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Effect of precursor solution pH on the structural and crystallization characteristics of sol–gel derived nanoparticles

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Abstract

This paper concerns with the effect of pH on the structure and crystallization behavior of particulate sol–gel derived zirconium titanate. According to differential scanning calorimetry, it was found that the thermal stability of the synthesized amorphous particles was enhanced by increasing the precursor solution pH value from 4 to 10, as confirmed by X-ray diffraction. Transmission electron microscopy studies on the xerogel and crystallized nanoparticles showed that the pH value does not fairly affect their size and morphology; thus, these structural features cannot have a meaningful contribution to the detected crystallization difference. The realized thermal behavior was explained based on a mechanism relating to the adsorption of hydroxide ions (OH^-) existing in the medium to metallic hydroxide precipitates synthesized during the sol–gel process. In this regard, it was speculated that the more the pH value is increased, as reasonably accompanied by the more hydroxide adsorption, the more the crystallization event is inhibited.

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Keywords: Ceramics; Sol-gel processes; Phase transitions; Transmission electron microscopy

1. Introduction

Zirconium titanate is one of the candidate ceramics for electronic, optical, catalytic, chemical, and biomedical applications [1–3]. One of the feasible methods to produce ceramic powders is the sol–gel route, so that the synthesized amorphous structures crystallize at temperatures considerably lower than those obtained by other processes [4–6]. Sol–gel synthesis can be performed by hydrolysis and condensation of inorganic salts or alkoxides. The procedures starting from the former precursors are categorized as particulate sol–gel processes, in which nanoparticles are directly synthesized and then dispersed in the medium.

Recently, a successful particulate sol–gel method using metallic chloride precursors was introduced to synthesize zirconium titanate in an aqueous solution of pH = 7 [7]. The structural and surface characteristics of coatings obtained by this method have been reported [8–11]. Moreover, the corrosion behavior and biocompatibility of a medical-grade stainless steel coated with these coatings, in the forms of oxide and hybrid, have been investigated [12,13]. However, to our knowledge, little work has been reported on the effect of the pH value of the synthesis solution on the structure and crystallinity of particulate sol–gel products. This work evaluates the influence of pH (4, 7, and 10) on the structure and crystallization properties of zirconium titanate nanoparticles prepared by the above-mentioned sol–gel process.

2. Experimental procedures

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An equal-molar solution of $ZrCl_4$ (Alfa Aesar, 99.5 %) and $TiCl_4$ (Alfa Aesar, 99.99 %) was prepared using deionized water, which led to a pH value of almost 1. Then, by the dropwise addition of a 2M NaOH solution, the pH of the precursor solution was increased to 4, 7, and 10. The obtained hydrogels were rinsed several times with deionized water to remove chloride ion. To assess the crystallization behavior of the xerogels dried at 50 ºC, differential scanning calorimetry (DSC, Netzsch, STA 449 F1 Jupiter ®) was employed at a heating rate of 10 °C/min. To confirm the drawn thermal conclusions, X-ray diffraction (XRD, Bruker AXS Inco., Cu Kα radiation) profiles of the powder specimens annealed at a temperature, selected according to the DSC results (650 ºC), for 10 minutes were recorded. A transmission electron microscope (TEM, JEOL JEM-2100, 200 kV) was also used to observe the powder particles in the synthesized hydrogels and the samples after crystallization.

3. Results and discussion

During the DSC scan of the xerogel prepared at pH = 7, a broad endothermic peak at about 120 ºC was observed, due to the removal of residual water and chloride [7]. A sharp exothermic peak was also observed at around 690 ºC, which was attributed to crystallization, as confirmed by XRD and TEM studies. However, as noted in the experimental section, the materials synthesized in the various pH values are studied in the present work. The DSC profiles of the xerogels prepared at the different pH values, albeit in a temperature range in which crystallization occurs, are shown in Fig. 1. Indeed, since nanoparticles during sol–gel processing are nucleated from a liquid phase at room temperature, the xerogels have an amorphous structure. By heating and exceeding the temperature range of the amorphous stability, structural ordering and crystallization occur. As can be seen in the DSC profiles, the

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crystallization peak temperatures for the samples synthesized at pH = 4, 7, and 10 are 665, 690, 706 ºC, respectively. This is confirmed by the XRD experiments done on the samples annealed at 650 ºC for 10 minutes (Fig. 2), suggesting that crystallinity is decreased with increasing pH. Note that these temperature and time are selected to make a crystallinity contrast in the samples. Thus, it is found that by increasing the pH value, the crystallization peak temperature is shifted to higher temperatures, i.e. the stability of the prepared amorphous phase increases.

Since the powder particle morphology and size, especially in the nano-metric scale, can affect the thermodynamics and kinetics of phase transformations including crystallization, TEM micrographs were taken of the synthesized xerogels (Fig. 3). The higher magnification photographs, in which single particles are evident, were taken of the hydrogels after adding carboxymethyl cellulose which makes the nanoparticles be negatively charged and depresses their hydrophobicity and agglomeration [8,9]. As can be seen, all of the samples present similar features, i.e. a large tendency to agglomeration (due to their nano-metric size and high surface energy), a relatively spherical morphology, a mean particle size of about 5 nm, and an amorphous structure (realized from the selected area diffraction (SAD) patterns presented as inserts). To study theses features after crystallization, TEM micrographs were taken of the samples synthesized at pH = 4, 7, and 10 after annealing at 675, 705, and 720 ºC, the end temperatures of the crystallization ranges in the DSC curves, respectively (Fig. 4). Again, no meaningful difference is detected, suggesting that the pH value of the synthesis solution has no detectable effect on the powder morphology and size, before and after crystallization. Thus, these characteristics cannot be used to explain the difference observed in the thermal

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behavior of this particulate sol–gel system, despite employed to do so in some polymeric sol–gel systems, as briefly focused on below.

In the sol–gel synthesis of La_2CuO_4, using lanthanum nitrate and cupric nitrate as the raw materials, water as the solvent, citric acid as the complexing agent and ammonia to control pH, the particle size and crystallinity firstly increased and then decreased with increasing the precursor solution pH from 1 to 2.5, as explained with the dissociation of citric acid [14]. Moreover, pH significantly affected the formation, morphology, and phase purity of sol–gel derived calcium hydroxyapatite [15]. In the sol–gel reactions of titanium alkoxides and water, it was found that pH influenced the size and specific surface area of as-synthesized and annealed products [16].

It is believed that the behavior of hydroxide ions (OH^-) and protons (H^+) in the sol–gel system causes the observed crystallization trend. The reaction of water and metallic chlorides produces amorphous hydroxides during sol–gel processing, through the following equation:

$$ZrCl_4 + TiCl_4 + 8H_2O \rightarrow ZrTi(OH)_8 + 8H^+ + 8Cl^- \quad (1)$$

At very low pH values, H^+ ions are adsorbed to the –OH groups of the metallic hydroxide precipitates by hydrogen bonding. By increasing pH, the progress in the adsorption of OH^- ions to the Ti(IV) and Zr(IV) sites of the synthesized hydroxide precipitates dominates, particularly in the pH range studied in this work. It is believed that the adsorption of OH^- ions principally retards the nucleation and thereby crystallization of oxide [17], since crystallization demands the elimination of excess oxygen and hydrogen in the produced hydroxides, via Reaction 2, apart from short-range diffusion-controlled ordering of the ions in the suitable sites of the crystal structure. This is also supported by the fact that by increasing

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pH, the excess of oxygen (O^- and O_2^-) is more gradually eliminated in sol–gel products [18,19].

$$ZrTi(OH)_8 \rightarrow ZrTiO_4 + 4H_2O \quad (2)$$

Thus, it is speculated that the more the pH value is increased, as reasonably accompanied by the more hydroxide adsorption, the more the crystallization event is retarded.

4. Summary

This paper investigated the effect of pH on the structure and crystallization properties of sol–gel derived nanoparticles. It was found that the pH value did not influence the size and morphology of the xerogel and crystallized nanoparticles. However, the crystallization peak temperature of the synthesized amorphous xerogels was enhanced by increasing the pH value of the solution, as explained based on a mechanism dealing with the adsorption of hydroxide ions (OH^-) to the metallic hydroxide precipitates.

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Figures

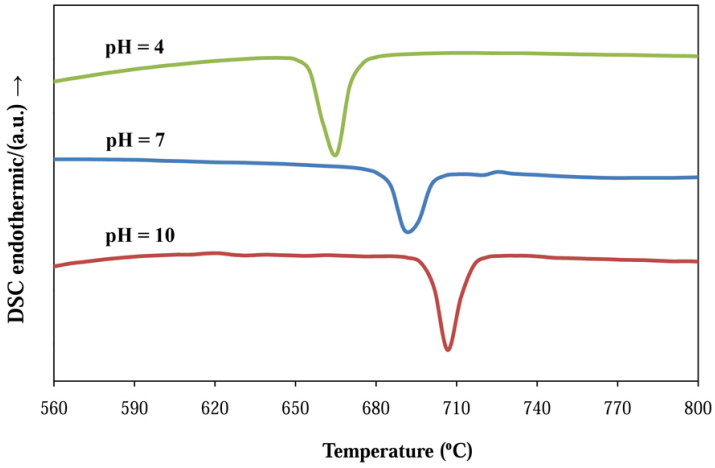

Fig. 1. DSC profiles of the xerogels prepared at the different pH values.

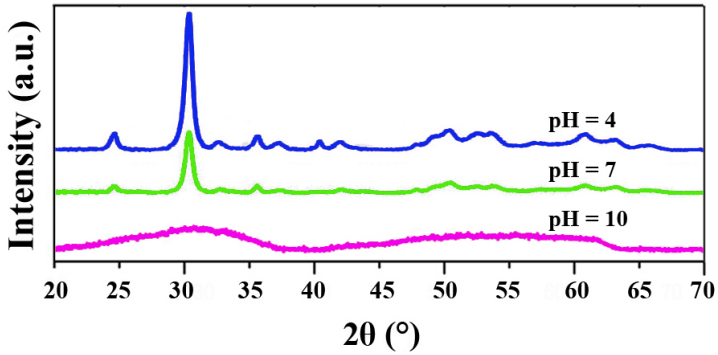

Fig. 2. XRD patterns of the powder samples synthesized at the different pH values after annealing at 650 ºC for 10 minutes.

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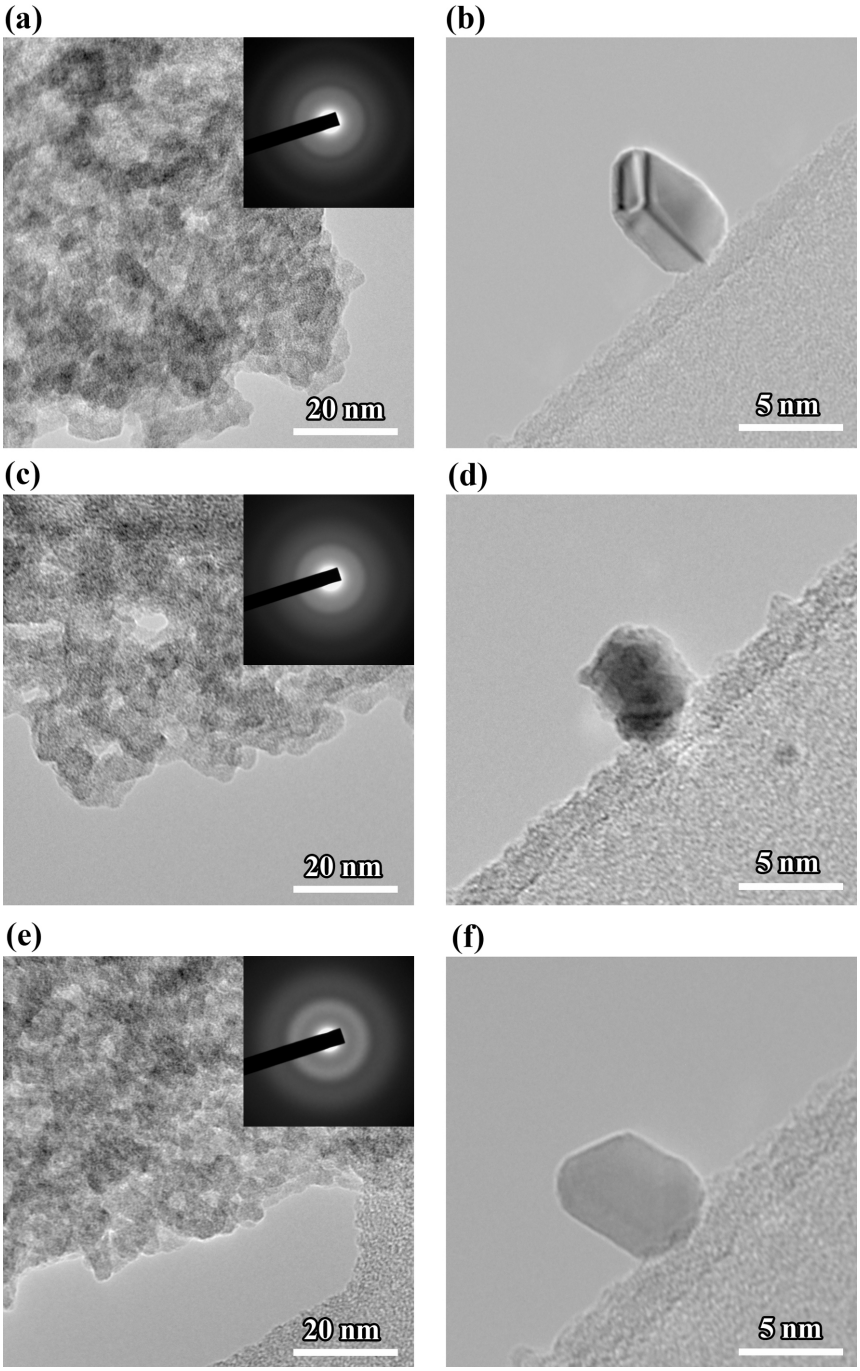

Fig. 3. TEM micrographs of the xerogels synthesized at pH = 4 (a and b), pH = 7 (c and d), and pH = 10 (e and f); the inserts in the high-magnification images are the related SAD patterns.

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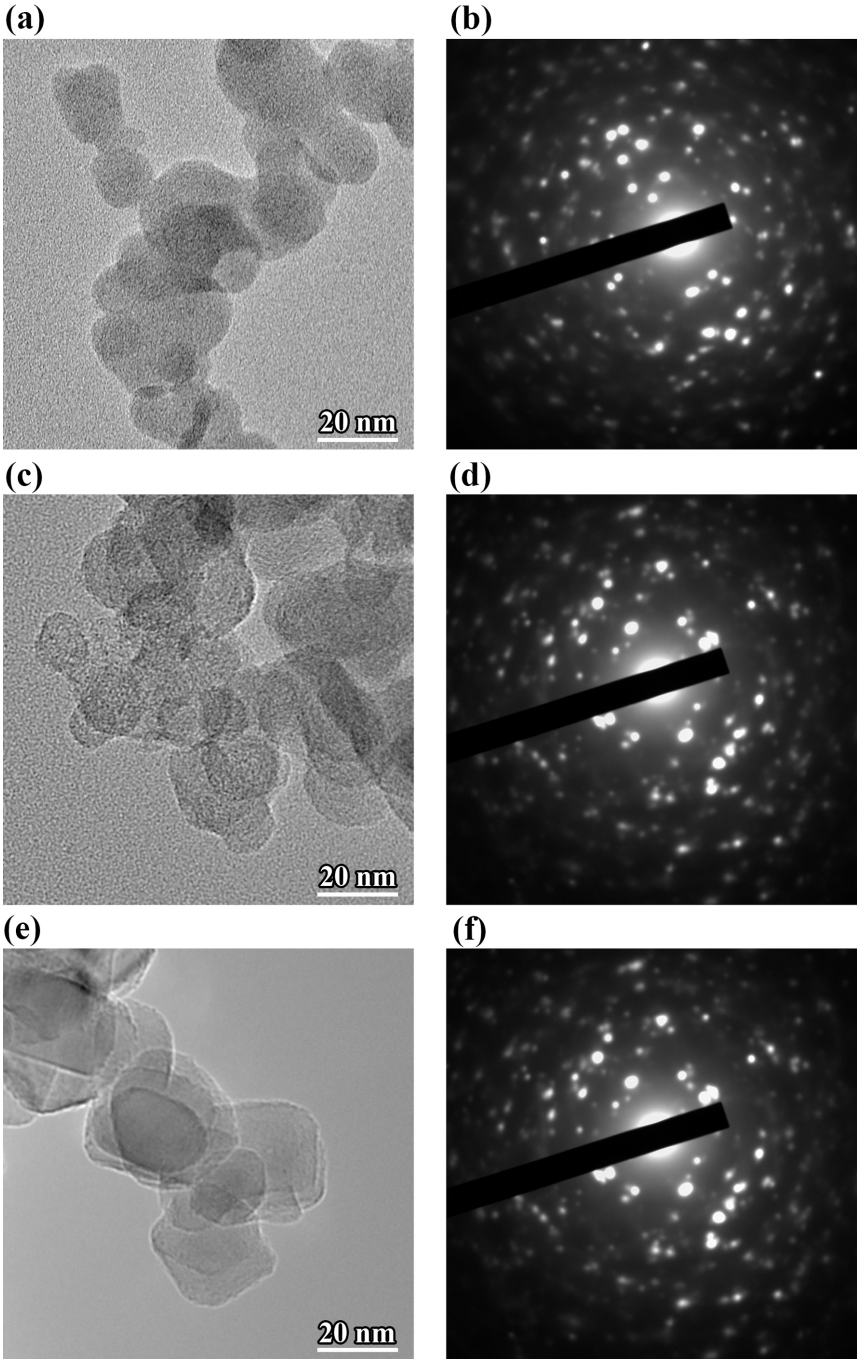

Fig. 4. TEM micrographs and SAD patterns of the samples synthesized at pH = 4 (a and b), pH = 7 (c and d), and pH = 10 (e and f) after annealing at 675, 705, and 720 ºC, respectively.