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Ceramic materials based on lanthanum zirconate for the bone augmentation purposes: materials science approach

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Abstract

The creation of new non-toxic materials that combines high osteointegration and strength characteristics is an urgent contemporary challenge. The use of complex oxides, such as lanthanum zirconate ($La_2Zr_2O_7$), as non-reservable alloplastic implant materials is a novel and promising way of fulfilling this challenge. In this work, the ceramic materials based on undoped and alkali-earth (Ca, Sr) doped $La_2Zr_2O_7$ were obtained. The main physical and chemical characteristics of the ceramic materials were determined. The effects of synthesis method and dopant nature on the target characteristics of potential allografts were established.

Keywords

$La_2Zr_2O_7$
bioceramics
augmentation
implant
osteoreplacement material

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Key findings

- The sol-gel method is more preferable, requiring less time to obtain a single-phase composition.
- The density of the prepared ceramic samples was 3.56–4.16 g/cm^3.
- The porosity of the prepared ceramic samples was 30–42%.

1. Introduction

A wide range of tasks related to the field of biomedical materials science includes the unresolved problem of effective implant osseointegration [1–8]. Currently known materials which can potentially be used as bone allografts have a number of disadvantages, such as reduced biocompatibility, allergic and toxic reactions [9–20]. This suggests that the creation of new non-toxic materials that combines high osteointegration and strength characteristics is an urgent task. The solution of it will provide conditions for adequate compensation of bone defects with subsequent remodeling of the adjacent bone tissue.

As it was shown in the literature, the use of calcium-doped lanthanum zirconate as a non-reservable alloplastic implant is possible and demonstrates positive results in the process of bone remodeling [21]. The choice of this material was due to the fact that the crystal structure of lanthanum zirconate (Figure 1) is tolerant to various substitutions, including calcium and strontium ions. Moreover, it was shown that strontium incorporation into calcium phosphate ceramics results in improved biocompatibility, osteoconductivity and strength [22]. However, despite promising preliminary results, this approach requires comprehensive development both in terms of traumatology, physiology, and chemical materials science. To date, the influence of metal nature on the processes of osseointegration remains unclear. In particular, the possibility of ion exchange of augment and bone tissue has not been studied. There are no data on bone remodeling markers in the experiment. The degree of biomechanical correspondence of the augment based on lanthanum zirconate and bone tissue has not been established.

In the present study, the ceramic materials based on undoped and alkali-earth (Ca, Sr) doped lanthanum zirconate were successfully obtained. The main physical and chemical characteristics of the prepared ceramic materials were determined, and the effects of the synthesis method and dopant modification on the target characteristics of potential allografts were established.

2. Experimental

The complex oxides $La_2Zr_2O_7$, $La_{0.9}Ca_{0.1}Zr_2O_{6.95}$ and $La_{0.9}Sr_{0.1}Zr_2O_{6.95}$ were obtained by three different ways. The sol-gel synthesis method (Figure 1d) was taken from

[23]. The solid-state method was performed by mill and using agate mortar (Figure 1c). The powders of initial materials, La_2O_3, ZrO_2, $CaCO_3$, $SrCO_3$, were previously dried, weighed and mixed in stoichiometric quantities. The calcination was performed in the temperature range from 800 to 1300 °C with a step of 100 °C and 24 h dwells. The milling of powders was made after each calcination step.

The X-ray diffraction (XRD) studies were performed by a Bruker Advance D8 Cu Kα diffractometer with a scanning step of 0.01° and at a scanning rate of 0.5°/min. The morphology and chemical composition of the samples were studied using a scanning electron microscope Phenom ProX Desktop (SEM) equipped with an energy-dispersive X-ray diffraction (EDS) detector.

3. Results and discussions

In the experiment, nine powder samples were obtained. Each $La_2Zr_2O_7$, $La_{0.9}Ca_{0.1}Zr_2O_{6.95}$ and $La_{0.9}Sr_{0.1}Zr_2O_{6.95}$ composition was produced by three different methods: sol-gel (SG) method, solid state (SS) method using a mortar for grinding and solid state method using a ball mill. First, the XRD-check for the phase formation process was performed after 1100 °C heat treatment. For the compositions obtained by the SG method, all peaks were indexed in the Fd3m space group. However, they were broad, so the increase in the sintering temperature was required. After the same synthesis step (1100 °C), the compositions obtained by both variations of solid state method were not single phase. The peaks belonging to the metal oxides were detected together with the peaks of the target complex oxide phase.

The second XRD-check was performed after the next stage of treatment (1200 °C, 24 h). The peak broadening for the SG-compositions were observed. However, they were less pronounced in comparison with the previous stage. The intensity of metal oxide peaks in the XRD-data for the SS-compositions was lower than it was after the previous stage, but all compositions were not single phase yet. The third XRD-check was made after 1300 °C treatment for 24 h. The SG-compositions were single-phase, the peaks were not broadened. The SS-compositions obtained using the mill were single phase as well. As an example, Figure 1e presents the photo of the powder sample of $La_2Zr_2O_7$, and the corresponding XRD-data is shown in Figure 1a. The SS-compositions obtained using the mortar contained both complex oxide and initial reagents. The single-phase compositions were obtained only after 1600 °C treatment for 24 h. It should be noted that doping leads to a slight decrease in the unit cell parameters (10.810 Å for $La_2Zr_2O_7$, 10.797 Å for $La_{0.9}Ca_{0.1}Zr_2O_{6.95}$, 10.805 Å for $La_{0.9}Sr_{0.1}Zr_2O_{6.95}$).

Thus, we can conclude that the presence of alkali-earth dopants in the structure of lanthanum zirconate does not affect the final annealing temperature that is necessary for obtaining a single-phase composition. The use of SG and SS-mill synthesis methods allow single phase compositions at the lower temperatures to be obtained. At the same time, the SG-method is more preferable due to less time it takes to obtain single-phase compositions.

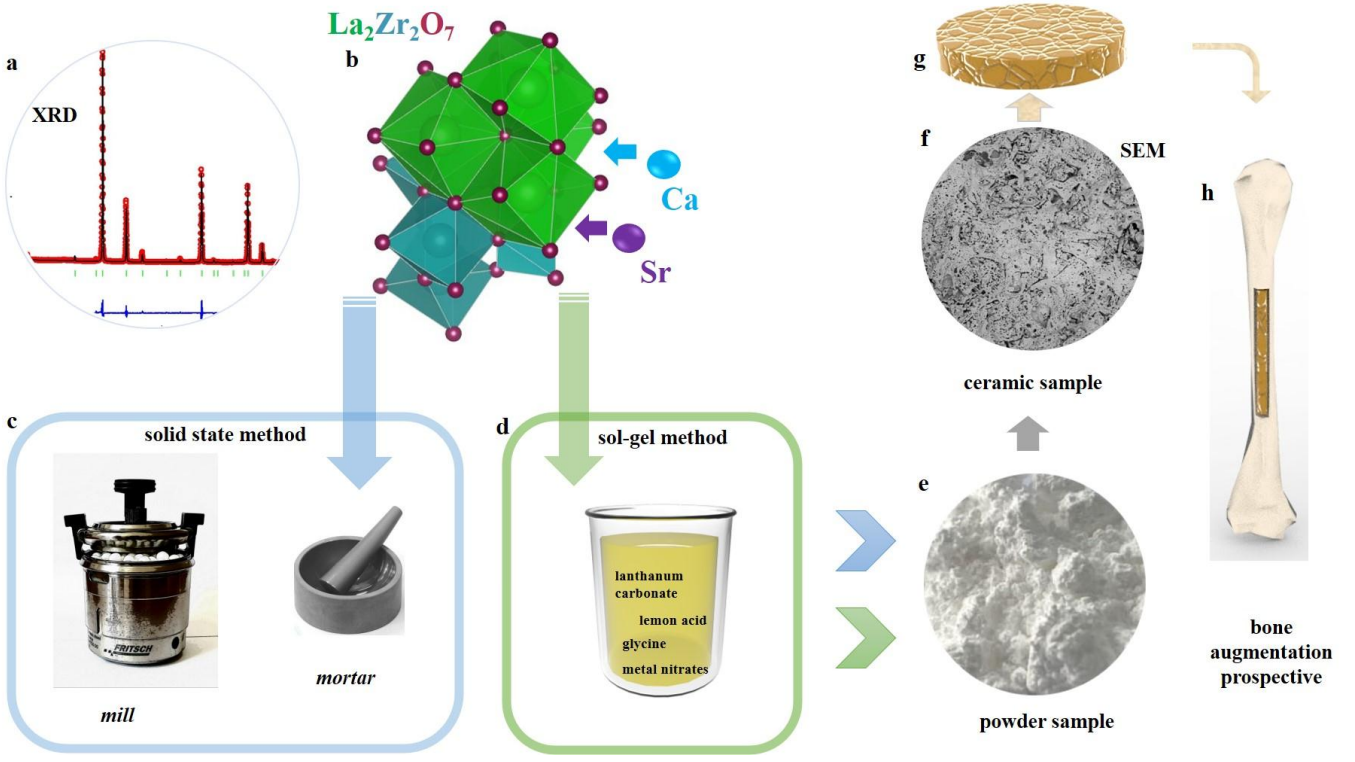

Figure 1 The XRD-pattern (a), crystal structure (b), photo of powder sample, image of surface of ceramic sample (f) of composition $La_2Zr_2O_7$; schemes of solid state (c) and sol-gel (d) synthesis methods; image of ceramic pellets (g) and of bone with augmentation.

Table 1 The density (g/cm³) and porosity (%) of the fabricated ceramic samples.

Composition	Density	Porosity
$La_2Zr_2O_7$ (SG)	4.02	33
$La_{0.9}Ca_{0.1}Zr_2O_{6.95}$ (SG)	3.94	36
$La_{0.9}Sr_{0.1}Zr_2O_{6.95}$ (SG)	4.16	30
$La_2Zr_2O_7$ (SS-mill)	3.89	35
$La_{0.9}Ca_{0.1}Zr_2O_{6.95}$ (SS-mill)	3.41	42
$La_{0.9}Sr_{0.1}Zr_2O_{6.95}$ (SS-mill)	3.56	40

The morphology of the powder samples was studied using the scanning electron microscopy (SEM). The doping did not significantly affect the dispersity of the samples. The SG-compositions consisted of irregular round-shaped grains with a size of 30–50 μm, forming agglomerates of up to 100 μm. The SS-compositions were represented by the grains with ~3–5 μm, forming agglomerates of ~10–15 μm. The grain boundaries for all samples were clean. The chemical composition and the elements distribution were determined by energy-dispersive spectroscopy (EDS) analysis performed on polished cleavage of the ceramic samples. The ceramic samples were prepared by pressing of cylindrical pellets (pressure ~7 MPa) (Figure 1g) and sintering them at 1400 °C for 24 h. The image of the surface of ceramic $La_2Zr_2O_7$ sample is shown in Figure 1f. Homogeneous distribution of the elements was observed; the concentration of dopant at the grain boundaries and in the bulk of the grain was comparable.

The relative density and porosity of ceramic samples are presented in Table 1. As we can see, the density of SG-compositions is higher as compared with the density of SS-compositions. The porosity of the SG-compositions is lower; however, it is high enough. It is obvious that to increase the ceramic density, it is necessary either to use sintering additives or to modify the method of synthesis. However, the requirements for bone augmentation ceramics (Figure 1h) are different and they depend on many factors including the type and condition of the bone and the size of the implant.

4. Conclusions

In this paper, the materials science approach to the problem of obtaining novel ceramic materials for the bone augmentation purposes was implemented. The ceramics based on undoped and alkali-earth (Ca, Sr) doped lanthanum zirconate were obtained by three different methods: sol-gel method, solid state method in the mortar and solid state method in the mill. It was shown that the presence of an alkali-earth dopant in the structure of lanthanum zirconate does not affect the final annealing temperature required for obtaining single-phase compositions in less time. However, the sol-gel method is more preferable it allows synthesizing a single-phase composition. The density of ceramic samples obtained using the solid state method (3.56–3.89 g/cm³) was lower in comparison with the samples obtained by the sol-gel method (3.94–4.16 g/cm³). The porosity was lower for the latter. We can conclude that effects of the synthesis method and the presence of a dopant in the structure on the basic properties of ceramic samples were established. However, this work is only a first step to obtaining novel highly effective ceramic materials for the bone augmentation.

Supplementary materials

No supplementary materials are available.

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Conflict of interest

The authors declare no conflict of interest.

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