Thermochimica Acta, 192 (1991) 29–34
Elsevier Science Publishers B.V., Amsterdam

A study of the effects of CeO_2 on the crystallization of CaO/P_2O_5 glass [α]

Jinn-Shing Lee [a,b], Jaw-Chay Perng [b], Ching-Wang Huang [b] and Wei-Ping Pan [c]

[a] *Chung Shan Institute of Science and Technology, Long-Tan, Taiwan 32526 (Taiwan)*
[b] *Department of Chemistry, Chung Yuan University, Chung Li, Taiwan 32033 (Taiwan)*
[c] *Department of Chemistry, Western Kentucky University, Bowling Green, KY 42101 (USA)*

(Received 17 May 1991)

Abstract

In previous studies, the effects of rare earth oxides on the physical properties of CaO/P_2O_5 glass-ceramics have been investigated. It was found that the addition of rare earth oxides elevated the physical properties of CaO/P_2O_5 glass-ceramics. CeO_2 played a key role as the nucleation agent.

The main objective of the experiment is to examine the effect of the addition of CeO_2 on the crystallization of CaO/P_2O_5 glasses. Addition of CeO_2 appears to produce a higher temperature of maximum nucleation rate (615 °C) than that of CaO/P_2O_5 glasses (580 °C). The activation energy of crystal growth and morphology of crystal growth are also presented. It is found that the surface crystallization occurs in the presence of CeO_2.

INTRODUCTION

Hydroxyapatite is known to be one of the most biologically compatible materials to human bone. However, high-strength sintered products of hydroxyapatite have not yet been developed [1]. Nonetheless, CaO/P_2O_5 glass-ceramics, which are biologically compatible with living bone, have been used in implants [2]. Glasses containing Al_2O_3 and SiO_2 have been studied [3] as possible implants but were found to have physical properties that were inappropriate for such a procedure. The purpose of this research was to enhance the bending strength of CaO/P_2O_5 glass-ceramics using conventional pressure at room temperature and sintering.

Thermal analysis has been successfully used to study the kinetics of chemical reactions and the crystallization of glass [4]. Many researchers describe methods for determining the activation energy for crystal growth and the mechanism of crystallization for bulk or surface nucleation from DTA curves [5–8]. Recently a method has been found to evaluate the crystallization peak from DTA. The kinetic parameters were used to find the

---

[α] Presented at the 19th Annual NATAS Conference, Boston, MA, 23–26 September 1990.

mechanism of crystal growth in glasses and from the DTA curve the fastest nucleation temperature of glass was obtained.

EXPERIMENTAL

Samples of glass with different compositions were prepared by heating in Pt crucibles in a furnace at 1350 °C for 2 h. The melts were then quenched in distilled water. The quenched glasses were then crushed and sieved to a powder of less than 200 mesh. The test species for physical properties were prepared by adding organic binder, 1% by mass, to the glass powder and then forming a rod out of this mixture at room temperature. For nucleation and heat treatment, the temperature was held at 600 °C for 10 h and at 700 °C for 2 h. Vicker's hardness test was used to evaluate hardness and a four point bending strength test was used to evaluate bending strength. Density was determined by using Archimedes principle in a medium of deionized water.

A Rigaku-Denki differential thermal analyzer model 8121 was used with heating rates from 2 to 20 °C min^{-1}. The experiments were run on samples (about 30 mg) of fine (−325 mesh) and coarse (−30 + 50 mesh) powder and α-A_2O_3 powder was used as a reference material.

RESULTS AND DISCUSSION

Physical properties

The average bending strength of the CaO/P_2O_5 glass-ceramics was found to be improved by adding a nucleating agent (see Fig. 1). Samples which contained the nucleating agent, 3% by mass, appeared to display a significant improvement in their bending strength, especially the CeO_2 sample.

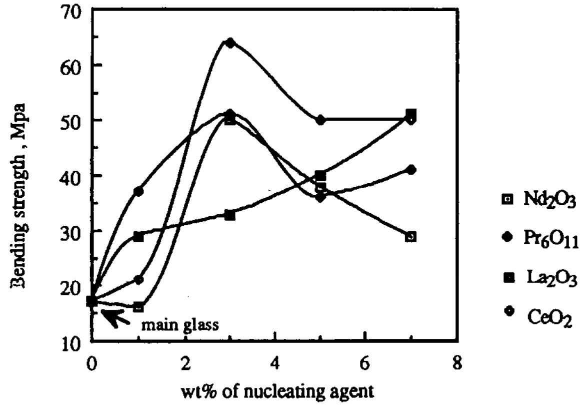

Fig. 1. Bending strength versus percentage mass of nucleating agent.

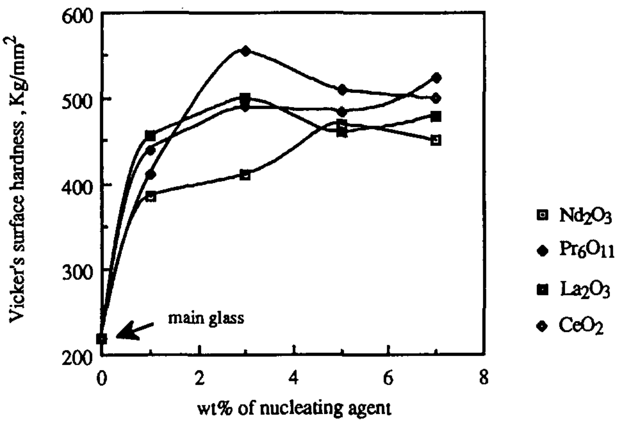

Fig. 2. Vicker's surface hardness versus percentage mass of nucleating agent.

Figure 2 displays a plot of Vicker's hardness versus the percentage by mass of nucleating agent for four different samples and further illustrates that the Vicker's hardness of the samples increases and then levels off at a high value. The density of the samples tended to decrease slightly when a nucleating agent was present (see Fig. 3). From an engineering point of view, a reduction in the mass is advantageous.

The addition of the nucleating agent caused the DTA exotherm to shift to temperatures 5–30 ° C higher (see Fig. 4). This indicates that the temperature or time of the heat treatment process has to increase.

From the data collected on the physical properties, we found that the addition of a rare-earth oxide nucleating agent improves the physical properties of CaO/P_2O_5. We also obtained the best result from the CeO_2 sample (3% by mass) heated to 700 ° C.

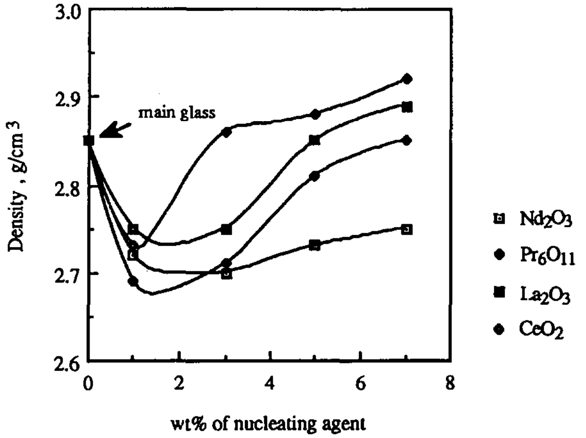

Fig. 3. Density versus percentage mass of nucleating agent.

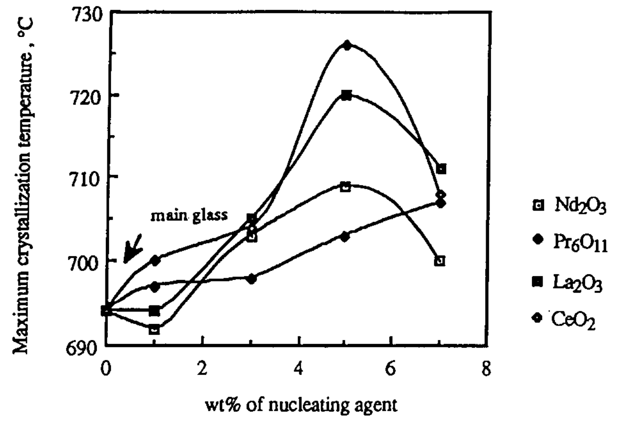

Fig. 4. Maximum crystallization temperature versus percentage mass of nucleating agent.

Crystal growth and nucleation

As crystallization occurs in glass, the heat of crystallization gives rise to an exothermic peak in the DTA curve. The kinetic parameters can be calculated from DTA curves by the equations [9–11]

$$\ln \Delta T = -mE/RT + \text{constant} \qquad (1)$$

$$\ln h = -E'/RT_p + \text{constant} \qquad (2)$$

$$\ln h/T_p^2 = -E''/RT_p + \text{constant} \qquad (3)$$

where E is the apparent activation energy, m is the order of reaction, T_p is the peak temperature of the DTA curve, and h is the heating rate. From eqn. (1), the value of mE can be calculated from the slope of the straight line obtained by plotting $\ln \Delta T$ against $1/T$. From eqn. (2), the activation energy (E') can be calculated from the slope of the straight line obtained by plotting $\ln h$ against $1/T_p$. Thus, the kinetic parameter, m is obtained by comparing mE to E'. The activation energy (E'') also can be calculated from eqn. (3). All these results are compiled in Table 1. The values of m suggest that the surface devitrification takes place in the presence of CeO_2

TABLE 1

Values of E and m [a]

Sample	E''	E'	mE	m
CaO/P_2O_5 glass	86	88	145	1.64
CeO_2, 3%CaO/P_2O_5 glass (by weight, −325 mesh)	106	108	65	0.60
CeO_2, 3%CaO/P_2O_5 glass (by weight, −30+50 mesh)	102	105	54	0.52

[a] See text for definitions of parameters.

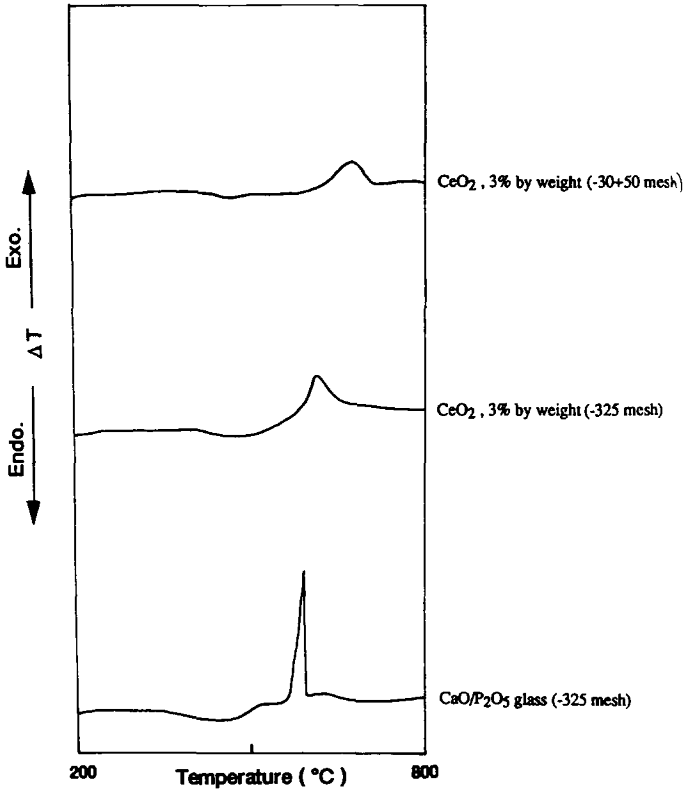

Fig. 5. DTA curves of glass samples with 10 °C min^{-1} heating rate.

with CaO/P_2O_5 glass. However, the bulk devitrification occurs in the CaO/P_2O_5 glass without the presence of CeO_2. The DTA results also showed a sharp peak which indicated the bulk devitrification in the CaO/P_2O_5 glass (see Fig. 5).

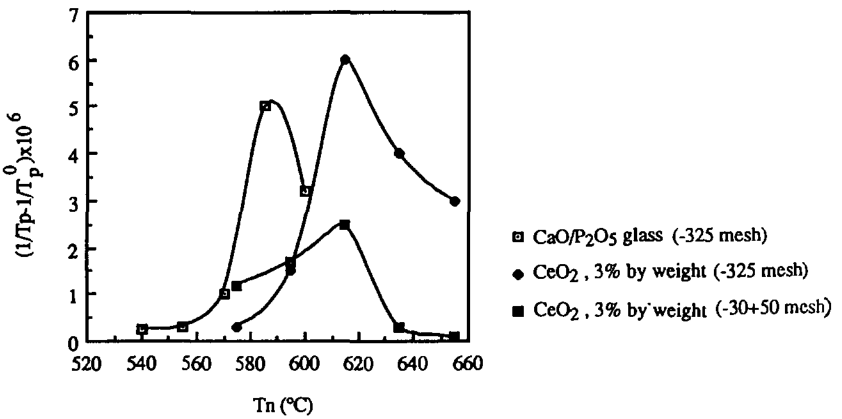

Fig. 6. Nucleation rate–temperature curve.

The kinetic rate constant of nucleation (I) can be calculated by using the approximated equation

$$\ln I = E/R\left(\frac{1}{T_p} - \frac{1}{T_p^0}\right) + \text{constant}$$

If we plot $((1/T_p) - (1/T_p^0))$ versus the temperature (T_n) for the nucleation heating program, we obtain a curve for the nucleation rate–temperature (Fig. 6). From this curve we see a maximum at 615 °C for the CeO_2 glass sample and a maximum at 585 °C for the main glasses which is very near their glass transition temperatures.

CONCLUSIONS

The physical properties of CaO/P_2O_5 glasses were enhanced by the addition of rare earth oxides as nucleating agents, but the activation energy for crystal growth was elevated and the mechanism for crystal growth was changed. The maximum nucleation temperature of glasses was found to be near their glass transition temperatures. By comparing the maximum nucleation temperature of CaO/P_2O_5 glass and the CaO/P_2O_5 glass with the nucleating agents we find that the appropriate heat treatment temperature was shifted 30 °C higher.

REFERENCES

1 K. Knodo, M. Okuyama, H. Ogaawa and Y. Shibata, Comm. Am. Ceram. Soc., November (1984) C-222.
2 Y. Abe and H. Fukui, Skika Kyoka-Zasshi, 16, 36 (1975) 196.
3 Y. Abe and H. Satio, Yogyo Kyokaishi, 2, 85, (1977) 45.
4 A. Marotta, A. Buri and F. Branda, Thermochim. Acta, 40 (1980) 397.
5 T. Ozawa, Polymer, 12 (1971) 150.
6 J. Sestak, Phys. Chem. Glasses, 15 (1974) 137.
7 A. Matrotta and A. Buri, Thermochim. Acta, 25 (1978) 155.
8 J. Augus and J.F. Bennett, J. Therm. Anal., 13 (1978) 283.
9 M. Aviami, J. Chem. Phys., 9 (1941) 177.
10 A. Marotta and A. Buri, Thermochim. Acta, 25 (1978) 155.
11 A. Marotta, S. Saiella, F. Branda and A. Buri, Thermochim. Acta, 46 (1981) 123.