



Addition of Alumina to Nanoporous Calcium Titanium Phosphate Glass-Ceramics and its Effects on Crystallization Behavior

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ABSTRACT

Microporous Calcium Titanium Phosphate glass-ceramics have many uses in high-tech industries. For example, they have applications in catalysts industry. In this study, different molar percentages of alumina were added to a glass with P_2O_5 30, CaO 45, TiO_2 25 (mol%) composition. The samples were melted at 1350°C and crystallization heat treatment was performed on the glasses after cooling to make glass-ceramics. The Differential Thermal Analysis (DTA) was used to determine nucleation and crystallization temperature. The DTA curve of the sample had 4 molar% alumina had the sharpest crystallization peak. The CP and CTP phases were the most crystalline phases in all samples. The soluble CP phase disappeared and the porous structure of the CPT crystals remained through the acid washing of the samples. The results showed that the addition of alumina decreased the crystallization temperature, time and temperature of crystallization, and also increased the average size of porosities (from 12 to 16 nm).

1. INTRODUCTION

Nanoporous glass-ceramics have advanced applications in various industries. They can be used in sensors [1], biomaterials [2], as well as immobilization of enzymes [3], catalysts [4], and lithium-ion batteries [5]. Calcium titanium phosphate (CTP) glass-ceramics are produced by glass heat treatment in the nominal composition of 45CaO-25TiO₂-35P₂O₅ [6]. They generally include different phases that can be referred to Nasicon-type CaTi₄(PO₄)₆ (CTP) crystals and some crystalline titanium and calcium phosphates (CP) phases. The porous material can eventually be obtained by removing these phases because the calcium phosphate phases in this ceramic glass are soluble in some acidic solutions, which can be eliminated by washing them in acid, [7]. For some applications, pores need to be controlled and resized. Some reports have shown that porosities can be resized by subsequent heat treatment. However, the surface chemistry of the pores has changed and may not be suitable for using this type of operation [8]. It has already been reported that porosities can be increased by adding cerium oxide [9]. In this study, it has been tried to increase the porosity size not sharply but moderately

and also, improve the glass in the glass. It was found that the crystallization could be improved and the pores eventually changed by adding alumina to the base glass. In this research, the crystallization behavior of ceramic glass has been investigated in the presence of alumina.

2. EXPERIMENTAL PROCEDURES

2.1. Preparation of Glass-Ceramics

The chemical composition of the base glass is 45CaO-25TiO₂-35P₂O₅ +2Na₂O (mol%). The base glass was prepared according to Hosono's report [10]. The raw materials that were used to make the glass were reagent grade, CaCO₃ (Merck 102069), TiO₂ (Merck 100808), P₂O₅ (Merck 100540), and Al₂O₃ (Merck 106396). The first sample had 2mol% Al₂O₃ (Al2), the second had 4mol% Al₂O₃ (Al4), and the third had 6 mol% Al₂O₃ (Al6). The base glass (G) had no Al₂O₃. The batch of glass was first poured into an alumina plant to melt the glass and then, it transferred to an electric furnace. The furnace temperature was increased to 1450°C and the samples were kept at the maximum temperature for 2h. The melt was then poured into a pre-heated steel mold. The glass was kept at the maximum temperature for less

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than 2h to prevent corrosion by the molten glass. The crucible were shaken for 2 minutes before casting into the furnace to achieve a homogeneous melt. The glass samples were then transferred to another furnace at 600°C and allowed to cool in the furnace. The heat treatment should be performed on glass samples for the growth of crystals to make a glass-ceramic,. The crystalline glass samples were kept in the hydrochloric acid solution for one week after heat treatment to dissolve the dissolvable phase and leave the porous structure. The porous structure will be a porous glass-ceramic.

2.2. Nucleation and Crystallization

The nucleation heat treatment must be initially performed on the glass samples to produce glass - ceramic. This operation is consist of holding the samples at the appropriate nucleation temperature. Nucleation temperatures are typically selected between the glass temperature (T_g) and the dilatometry temperature (T_d) ($(T_g+T_d)/2$). The samples must first be kept at nucleation temperature at variable times and then subjected to the DTA test to determine the appropriate time for nucleation. After nucleation treatment, crystallization of the samples should be preformed at onset of the crystallization peak temperature where the crystallization begins (T_p-30). Then, samples crystallized at different temperatures subject to XRD analysis. Moreover, the samples should be crystallized at different period of times and the optimum crystallization time will be selected according to the amount of crystallinity .

2.3. Thermal Analyses

DTA technique (Shimadzu-DTG60AH) was used to study the thermal behavior of glass samples. The reference material in this technique was α - Al_2O_3 and the heat rise rate was set to $10^\circ C \cdot min^{-1}$. The glass transition temperature (T_g) and the dilatometric temperature (T_d) were determined by considering the endothermic peak position in the DTA pattern [11]. The minimum temperatures at the endothermic peak, the dilatometric temperature, and the beginning of the endothermic peak were the glass transition temperatures. These temperatures were used to determine the phase separation range as well as the nucleation temperature. According to previous research, the DTA of the sample with the thinnest exothermic peak was identified as the best sample for nucleation [12].

2.4. XRD analysis

The phase analysis of the crystalline samples is performed using an XRD device. For this purpose, the samples were first powdered and tested using the XRD (Siemens-D500) at 20kV and in the 2θ ranges from $10^\circ - 60^\circ$.

2.5. Microstructure and Porosity Characterization

The samples were first polished, and then, etched in dilute hydrofluoric acid solution to investigate their microstructure. The etched samples were coated with gold using a sputtering device. Field Emission Electron Microscopy (FESEM) (Hitachi-S-4800) was then used to observe their microstructure. Moreover, porosity was determined through the BT method (Belsorp mini II).

3. RESULTS

3.1. Phase Separation

Fig. 1 shows the DTA results of the samples. The DTA exothermic peaks correspond to crystallization in glass samples. As can be observed in DTA traces, the sharpest exothermic peak with the lowest temperature belongs to the sample with 4% mol Al_2O_3 (Al4).

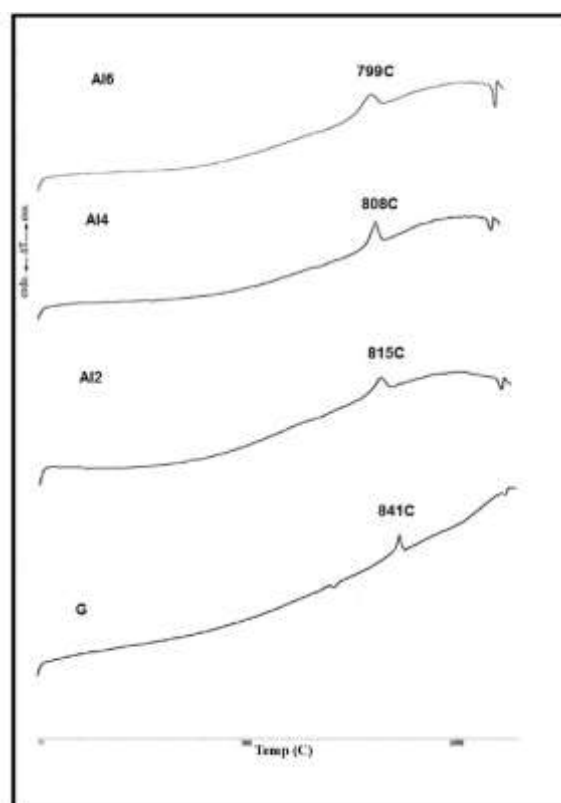


Figure 1. DTA traces of glass samples (G, Al2, Al4, and Al6)

According to the Ray and Day method [12], Al4 has the best crystallization behavior among the samples. Therefore, Al4 was suitable and selected for further studies. The base glass was crystallized according to the method of Hosono for comparison [6].

The phase separation was not observable in the glass samples even at very high magnifications by FESEM. Therefore, heat treatment was first performed at the

appropriate temperature range to encourage the phase separation process in the glass samples. It should be noted that there is a direct correlation between nucleation and phase separation in the glass-ceramics, i.e., first, there should be a phase separation in the glasses for good nucleation [9]. It was suggested that the nucleation needs a pretreatment for phase separation. The range of phase separation is between T_g and T_d . The mentioned temperatures as determined by DTA are summarized in Table 1.

TABLE 1. Glass transition (T_g) and dilatometric softening (T_d) and nucleation (T_n) temperatures of glass samples

Sample	Temperature ($^{\circ}\text{C}$)				
	T_g	T_d	T_n	T_p	T_l
G (Base Glass)	~675	~705	690	841	1070
Al2	~668	~683	682	815	1072
Al4	~660	~675	668	808	1070
Al6	~653	~667	693	799	1071

Fig. 2 shows the DTA traces for the nucleated samples at different lengths of time.

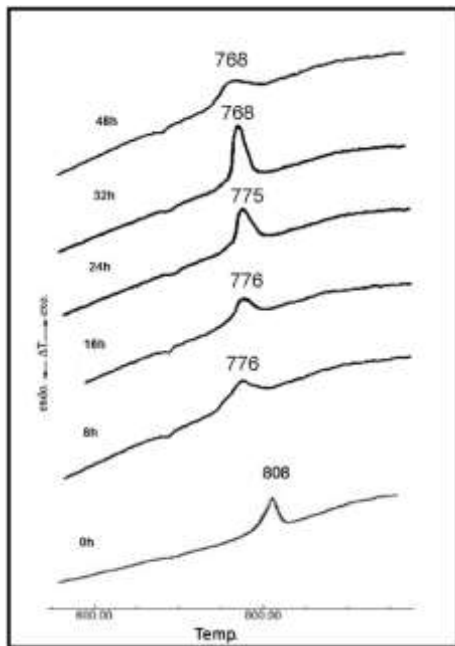


Figure 2. DTA traces for Al4 samples after nucleation heat treatment for different lengths of time (0, 8, 16, 24, and 32h)

The nucleation process was found to be effective since T_p decreased with increasing the nucleation time [7]. The T_p became wider and began to fade after 32 hours of nucleation. Therefore, it is concluded that 32 hours of nucleation is appropriate.

The microstructure of the samples was observed using FESEM to confirm the results of the DTA. Fig. 3 shows the FESEM images of the samples nucleated in different lengths of time. A sample containing 4% alumina (Al4), which had been nucleated for 32h, had a separated microstructure. This type of separation appears to be spinodal because it is more specific with longer holding time at the nucleation temperature. FESEM images of the base glass sample are shown in Fig. 3 (G32) after 32h of nucleation at 690°C for comparison. The appropriate temperature and time for nucleation of the base glass were previously reported by other researchers [7].

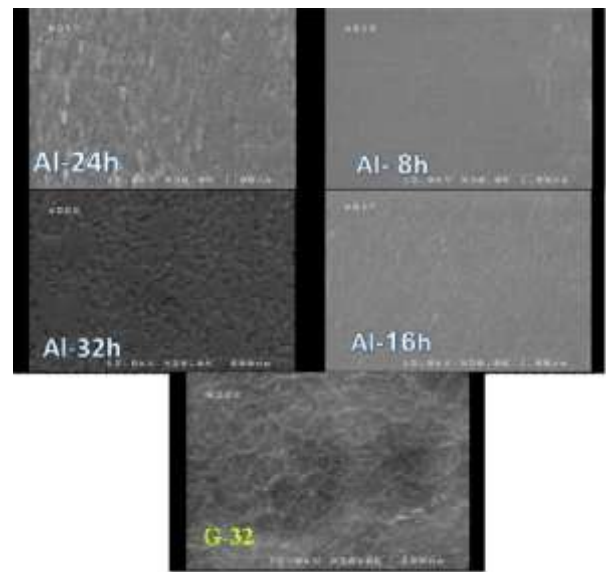


Figure 3. FESEM micrographs for the nucleation heat treatment of base glass (G) and Al4 for different lengths of time (8, 16, 24, and 32h)

3.2. Crystallization

The exothermic peaks in the DAT pattern usually reflect the crystallization in the glass samples. According to previous reports, the crystallization in this system is the bulk crystallization type [9]. Samples should, therefore, be crystallized in bulk. Glass parts were subjected to crystallization for this purpose. Interestingly, the glass changed color after crystallization operations, indicating the crystallization of glass samples.

The results showed that the optimum nucleation temperature was 668°C and the optimum nucleation time was 32h. If the crystallization process is performed at the above-mentioned temperature peak (808°C), it will eventually lead to the formation of large crystals and coarse-grained microstructures. Therefore, the crystallization process should be carried out at lower temperatures. According to Fig. 1, it is clear that crystallization begins at a temperature of about 740°C .

The sample was subjected to crystallization between T_c and (T_c-30) to accurately determine the crystallization temperature, which appears to be the beginning of crystallization. For this purpose, the samples were first nucleated at 668 for 32h, and then, kept at different temperatures for 3h to get crystallized.

Fig. 4 shows the XRD patterns of some heat-treated samples according to the above program. Since glass-ceramic microstructure will ultimately determine the size of pores, it should be fine-grained as far as possible. For this purpose, the crystallization temperature should be set as low as possible. According to the XRD results, it is clear that the crystallization started at 755°C because it showed the peaks of its crystalline phases.

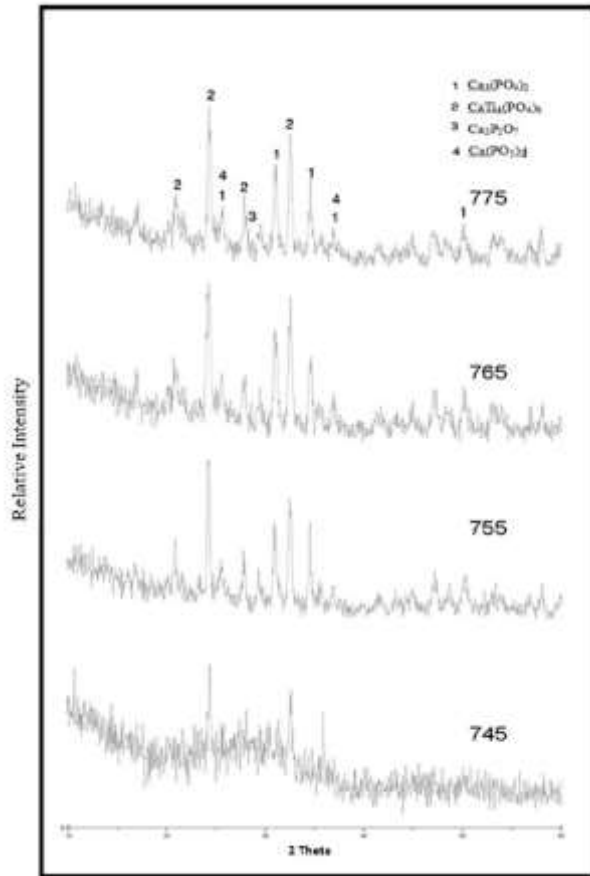


Figure 4. XRD patterns for samples heat-treated at different temperatures (745°C, 755°C, 765°C, 775°C) for 3h after nucleation at 668°C for 32h

Therefore, the temperature of 755°C was determined as the appropriate crystallization temperature. In addition, to determine the optimal nucleation time, the samples were first nucleated at 668°C for 32h, and then, crystallized at 755°C for various intervals.

Fig. 5 shows the XRD patterns of the samples. The XRD results show that the crystallization rate increases steadily from 45min to 48h. Looking closely at the results, it can be seen that the 24-hour XRD pattern is not significantly different from 48 hours. On the other hand, the FESEM results (Fig. 6) showed that the crystals grow larger from 24h to 48h. Therefore, a 24-hour crystallization time seems appropriate to prevent excessive growth of crystals.

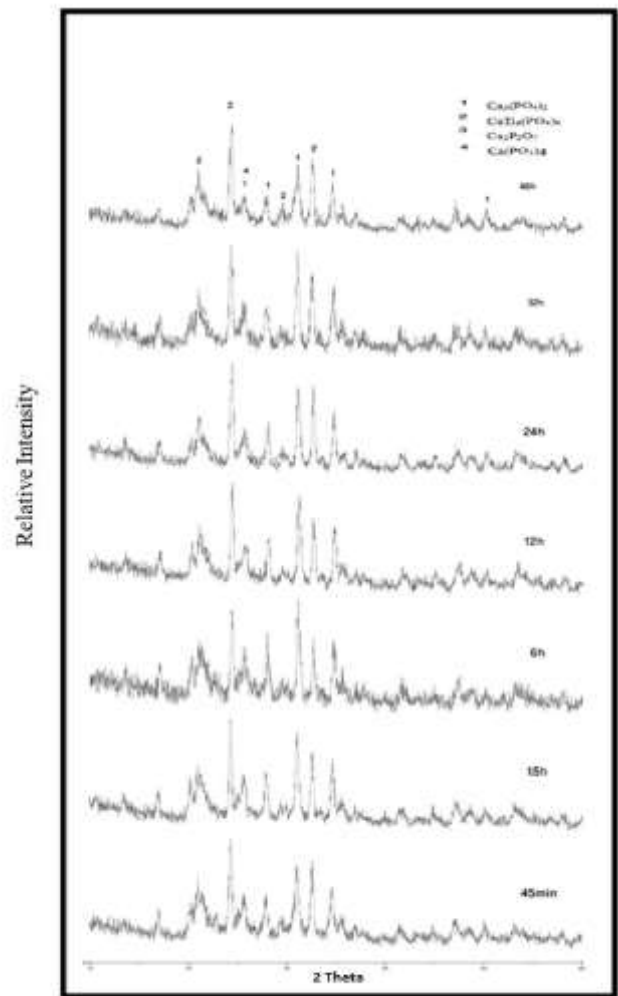


Figure 5. XRD patterns for nucleated samples at 668°C for 24h, and afterward, crystallized at 755°C for different lengths of time (45min, 1.5, 6, 12, 24, 32, and 48h)

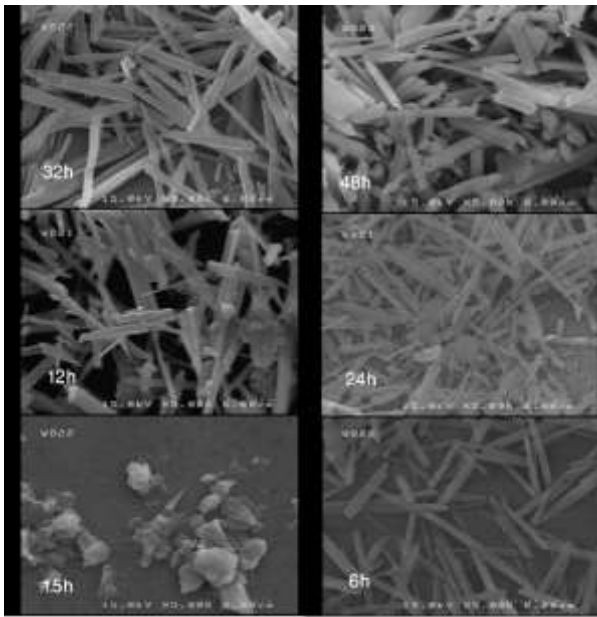


Figure 6. FESEM micrographs for nucleated samples at 668°C for 24h, and subsequently, heated at 755°C for different lengths of time (1.5, 6, 12, 24, 32, and 48h)

3.3. Leaching and Porosimetry

The prepared glass-ceramics were kept in a 1M HCl solution for one week at ambient temperature. Fig. 7 shows the porous microstructure of glass-ceramic (G) and alumina-containing glass-ceramic (Al4) after acid washing. The results of porosity analysis are presented in Table 2 through the BET method. Furthermore, Fig. 8 shows the XRD results of the Al4 sample before and after the acid washing.

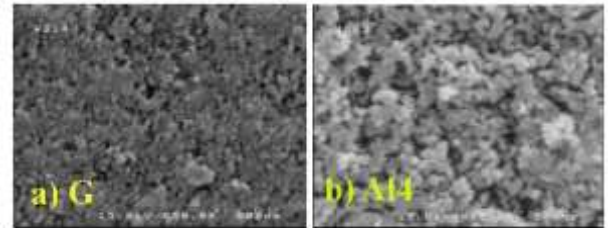


Figure 7. FESEM micrograph of crystallized samples after holding in HCl for one week: a) G and b) Al4

TABLE 2. BET results for porous glass-ceramics

Sample	G	Al4
Average pore size (nm)	12.3±2	16.1± 2
Specific surface area (m ² .g ⁻¹)	26± 3	14± 2

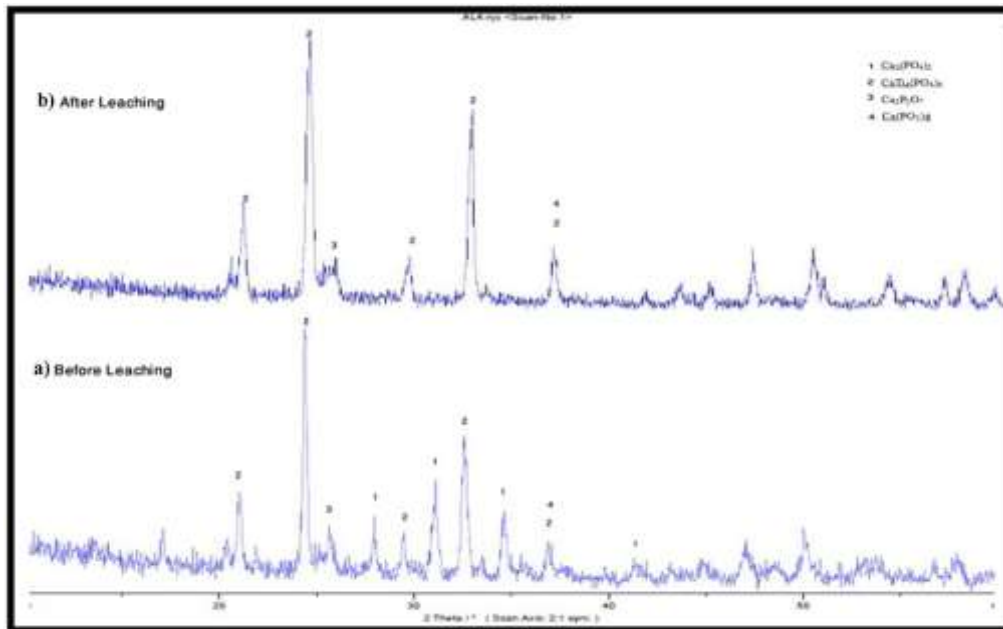


Figure 8. XRD patterns of Al4 nanoporous glass-ceramic before and after soaking in HCl for one week

4. DISCUSSION

All glasses have a violet color. This color was attributed to the existence of Ti^{4+} in the glasses [6]. There was not any change of color with adding Alumina. The glass containing 6% alumina had a more viscosity that was poured from the crucible harder than others.

The T_1-T_g increased with the addition of alumina to the base glass, which indicates the improvement of glass making. Better glass making resulted in harder crystallization and creation of larger crystals rather than finer crystals, which ultimately increased the size of the pores. This is also confirmed by the BET results (Table 2). On the other hand, the improved glass formation in this system avoided unwanted initial crystallization. Thus, the crystallization can be done arbitrarily and with greater precision.

There are a few papers that investigated the structure of the base glass-ceramic [2], which often consist of Nasion-type $CaTi_4(PO_4)_6$ crystals and some crystalline titanium phosphates with calcium phosphate phases. T_g decreases by adding Al_2O_3 (Fig. 1). Researchers reported that T_g should increase by the addition of Al_2O_3 in phosphate glasses [13], but it seems this is not a general result. The nature of aluminophosphate glasses structures is highly dependent on the glasses composition [14]. So, it seems that a structural study is necessary to understand the main reason for the increase of T_g by adding Alumina. That study was not in the scope of this research, but further studies are under progress by the researchers of this paper. Nucleation is very important in the phosphate glass-ceramics. Fig. 3 showed that phase separation was intensified by nucleation heat treatment after a relatively long time (32 hours), but the glass may start to crystallize after a very long period of nucleation heat treatment (48 hours). Thus, it seems that 32 hours of nucleation time was quite enough. It seems that the Al_2O_3 addition keeps the interconnected spinodal microstructure by comparing the base glass with the A14 sample in Fig. 3.

Fig. 5 shows that the formation and the growth of the major phases, $CaTi_4(PO_4)_6$, and $Ca(PO_3)_2$ are simultaneous, and Fig. 6 confirmed this observation. The comparison of Fig. 6 (1.5 hours vs. 24 hours) shows the crystallization of the samples after 1.5 and 24 hours heat treatment, respectively. The results show that the equiaxed particles eventually adopted to plate-like shapes, whereas the fibrous particles preserved their fibrous or rod-shaped morphology. There is no evidence of other phases like anatase. Also, the $\beta-Ca_2P_2O_7$ phase is very small. This is an appropriate result because $Ca_2P_2O_7$ is soluble in acid. Therefore, it can increase the pore size after leaching [15].

In the previous methods used by researchers to increase the porosity, the subsequent heat treatment process resulted in the formation of unwanted phases such as the anatase and $Ca_2P_2O_7$ phases. These phases changed the

surface chemistry and made the product inappropriate for some applications [8].

According to Fig. 7 (a), it can be seen that most pores are smaller than 100 nm. In Fig. 8, it can be seen that $CaTi_4(PO_4)_6$ and $Ca(PO_3)_2$ are the major and minor phases remaining after the soaking process and there is no evidence of the presence of the $\beta-Ca_3(PO_4)_2$ phase. According to BET results, the average pore size is 16.1 ± 2 nm in the A14 sample, which means the porous glass-ceramic was in the nano range. The specific surface area for this specimen was 14 ± 3 $m^2.g^{-1}$. The average pore size and the specific surface area are 12.3 ± 2 and 26 ± 3 $m^2.g^{-1}$, respectively in the base glass-ceramic (G). The pore size moderately increased by adding Al_2O_3 to the base glass. This is due to the harder crystallization, and consequently, the creation of larger crystals. These larger crystals dissolve in the acid and leave larger pores. Since there were no new additional phases in the method described in this study, the surface chemistry of the pores was similar to the base glass-ceramic, and did not change.

5. CONCLUSION

In this research, the effect of adding alumina to the base glass was investigated on the ceramic glass system. According to the studies, the glass transition temperature and the crystallization temperature of the glass samples were decreased by adding alumina to the glass. The sample containing 4% mol alumina had good crystallization behavior, which was selected for the studies. The appropriate nucleation temperature for the sample was $667^\circ C$. The time required for nucleation was 24h, while the base glass had a glass transition temperature of $675^\circ C$ and the optimum nucleation time of 32h. The most important phases created in the glass-ceramics after being washed with hydrochloric acid were the $CaTi_4(PO_4)_6$ and $Ca(PO_3)_2$ phases. It was shown that the porosity size increased from 12.3 to 16.1 and the specific surface area was also reduced from 26 to $14 m^2.g^{-1}$ by adding 4% alumina molar to the porous glass-ceramic.

6. ACKNOWLEDGEMENTS

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