Mechanical and dielectric properties of porous lanthanum orthophosphate materials with TiO₂ addition via foam-gelcasting

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ABSTRACT

Lanthanum orthophosphate (LaPO₄) powder was prepared by a solid–liquid precipitation reaction of lanthanum carbonate powder with H₃PO₄ in order to fabricate porous LaPO₄ materials. The phase transition and morphology evolution of the reaction products were found to be dependent mainly on the mass ratios of reactants and calcination temperatures. Porous materials using as-synthesized single-phase LaPO₄ powders and TiO₂ additives via direct foam-gelcasting exhibit large spherical-shaped cells without preferred orientation. The bulk density increases with the increase of sintering temperatures, as evidenced by bigger strut thickness, smaller cell and window sizes and lower inter-connectivity. Porous LaPO₄ bulk ceramic with 5 wt% TiO₂ addition sintered from 1100°C to 1500°C shows a porosity within 66.80–82.03% and a compressive strength from 4.0 to 17.2 MPa. The compressive strength dependence on the relative density follows a power-law relationship with an exponent value of −2.45. While imaginary parts of dielectric permittivity of the porous LaPO₄ materials measured over the X-band frequencies (8.2–12.4 GHz) depend weakly on the frequency and TiO₂ addition, the real parts are affected strongly by TiO₂ addition and sintering temperatures and fall within the range between 1.9 and 3.5 in this study.

1. Introduction

Lanthanum orthophosphates (LaPO₄) as advanced ceramic materials possess high thermal stability and excellent oxidation resistance at elevated temperatures [1]. They have a layered crystallographic structure that imparts machinability and toughness to the composites [2]. Its porous counterparts have many additional advantages such as low density, high specific surface area, improved thermal insulation and low dielectric constant. Preparation of such porous materials involves, in general, synthesis of LaPO₄ powder and manufacture of bulk ceramics.

The LaPO₄ powder can be synthesized by the solid–liquid precipitation [3,4] or solvothermal reaction [5] using H₃PO₄ and La₂O₃ or La(NO₃)₃ as the raw materials. The phase transformation and morphology of the final products were influenced by calcination temperatures, synthesis methods, processing conditions and types of raw materials [6,7]. The porous lanthanum orthophosphate materials have been fabricated by template and sol–gel routes so far [8,9]. Porous LaPO₄ ceramics sintered at 1200°C have the micro-hardness less than 350 HV with a porosity of ~13% [10]. The porosity of Al₂O₃/LaPO₄ composite ceramics with narrow pore-size distribution prepared by cold isostatic pressing was only ~40% [11]. The water–based foam–gelcasting method possessing the advantages of both direct foaming and gelcasting methods has attracted wide attention as a simple, versatile and low-cost fabrication method for highly porous ceramics [12].

Dielectric properties of dense LaPO₄ materials in the low-frequency range (10⁵–10⁷ Hz) [13] and microwave band (8–14 GHz) [14,15] have been investigated. However, detailed studies on dielectric properties of porous LaPO₄ materials are scarce. The present work focuses on the effect of TiO₂ addition on the mechanical and dielectric properties of porous LaPO₄ materials, since TiO₂ addition can be beneficial to the desired mechanical strength and tailored dielectric constants as required in many applications [16,17]. The LaPO₄ powder was prepared by the reaction of lanthanum carbonate (La₂(OH)(CO₃)₃) powder and diluted orthophosphoric acid. The effects of TiO₂ addition in porous LaPO₄ materials on the phase composition and porosity were also investigated.

2. Experimental

2.1. Materials

Commercially available rutile powders with an average particle size of 3 μm, lanthanum carbonate powders, and orthophosphoric acid were employed as starting materials for synthesizing lanthanum phosphate powders. N-methyl acrylamide and N,
N’-methylene-bis-acrylamide were used as an organic monomer and crosslinker respectively for direct foam-gelcasting method. Ammonium persulfate was used as a reaction initiator and N,N,N’,N’-tetramethylethlenediamine was used as a catalyst during the in-situ gelation processing. Sodium hexametaphosphate was applied as a dispersant and sodium carboxymethyl cellulose was utilized as a rheological additive. Sodium dodecyl sulfate and lauryl alcohol were put into use as a foaming agent and foam stabilizer, respectively. The details of raw materials are listed in Table 1.

### 2.2. Preparation of porous LaPO₄ materials

The lanthanum phosphate powder was synthesized via a direct solid–liquid precipitation reaction. In order to obtain pure lanthanum orthophosphate powders with few or no by-products, 3, 4, 5 and 6 g orthophosphoric acids were mixed respectively with 10 g deionized water before 10 g lanthanum carbonate powders were slowly added into the diluted orthophosphoric acid under magnetic stirring to obtain the white precipitate. The suspension was kept in a water bath (~70°C) continuously for 4 h under magnetic stirring. At last, the white precipitate was dried at 150°C for 24 h before calcination at various temperatures of 600°C, 1000°C, 1200°C and 1500°C at 5°C/min and hold time of 2 h. The synthesized powders are designated as 10:10:3, 10:10:4, 10:10:5 and 10:10:6 samples, corresponding to the mass ratios of lanthanum carbonate, deionized water and orthophosphoric acid, respectively.

Porous LaPO₄ materials were manufactured by direct foam-gelcasting process [12]. A series of low viscous slurries were obtained by ball-milling for 4 h including 45 g deionized water, and 100 g mixed as-synthesized single-phase LaPO₄ powder and commercial rutile powder (containing 2, 4, 5 and 6 g TiO₂, respectively). The corresponding samples with various TiO₂ contents are designated as LT2, LT4, LT5 and LT6, respectively. Foamed slurries were stirred mechanically until the foam volume reached ~350 mL in a scaled beaker compared to the non-foamed suspension. The adequately stirred and well-foamed slurries were poured into a plastic mold and gelled in ~15 min. After demolding, the green bodies were dried at 50°C for 48 h, and then sintered at 1100°C, 1200°C, 1300°C, 1400°C and 1500°C respectively with 2°C/min and hold period of 2 h. The corresponding LT5 porous materials sintered at various temperatures are denoted as LT5-1100, LT5-1200, LT5-1300, LT5-1400 and LT5-1500, respectively.

### 2.3. Characterization

The phase structure of lanthanum phosphate powders after various calcination temperatures and porous LaPO₄ ceramics with TiO₂ addition was identified using X-ray diffraction (XRD, D8 Discover, Bruker, Germany) analysis in the spectra range of 2θ = 10-70° with a step length of 0.15°/s. The powder morphologies and microstructure of porous LaPO₄ samples were investigated with a scanning electron microscope (SEM, Sirion 6700 F, FEI, Netherlands). The elemental composition of the LaPO₄ powder was measured by an attached energy dispersive spectroscopy (EDS, Genesis 60 S). The weight and volume of a porous specimen are used to obtain its bulk density, and the porosity was established by the following equation: \( V = (1 - \rho / \rho_0) \times 100\% \) where \( \rho_0 \) is the bulk density of the porous sample and \( \rho_0 \) (5.12 g/cm³) is the density of dense LaPO₄ [18]. The compressive strength was tested on a mechanical testing machine (CMT4503, SANS, Shenzhen, China) using the specimens sized about 20 mm×20 mm×15 mm. The crosshead loading speed is 0.5 mm/min. The samples of sintered porous materials were machined with sizes of 10.16 mm × 22.86 mm × 3 mm and dried at 120°C for 0.5 h after ultrasonic cleaning in ethanol for 15 min. Then, the room-temperature dielectric property of the dried samples was measured by the waveguide method over the X-band frequencies (8.2–12.4 GHz) with a network analyzer (N5230 C, Agilent, USA).

### 3. Results and discussion

#### 3.1. Phases and morphologies of lanthanum phosphate powders

The XRD patterns of lanthanum phosphate powders calcined at 1500°C with various mass ratios of H₃PO₄ are...
shown in Figure 1. The monoclinic LaPO₄ (JCPDS # 32–0493) [6] is the dominant phase in all sample powders, while traces of La₃PO₇ (JCPDS # 49–1023) [19] for a mass ratio of 10:10:3 and La(PO₃)₃ (JCPDS file # 33–0718) [20] for 10:10:5 and 10:10:6 are also observed. Relatively pure monoclinic LaPO₄ phase was obtained only for a mass ratio of 10:10:4 (Figure 1(b)), so powder under this processing condition was used subsequently. Figure 2 illustrates the XRD patterns of the as-synthesized white precipitate calcined at various temperatures. The broad peaks demonstrate an incomplete crystallization of the hexagonal phase LaPO₄·0.5H₂O (JCPDS #46-1439) [6] dried at 150°C because of the following reaction:

\[
\text{La}_2(\text{CO}_3)_3(s) + 2\text{H}_2\text{PO}_4(l) \rightarrow 2\text{LaPO}_4 \cdot 0.5\text{H}_2\text{O}(s) \\
+ 3\text{CO}_2(g) \uparrow + \text{H}_2\text{O}(g) \tag{1}
\]

The XRD spectra of the powder calcined at 600°C shows broad and low-intensity peaks of monoclinic structure LaPO₄ owing to the dehydration of the hydrated lanthanum phosphates [21]:

\[
\text{LaPO}_4 \cdot 0.5\text{H}_2\text{O}(s) \rightarrow \text{LaPO}_4(s) + 0.5\text{H}_2\text{O}(g) \uparrow \tag{2}
\]

Such a hexagonal to monoclinic transformation is irreversible. Further elevated thermal treatment at 1000°C leads to sharp diffraction peaks of LaPO₄ phase and additional characteristic peaks of La(PO₃)₃ phase [21]:

\[
2\text{H}_2\text{PO}_4(\text{absorbed}) + \text{LaPO}_4(\text{solid}) \rightarrow \text{La}(\text{PO}_3)_3 \\
+ 3\text{H}_2\text{O}(g) \uparrow \tag{3}
\]

The XRD pattern for powder samples calcined at 1200°C is similar to that of 1000°C. According to Figure 1(b), after calcination at 1500°C, the phase of La(PO₃)₃ disappears [19,22]:

\[
\text{La}(\text{PO}_3)_3(s) \rightarrow \text{LaPO}_4(s) + 1/2\text{P}_4\text{O}_{10}(g) \uparrow \tag{4}
\]

The reaction and phase transformation mechanisms to generate LaPO₄ from La₂(CO₃)₃ and H₃PO₄ are believed to be similar to these reported previously, although different reactants were used in the literature [21,23].

The evolution characteristics in morphology of lanthanum orthophosphate powders calcined at various temperatures for 2 h are depicted in Figure 3. The powder calcined at 150°C is agglomerated and composed of many nano-sized needle-like assemblies in Figure 3(a). At 1000°C, the lanthanum orthophosphate particles have undergone significant shrinkage in the form of uniform spherical nanograins (Arrowhead “A” of Figure 3(b)) with diameters of ~300-500 nm. The spherical nanograins appear to be connected by low melting-point La(PO₃)₃ phases (Arrowhead “B” of Figure 3(b)). At 1200°C, hard agglomerates were generated due to grain coalescence to brick- or rod-like forms (Arrowhead “C” and “D” of Figure 3(c)). After calcination at 1500°C, these rod-like particles showed layered structures. The EDS analysis in Figure 3(e) revealed the mass contents of O, P and La elements are about 63.86%, 10.73% and 25.41%, respectively, which gives the atomic ratio close to 1:1:4 and a direct evidence that the powder is composed of stoichiometric LaPO₄.

### 3.2. Properties of porous bulk LaPO₄ materials

#### 3.2.1. Phase structure and microstructure

Figure 4 depicts the XRD patterns of the porous LaPO₄ materials with different TiO₂ contents sintered at 1500°C for 2 h. Polycrystalline LaPO₄ and rutile phases are detected. With increasing addition of rutile from Figure 4(a–d), the intensity of the rutile phase grows stronger, while the lanthanum orthophosphate phase in the presence of TiO₂ remains stable with no new compounds.

The bulk density and porosity of the LT5 specimens sintered at different temperatures are plotted in Figure 5. With increasing sintering temperatures from 1100°C to 1500°C, the porosity of porous LT5 ceramics decreases from 82.03% to 66.80% and the bulk density increases.
from 0.92 to 1.70 g/cm³. The TiO₂ additive is beneficial to a faster densification rate above 1300°C [24–26].

The microstructure of porous LaPO₄ materials sintered at various temperatures is presented in Figure 6. Spherical cells with no preferred orientation are observed and are likely to lead to isotropic properties, which is a typical characteristic of the direct foaming process for preparing porous materials. The pores in the porous LaPO₄ ceramics are mostly open cells connected with smaller
windows and only a small portion is closed cells (isolated pores) (Figure 6(a)). It is believed that the large spherical cells are generated by mechanical foaming, and the small windows are due to the merger of air bubbles. In the highly individual SDS-foamed slurries, the air bubble may grow in size and coalesces, leading to the porous ceramics with smaller strut thickness, larger cell and window sizes and bigger permeability [12,27]. Very small-sized pores located at the grain boundaries are also observed after sintering at 1100°C (see the inset in Figure 6(a)), which indicates a hierarchical pore structure. With the sintering temperature elevated to 1500°C shown in Figure 6(b), the size of cells and windows is decreased due to the densification. Closely packed spherical/equiaxial LaPO₄ grains are also confirmed. The mean grain size increases in the range from ~1 μm to ~5 μm. The SEM micrographs of porous LaPO₄ materials sintered at 1500°C for 2 h with respect to various contents of TiO₂ additives distinctly manifest uniformly distributed open porosity in sintered porous materials (Figure 6 (c,d)). The microstructures of porous LaPO₄ materials sintered at 1500°C indicate that samples with various TiO₂ contents exhibit almost a similar pore structure with no obvious difference. The amount of the TiO₂ additive has no significant effect on the bulk density after sintering at 1500°C [28].

3.2.2. Mechanical strength
Figure 7(a) illustrates the dependence of compressive strength of a porous LaPO₄ ceramic on the sintering temperature. The increase in sintering temperature leads to dense grains and the decrease of porosity,

Figure 6. SEM micrographs of porous LaPO₄ materials sintered at various temperatures for 2 h. (a) LT5-1100, (b) LT5-1500, (c) LT2-1500 and (d) LT4-1500.

Figure 7. (a) Compressive strength of porous LT5 ceramics sintered at various temperatures. (b) The relative compressive strength of porous LT5 ceramics as a function of relative density.
thereby improving the compressive strength. The compressive strength of LT5-1500 sample is as high as 17.2 MPa while the porosity was 66.80% due to the strengthening of sintering struts and less micro-cracked framework. The compressive strength of porous materials can be obtained according to the Gibson and Ashby model [29,30]: $\sigma/\sigma_0 = C(1-V)^{3/2} = C(\rho/\rho_0)^{3/2}$ where $\sigma$ and $\rho$ are the compressive strength and bulk density of a porous sample, respectively; $C$ is a constant; $\sigma_0$ and $\rho_0$ are the theoretical strut strength and density of dense LaPO$_4$, respectively. As shown in Figure 7(b), in the double log plot, the slope of compressive strength versus relative density of porous LT5 ceramics is 2.448. The variation between the exponent value determined in this work and that reported in the Gibson and Ashby model can be owing to the different microstructures. In addition, after sintering at 1500°C, the compressive strength of porous materials with various TiO$_2$ contents is believed to be close to each other due to the similar pore structures shown in Figure 6. The compressive strength is mainly related to the porosity according to the model.

3.2.3. Dielectric properties

Figure 8 displays the measured real and imaginary permittivity of the porous LaPO$_4$ samples with different TiO$_2$ contents sintered at 1500°C for 2 h in the X-band. The mean real part of dielectric permittivity increases slightly in the range from 2.9 to 3.5 as the TiO$_2$ content was added from 2 wt% to 6 wt% owing to the large dielectric constant of rutile ($\varepsilon' = ~100$ [16]). The waveguide method is easy to measure the complex permittivity, but the deviation of the imaginary permittivity is complicated, particularly when the dielectric loss is small. Figure 9 represents the measured real and imaginary permittivity of LT5 porous ceramics sintered at

![Figure 8](image8.png)

**Figure 8.** The measured real and imaginary permittivity of porous LaPO$_4$ ceramics in the X band with various TiO$_2$ contents sintered at 1500°C for 2 h.

![Figure 9](image9.png)

**Figure 9.** The measured real and imaginary permittivity of porous LT5 ceramics in the X band sintered at various temperatures.
various temperatures in the X band. The mean real permittivity of LT5 porous materials increased from 1.93 to 3.20 with the decrease of porosity from 82.03% to 66.80% when the sintering temperature is elevated from 1100°C to 1500°C. The real permittivity of porous materials is smaller than that of dense LaPO$_4$ ($\varepsilon_r = -11$ [14]) owing to the high porosity. The real permittivity is influenced by the TiO$_2$ contents and porosity variation. The imaginary permittivity is similar to the result shown in Figure 8. At some frequencies tested, the imaginary permittivity shows abrupt changes due to the measurement accuracy. Overall, the porous LaPO$_4$ materials have a low dielectric loss. The complex permittivity tailored by the TiO$_2$ addition and sintering temperatures will have potential applications for microwave-transmitting materials. The relationship between the effective permittivity and porosity of the LT5 porous ceramics is shown in Figure 10. The real permittivity of the LT5 porous ceramics can be concerned with that of fully dense ceramics and porosity according to the Maxwell-Garnett model and the Bruggeman model [31]. Due to the hierarchical pore structures, the mean real permittivity of LT5 porous ceramics is located below by the form of the Maxwell-Garnett model and above by the form of the Bruggeman model. Obviously, there is a large difference between the effective permittivity predicted by the two models and the experimental data. Therefore, it is necessary to find a suitable model to predict the relationship between the effective permittivity and porosity of the porous lanthanum orthophosphate ceramics in the next work.

4. Summary

Relatively pure lanthanum orthophosphate powder was synthesized by a solid–liquid precipitation reaction of La$_2$(CO$_3$)$_3$ powder, deionized water and H$_3$PO$_4$ with a reagent mass ratio of 10:10:4 and calcination temperature of 1500°C. The phase is transformed from hexagonal phase LaPO$_4$·0.5H$_2$O to monoclinic LaPO$_4$ phase with typical characteristics of layered structures. Highly porous LaPO$_4$ materials with controllable porosity and hierarchical pore structures were prepared by direct foam-gelcasting method using the as-synthesized LaPO$_4$ powder and commercial TiO$_2$ powder as raw materials. The porous materials exhibit approximately large spherical cells with isotropic properties. Open cells show smaller connected windows and thicker strengthening struts with the increase of sintering temperature. The compressive strength varies in the range of 4.0 to 17.2 MPa and the corresponding porosity decreases from 82.03% to 66.80% for porous LT5 ceramics as sintering temperature increases from 1100°C to 1500°C. The power-law relationship of the compressive strength on the relative density fitted in this work has an exponent of $\sim$2.45. The real permittivity tailored by the TiO$_2$ addition and sintering temperatures is ranging from about 1.9 to 3.5 and the change of imaginary part is complicated. The porous LaPO$_4$ materials prepared in this work will be potential for microwave-transmitting materials.

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Disclosure Statement

The authors declare no conflicts of interest.

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