



Determination of the Nucleation and Crystallization Parameters for Making Nanoporous Titanium Phosphate Glass-ceramics

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ABSTRACT

Nanoporous glass-ceramics were prepared with composition 45CaO-25TiO₂-35P₂O₅ (mol.%). Two molar percent of Na₂O was added as a flux to the composition. With the aforementioned composition, the glass was melted and crystallized into glass-ceramics containing β-Ca₃(PO₄)₂ and CaTi₄(PO₄)₆ as the main phases. The differential thermal analysis (DTA) was conducted to determine the suitable temperatures for nucleation and crystallization. Various times were examined for nucleation and the best nucleation time was chosen. The microstructure of final nucleated sample was observed by Scanning Electron Microscopy (SEM). Then, the glasses were crystallized and identified by X-ray Diffraction (XRD). The microstructures of crystallized specimens were studied by SEM. The glass-ceramics were leached in HCl, and the resulting β-Ca₃(PO₄)₂ was dissolved out leaving a porous structure as CaTi₄(PO₄)₆. It was found that specific surface area and average pore size diameter of the nanoporous glass-ceramics were controlled by the correct choice of heat treatment parameters. Using the optimal conditions for the production of nanoporous glass-ceramics with minimum pore size, 26±3 m²/g and 12.3±1nm were obtained for the specific surface area and pore diameter, respectively.

1. INTRODUCTION

Nanoporous phosphate glass-ceramics are applied in the production of catalyst supports and immobilization of enzymes¹. Calcium titanium phosphate porous glass-ceramics were first developed by Hosono² with a nominal composition of 45CaO-25TiO₂-35P₂O₅ (mol.%). The glasses produced in this system involved spinodal decomposition. After leaching in HCl acid, this type of glass-ceramic mainly comprises NASICON type CaTi₄(PO₄)₆ phase structured as in a porous medium. Later on, various studies focused on this system to better understand the properties of this type of glass-ceramic. Some researchers tried to reduce the medium size of the pores by adding other oxide³. Adding other oxide to the main system, may cause undesirable effect on the properties. Despite the variety of applications found for calcium titanium phosphate glass-ceramics, very few studies have so far been carried out on crystallization behavior as well as optimization of the heat treatment conditions in order to achieve minimum-

size porosity and thus maximum specific surface area. The goal of this study was achievement to the minimum-size porosity in the glass-ceramic system. In this study, multiple analyses were conducted to precisely examine the optimal conditions for heat treatment such as temperature, nucleation time and crystallization. Finally, the above optimal conditions were adopted to prepare a nanoporous glass-ceramic with minimum pore size ever obtained in this system.

2. MATERIALS AND METHODS

2.1. Preparation of glass-ceramic

According to previous research², a glass with the formulation of 45CaO-25TiO₂-35P₂O₅ was first prepared. In order to improve the melt behavior, 2 mol.% of Na₂O was added to the initial batch. The oxides were prepared from CaCO₃ (Merck 102069), TiO₂ (Merck 100808), P₂O₅ (Merck 100540) and Na₂CO₃ (Merck 106398). These raw materials were used at high purities (+99%).

At the next stage, the powders were mixed in a dry ball mill for 5 hours and 30 grams of the mixture inside an alumina crucible was transferred into a furnace with temperature of 1350 °C and kept at the maximum

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temperature for one hour. Before pouring the melt from the crucible into the mold, the molten glass in crucible was stirred to increase the homogeneity. Then, the molten glass was poured into a heated mold, immediately moved into the annealing furnace at 600 °C and allowed to be naturally cooled down to ambient temperature.

The resulting glass was used for the preparation of glass-ceramic. To obtain nanoporous glass-ceramic, the resulted glass-ceramics were kept in 1-mol hydrochloric acid for one week until β - $\text{Ca}_3(\text{PO}_4)_2$ phase was dissolved in the acid leaving $\text{CaTi}_4(\text{PO}_4)$.

2.2. Thermal analyses

The DTA (Shimadzu-DTG60AH) was performed on glass specimens to determine the temperatures of glass transition, softening and crystallization. Alpha alumina was the reference material, and the heating rate was 10 degrees per minute. The first threshold of endothermic peak in the DTA curve was considered as glass transition temperature (T_g) while its minimum value was considered as the softening temperature.

Due to the proximity of these temperatures, the median was considered as nucleation temperature and encourage of phase separation in the glass. According to the method proposed by Ray and Day⁴, the best nucleation conditions are met in a specimen with the narrowest and most extreme exothermic peak. Hence, the optimal nucleation takes place when the crystallization peak is at its narrowest and most extreme mode. On those bases, the optimal nucleation time was selected.

2.3. Phase analysis

In order to identify the crystallization phases, the heat treated samples were subjected to X-ray diffraction (XRD) (Siemens- D500) using $\text{Cu-K}\alpha$ radiation at 20 kV setting and in the 2θ range of 10–60°. Step size of scanning was 0.5 °/min.

2.4. Microstructural examinations and porosity characterization

The samples after polishing and etching were coated with a thin film of gold and subjected to SEM examination (Hitachi-S-4800). The specific surface area and average pore size were determined by BET method.

3. RESULT AND DISCUSSION

3.1. Nucleation behavior and crystallization

The glass specimens were dark purple, which suggested the presence of Ti^{3+} ions⁵. The glass viscosity was very low and the melt indicated high fluidity. This was why the specimen tended to have extreme crystallization^{6,7}. Therefore, the thickness of each specimen was minimized to increase the cooling level as well as the tendency to vitrification. The SEM analysis demonstrated that the phase separation was not occurred

for annealed glass specimen even at large magnifications. Hence, it was crucial to perform a heat treatment to encourage phase separation. The middle temperature of T_g and T_d was considered for heat treatment on nucleation. Fig. 1 displays the DTA curve for the base glass.

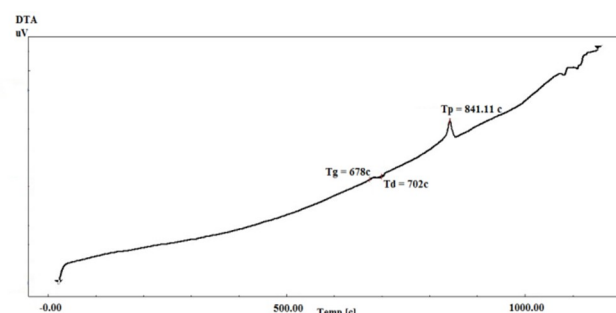


Figure 1. DTA trace for the base glass

T_g and T_d were 675 and 705 °C, respectively. Thus, the nucleation temperature (T_n) was designated to be 690 °C. In order to achieve optimal nucleation time, the base glass was heat treated at different times at 690 °C. Fig. 2 displays the DTA curve for the nucleated glasses.

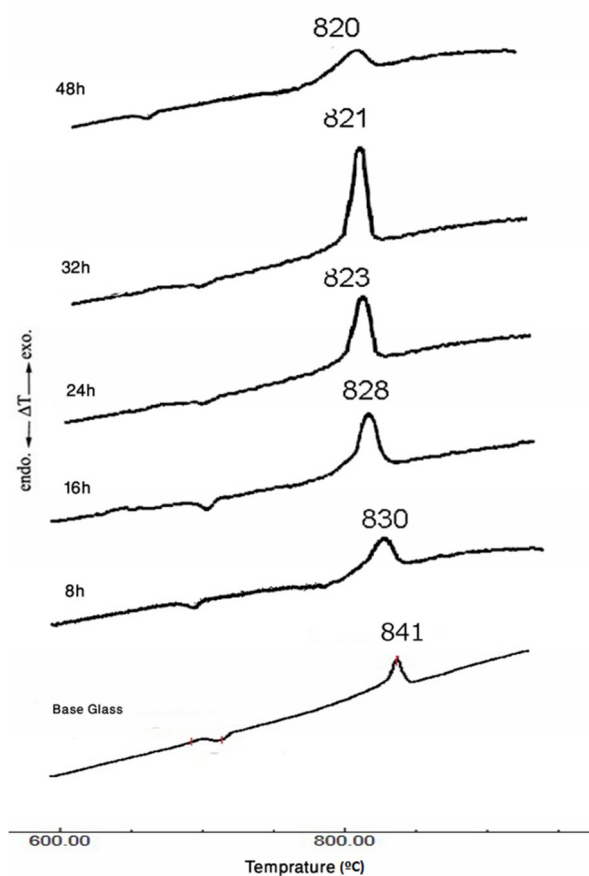


Figure 2. DTA traces for glass after different nucleation heat treatment times (8, 16, 24, 32 and 48 h)

Given the narrowing of the crystallization peak and its lowered temperature, the nucleation heat treatment was proven to be effective⁸. After 32 hours of nucleation, the crystallization peak started to flatten and shorten. Apparently, the optimal nucleation time was 32 hours. For further confirmation, the SEM was employed to observe the microstructure of nucleation specimens. As shown in Fig. 3, the effects of nucleation were barely visible within 8 hours, while the microstructure was well separated within 32 hours. Based on the nucleation form and opinions of other researchers^{3,9}, the nucleation was spinodal. After the crystallization heat treatment, the interlocking structure of a spinodal nucleation eventually produces an interconnected microstructure composed of β - $\text{Ca}_3(\text{PO}_4)_2$ and $\text{CaTi}_4(\text{PO}_4)_6$ crystals. It has also been revealed that separated microstructure is highly prone to crystallization since the separated boundaries provide ideal spots for heterogeneous nucleation¹⁰. Ultimately, this microstructure can greatly facilitate the volume crystallization of material.

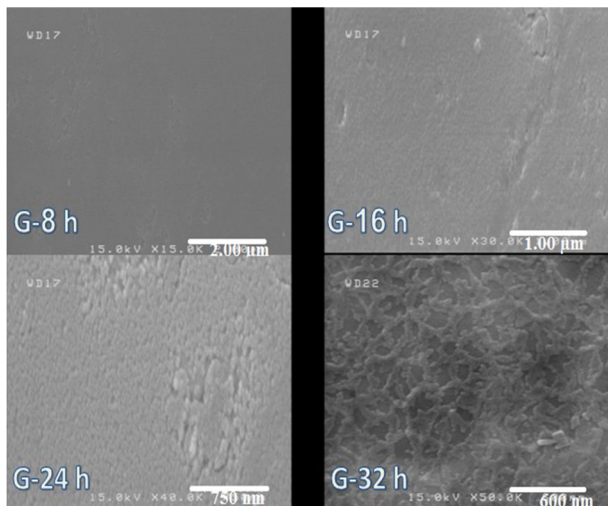


Figure 3. SEM micrograph of glass after different nucleation times (8, 16, 24 and 32 h)

In order to complete the crystallization, the nucleation needs to be followed by heat treatment within the range of crystallization peak. As shown in Fig. 1, the crystallization peak falls within the range of 841 °C. If the specimen falls within the crystallization peak of thermal treatment after nucleation at optimal time and temperature, a coarse-grained microstructure will eventually form due to extreme crystallization^{11,12}. This coarse-grained microstructure will prevent the production of a nanoporous glass-ceramic. Therefore, it is critical to select the appropriate crystallization temperature and time. For this purpose, four temperatures were selected at the onset of the crystallization peak between 765 to 795 °C. In order to determine the optimum temperature after nucleation heat treatment under optimal conditions, the specimens

were kept at the mentioned temperatures for three hours. The XRD analysis of specimens (Fig. 4) after crystallization at different temperatures showed that the temperature of 775 °C was the optimum crystallization temperature since crystallization peaks can well be detected at this temperature. At temperatures above the 775 °C, the crystallization intensifies and as mentioned earlier, leads to a coarse-grained microstructure. At this stage, it is essential to determine the appropriate time for the crystallization process. After nucleation under optimum conditions, the specimen was crystallized at 775 °C, $t=45$ m to $t=48$ h.

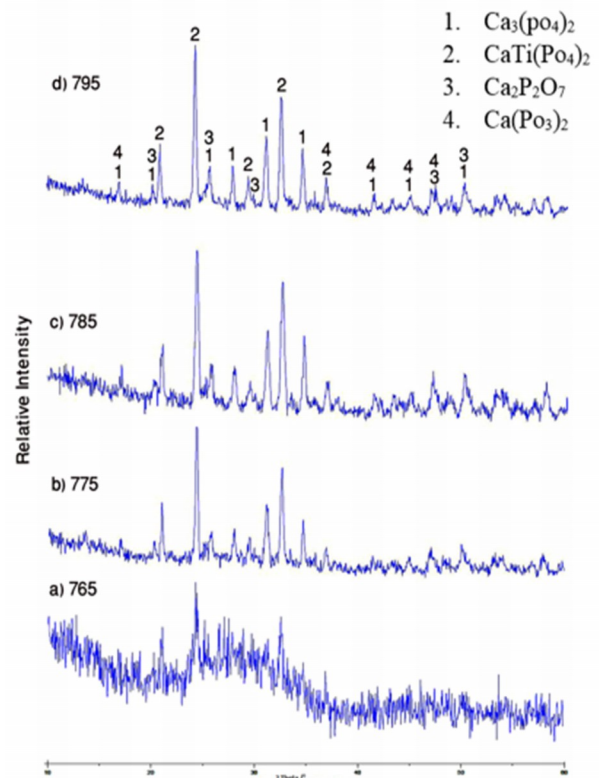


Figure 4. XRD patterns for specimens heat treated at different temperatures ((a) 765, (b) 775, (c) 785 and (d) 795 °C) for 3 h after nucleation at 690 °C for 32 h

Fig. 5 displays the XRD pattern for the crystallized specimens. Generally viewed, there is an evident decline in the background peaks and intensification of crystallization peak. The crystallization peaks are completely visible for $\text{Ca}_3(\text{PO}_4)_2$ - β and $\text{CaTi}_4(\text{PO}_4)_6$ phases. In addition to the above two phases found generally in the spectra, there are evident indicating the presence of $\text{Ca}_2\text{P}_2\text{O}_7$ and $\text{Ca}(\text{PO}_3)_2$ as partial phases. Some of these partial phases, including $\text{Ca}_3(\text{PO}_4)_2$ - β , are soluble in acid. As can be seen in the spectra shown in Fig. 5, there are no significant differences between spectra for 24 and 48 hours. Therefore, the optimal crystallization time seems to be 24 hours.

This choice was ensured by investigating the microstructure of the specimen through SEM images. Fig. 6 shows these images. Evidently, the thickness of crystals was only increased between 24 to 48 hours, which ultimately made it impossible to achieve a nanoporous microstructure. Accordingly, it was confirmed that $t=24$ hours was appropriate time for crystallization of glass-ceramic specimens.

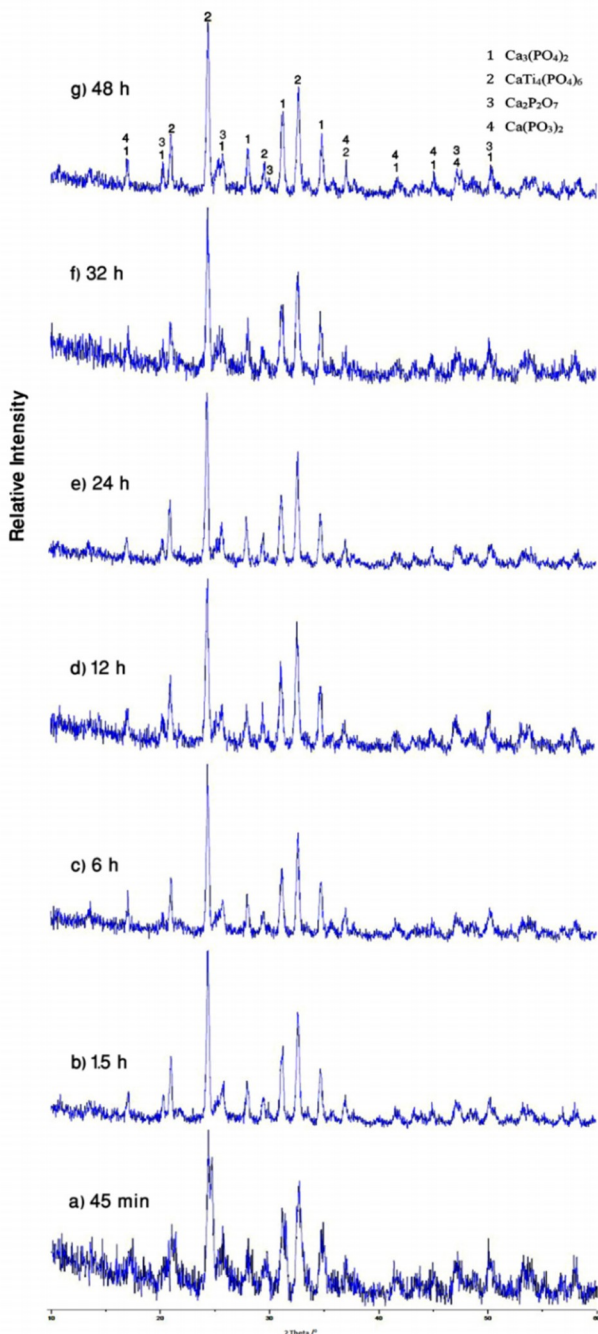


Figure 5. XRD patterns for specimens nucleated at 690 °C for 32 h and subsequently heated at 775 °C for different times ((a) 45 min, (b) 1.5, (c) 6, (d) 12, (e) 24, (f) 32 and (g) 48 h).

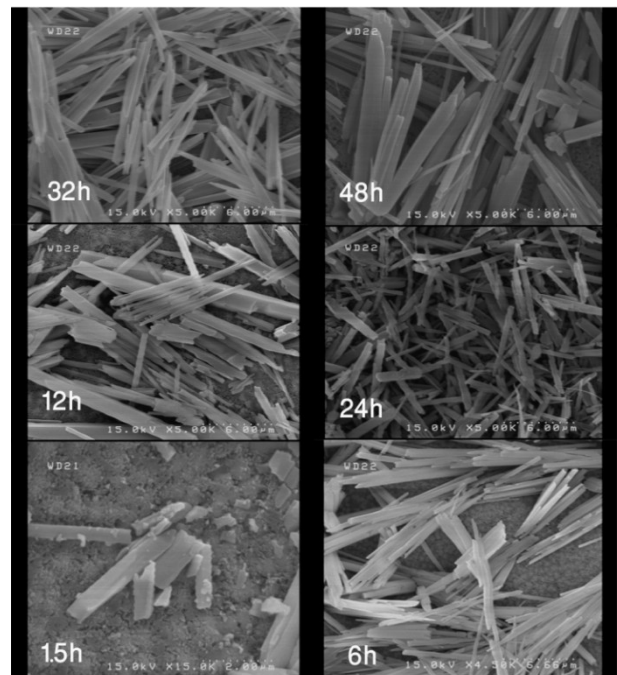


Figure 6. SEM micrographs for specimens nucleated at 690 °C for 32 h and subsequently heated at 775 °C for different times (1.5, 6, 12, 24, 32 and 48 h)

3.2. Achieving and measuring porosity

Having been produced, the glass-ceramics were immersed into a 1-mol HCl acid for one week. Fig. 7 displays the microstructure of the glass-ceramics after leaching.

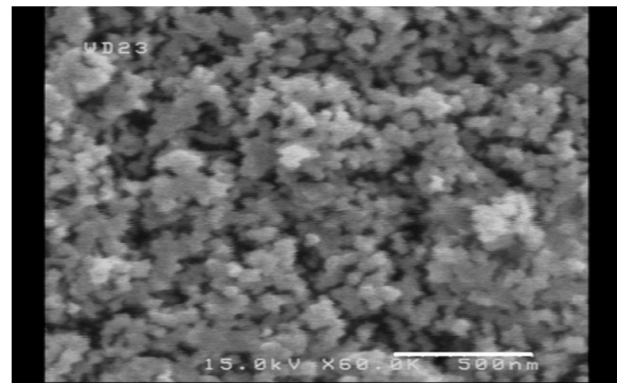


Figure 7. SEM micrograph of the porous glass ceramic

As can be seen, the specimens have desirably become porous. The pore size is generally below the 100 nm. Unlike the rod-shaped crystals prior to leaching, the pores are spherical. The spherical shape of the pores promises maximum specific surface area. Fig. 8 displays the XRD spectra for glass-ceramics before and after leaching. Phases β - $\text{Ca}_3(\text{PO}_4)_2$ and $\text{Ca}_2\text{P}_2\text{O}_7$ were eliminated during the leaching, only leaving the primary peak for $\text{CaTi}_4(\text{PO}_4)_6$ after leaching. The peaks of partial phase $\text{Ca}(\text{PO}_3)_2$ are also visible. Table 1 shows the

results of BET for the porous specimen. The average pore size was 12.3 nm, which is the smallest pore size ever reported in this glass-ceramic system. Moreover, it demonstrated the optimal crystallization conditions. The

specific surface area was 26 m²/g, which can be an appropriate value for the applications mentioned in previous sections.

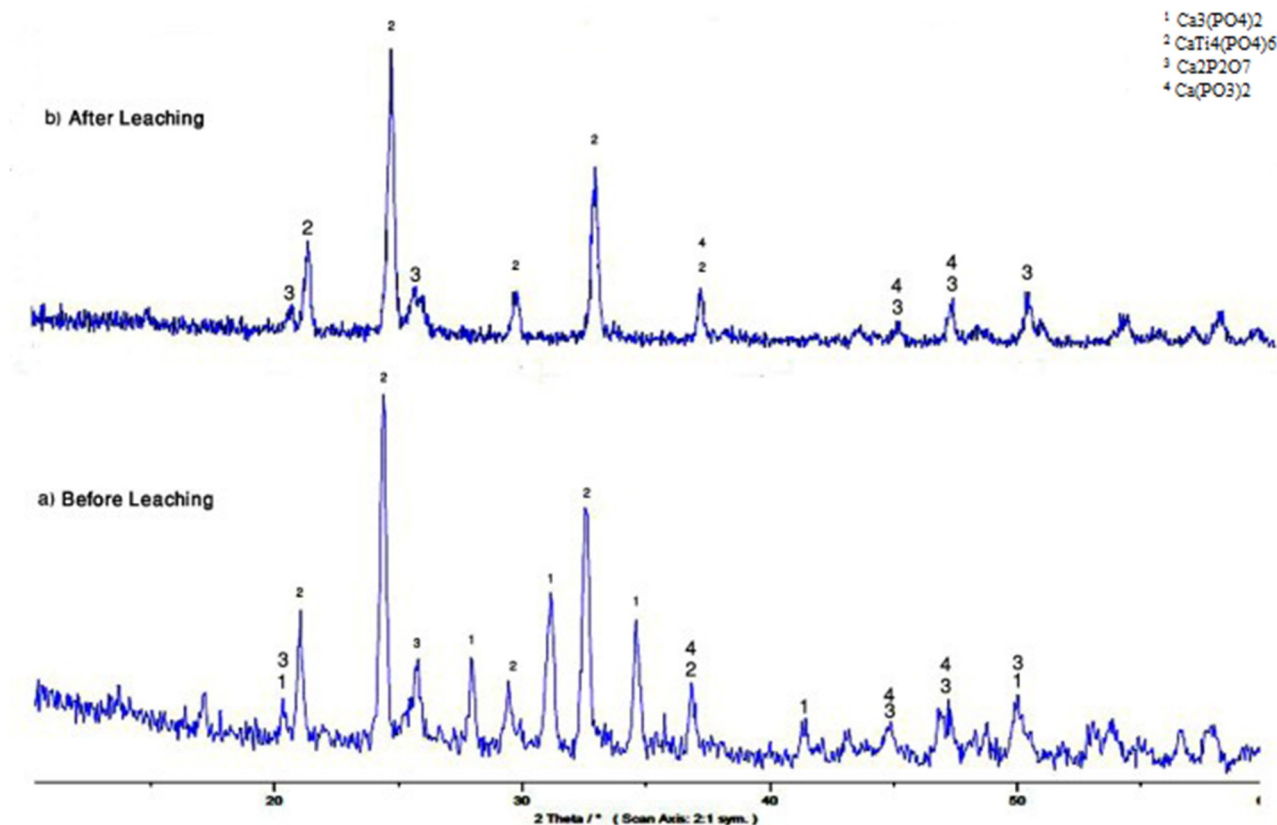


Figure 8. XRD patterns of glass ceramic, a) before leaching and b) after leaching

4. CONCLUSIONS

This study focused on the role of phase separation in nucleation of CaO-TiO₂-P₂O₅. It was found that the best nucleation temperature and time for achieving minimum porosity were 690 °C and 32 hours. Moreover, various analyses were conducted which confirmed that the 775 °C and 24 hours were the optimal temperature and time for crystallization of titanium calcium phosphate glass-ceramics. By applying the optimum conditions, the minimum pore size was obtained as 12.3 nm and the maximum surface area of 24 m²/g was achieved. The residual phase in the porous glass-ceramic mainly involved CaTi₄(PO₄)₆, which can ideally be applied in various backgrounds of phosphate nanoporous glass-ceramics.

5. ACKNOWLEDGMENTS

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