After annealing, due to the recovery of the crystal lattice, the unit cell volume increased to 543.40 Å\(^3\).

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Fig. 2. ATR spectra of the milled samples with different degrees of substitution (a) Z0, (b) Z0.25, (c) Z0.5, and (d) Z1.
progressive incorporation of Cl− generated a new broad diffuse band at 3430 cm\(^{-1}\) which is due to the OH− neighboring Cl− in a hydrogen-bonded configuration O—H…Cl. Moreover with the addition of Zr, the band at 638 cm\(^{-1}\) disappeared completely and a new band appeared at 669 cm\(^{-1}\), 707 cm\(^{-1}\) and 729 cm\(^{-1}\) for Z0.25, Z0.5 and Z1, respectively, which is attributed to the bending of single OH− ions in a predominantly Cl− chain [20]. The PO\(_4\)-derived bands occur at 1086–1008 cm\(^{-1}\) (\(\nu_3\)), 960 cm\(^{-1}\) (\(\nu_1\)), 584 and 555 cm\(^{-1}\) (\(\nu_4\)), and 462 cm\(^{-1}\) (\(\nu_2\)) [19].

The two regions of carbonate vibrations in apatite are: (i) 1448–1407 cm\(^{-1}\) attributed to \(\nu_3\) and (ii) 890–850 cm\(^{-1}\) attributed to \(\nu_2\) vibrations of the carbonate groups (B-type substitution) [21].

The morphological features of the synthesized nanopowders are shown in Fig. 3. From Fig. 3a, the powders consist of large agglomerates of nanocrystalline elongated crystals which is similar to the observations of Graeve et al. [22]. During annealing, the needle-like structure transforms into a flaky-like structure (Fig. 3b). The EDS spectrum in Fig. 3c indicates that calcium, phosphorus, oxygen, chlorine, carbon and zirconium are the main elemental constituents. Owing to the presence of water as a by-product during milling, no chemically stable contaminants were observed. From the TEM images in Fig. 3d and e, Z0 consists of randomly shaped fine particles with widths of 7–10 nm and lengths of 12–19 nm. The TEM images of Z1 in Fig. 3g and h reveal the same morphology as the FE-SEM observations, with the presence of nanoneedles of an average size of around 40–60 nm in length and 10–20 nm in width. In general, CA crystallizes in a pseudo-hexagonal structure and consequently illustrates diverse spatial arrangements of calcium and phosphate groups due to the two different types of binding sites for the approaching growth units. As compared to the hexagonally arranged \(ab\) crystal facets, the rectangular \(ac\) or \(bc\) crystal facets are rich in calcium ions or positive charge [23]. Therefore, the preferential replacement of Zr into the \(ac\) or \(bc\) apatite crystal facets (rich in calcium ions) causes a \(c\)-axis oriented crystal growth of the nanoneedles. More detailed analysis was achieved using HR-TEM lattice images (Fig. 3f and i). The lattice fringes had a spacing of 0.84 nm for Z0 and 0.87 nm for Z1, which belongs to \(d_{100}\). However, no lattice fringes in other directions were identified (see Supplementary data 4).

4. Conclusions

The structural and morphological features of the mechanochemically synthesized n-ZCCA were investigated. Results showed that the acidic reagents play an important role for promoting gradual
reactions during the mechanochemical process. A significant increase in the peak intensity, a thermal recovery of apatite crystal lattice as well as some phase transitions occurred during the annealing process at 800 °C for 1 h. Moreover, the breadth of the diffraction peaks of the heat treated samples declined drastically which can be justified due to a sharp rise in the crystallite size and a notable decrease in the lattice strain. The incorporation of Zr into the apatite lattice led to the shrinkage of lattice constants. The TEM images of the nanoneedle morphology showed a homogeneous size/shape distribution.

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Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at http://dx.doi.org/10.1016/j.matlet.2015.02.125.

References