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KINETIC STUDIES OF CRYSTALLIZATION IN $Ca_{1-x}Mg_x(PO_3)_2$ GLASSES

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Abstract

The crystallization kinetics of $Ca_{1-x}Mg_x(PO_3)_2$ glasses was studied for powder and bulk samples of the compositions x=0, 0.5 and 1.0 by means of DSC. The activation energy calculated by the Freedman method or the Kissinger method is smaller for the mixed glass $Co_{0.5}Mg_{0.5}(PO_3)_2$ than for the glasses with x=0 and 1.0. For most of the samples, the two-parameter Šesták-Berggren equation gives a better description of the crystallization kinetics; only for powder $Ca(PO_3)_2$ and bulk $Mg(PO_3)_2$ does the Johnson-Mehl-Avrami model fit better with the experimental data.

Keywords: crystallization, glass, kinetic study

Introduction

Calcium phosphates belong among materials studied for their application in medicine as biomaterials with unique properties [1] in both crystalline and glassy phases. Hydroxyapatite and calcium metaphosphate are the most interesting compounds investigated for this purpose in recent years [2, 3].

The metaphosphates have an ability to form a glassy state on fast cooling of their melts. Many applications of ceramic materials involve the glass to ceramic transition, because bulk pieces can be made by melting the batch and forming the bulk by cooling the melt in a suitable form. We recently reported a study of the structure of $Ca_{1-x}Mg_x(PO_3)_2$ in the glassy and crystalline phases [4]. Homogeneous glasses are formed throughout the whole compositional region, whereas two crystalline phases are formed within the region x=0.3 0.7. The present paper reports a study of the crystallization kinetics of $Ca_{1-x}Mg_x(PO_3)_2$ glasses with the aim of establishing how the different crystal structures influence the course of crystallization in this system.

Experimental

Samples in the system $Ca_{1-x}Mg_x(PO_3)_2$ were prepared with the compositions x=0, 0.2, 0.4, 0.5, 0.6, 0.8 and 1.0. The preparation of these samples started from

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carbonates of calcium and magnesium and a phosphoric acid solution containing 85% of pure H_3PO_4. The starting compounds were mixed in the stoichiometric ratio corresponding to the following reaction:

$$(1-x)CaCO_3+xMgCO_3+2H_3PO_4 \rightarrow Ca(H_2PO_4)_2+CO_2+H_2O \qquad (1)$$

Phosphoric acid was added slowly to the starting suspension of carbonates premixed with a small amount of water. The suspension obtained was then dried at 60°C.

The dry product was slowly heated to 600°C and maintained at this temperature for 2 h. The resulting material was disintegrated in a vibrational mill and melted at 1250°C for 20 min, the melt was then cooled rapidly either by pouring into water or on a steel sheet. In this way, we obtained homogeneous transparent glassy samples. The amorphous nature of the glasses was confirmed by X-ray diffraction. The glassy samples used for investigation of the thermal properties were disintegrated in the vibrational mill. The powder obtained had a mean particle size of $d \cong 80$ μm and was used for all crystallization kinetics measurements. The powder samples (100 mg) were placed in small silica crucibles and all measurements were carried out in air.

The non-isothermal thermoanalytical curves were recorded on a Perkin-Elmer DTA–DSC instrument, model 1700, working in the DSC mode in the temperature region from 20 to 1000°C at a scan rate of 2, 5, 10, 15 or 20°C min^{-1}. The kinetic analysis of the DSC data and all calculations were performed with the TA-system software package [5].

Results and discussion

A typical DSC curve is shown in Fig. 1 for the glass composition $Ca_{0.5}Mg_{0.5}(PO_3)_2$. The curves of all the $Ca_{1-x}Mg_x(PO_3)_2$ glasses afforded three characteristic features: the glass transition temperature, T_g the temperature of onset crystallization, T_c, and the peak temperature of crystallization T_p. T_g was evaluated by the integral method [6] as the point of intersection of the enthalpic curves for the glass and undercooled liquid.

All the values obtained for T_g, T_c and T_p for $Ca_{1-x}Mg_x(PO_3)_2$ are listed in Table 1. It may be seen that T_g increases by Mg by about 15°C when Ca is replaced. The crystallization temperatures T_c and T_p change with composition much more, the former by 46°C, and the latter by 78°C. The differences in T_c and T_p between glassy samples of $Mg(PO_3)_2$ and $Ca(PO_3)_2$ reflect the differences in the melting points of the crystalline compounds $Mg(PO_3)_2$ and $Ca(PO_3)_2$, 1165°C [7] and 975°C [8], respectively. The course of crystallization in the two glasses also differs. The crystallization peak for the $Mg(PO_3)_2$ glass is broader, which is probably due to more complicated structural changes as the chain structure transforms into a ring-like structure characteristic of crystalline $Mg(PO_3)_2$ [7].

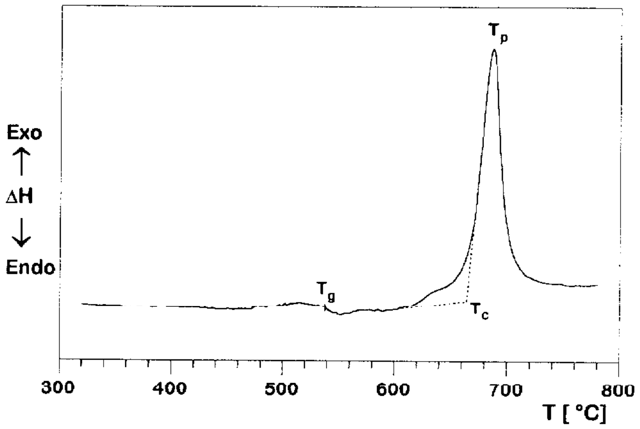

Fig. 1 Typical DSC curve obtained at a heating rate of 10 K min^{-1} for $Ca_{0.5}Mg_{0.5}(PO_3)_2$ glass

Table 1 Values of transformation temperature T_g, crystallization temperature, T_c, and peak temperature of crystallization, T_p, of $Ca_{1-x}Mg_x(PO_3)_2$ glasses obtained by cooling in water and measured at a heating rate of 10 K min^{-1}

x	0	0.2	0.4	0.5	0.6	0.8	1	ΔT^*
T_g/°C	533	535	537	533	535	540	548	15
T_c/°C	631	652	658	663	671	675	677	43
T_p/°C	647	672	677	682	693	700	725	78

*ΔT is the difference between the corresponding values for $Mg(PO_3)_2$ and $Ca(PO_3)_2$.

The course of crystallization also depends on the aggregate form of the sample. For the powder samples, it differs from that for the bulk samples. For the bulk samples, the crystallization peak is shifted to higher temperatures than those for the powder samples. This shift increases with increasing Mg content. A comparison of the courses of crystallization for the $Ca_{1-x}Mg_x(PO_3)_2$ bulk and powder glass samples can be seen in Fig. 2.

The modified kinetic equaiton applied for the studies of crystallization of glasses is usually in the following form [9]:

$$\Phi = \Delta H A e^{-\varepsilon} f(\alpha) \qquad (2)$$

where Φ is the heat flow, ΔH is the enthalpy of the crystallization process, A is the pre-exponential factor, α is the degree of crystallization and $\varepsilon = E/RT$ is the reduced activation energy. The function $f(\alpha)$ is a mathematical expression of the phenomenological kinetic model.

For some glasses, the most frequently applied kinetic equations are the Johnson-Mehl-Avrami (JMA) equation and the Šesták-Berggren (SB) equation.

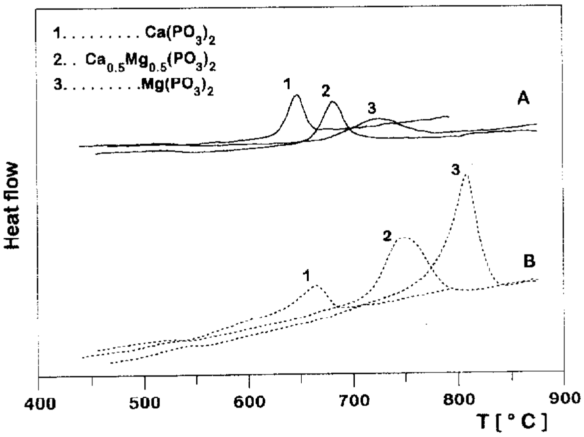

Fig. 2 Shift in crystallization peaks of powder (A) and bulk (B) $Ca_{1-x}Mg_x(PO_3)_2$ glasses with composition; heating rate 15 K min^{-1}

The JMA equation [10, 11] has the form

$$f(\alpha) = m(1-\alpha)[-\ln(1-\alpha)]^{1-1/m} \tag{3}$$

and the SB equation [12] has the form

$$f(\alpha) = \alpha^M(1-\alpha)^N \tag{4}$$

Because of the mutual interdependence of A and E in Eq. (2), the multiple-scan method is usually applied, with several sets of kinetic data taken at various heating rates. For calculation of the activation energy E, the methods of Friedmann [13] and Kissinger [14] were applied.

In the Friedmann method, the activation energy is calculated from the logarithmic form of Eq. (2):

$$\ln\Phi = \ln[\Delta HAf(\alpha)] - E/RT \tag{5}$$

as the slope of the plot of the normalized heat flow at a given crystallization degree, plotted *vs.* the reciprocal temperature.

The Kissinger method is based on the condition for the maximum of the DSC peak:

$$\ln\frac{\beta}{T_p^2} = \ln\frac{-f(\alpha_p)AR}{E} - \frac{E}{RT_p} \tag{6}$$

where T_p and α_p are the peak temperature and crystallization degree at the DSC peak, respectively, and β is the heating rate.

The values of E in the Friedmann method were calculated for different values of α in the interval $\alpha \in (0.1)$ for samples of $Ca_{1-x}Mg_x(PO_3)_2$ glasses with x=0, 0.5

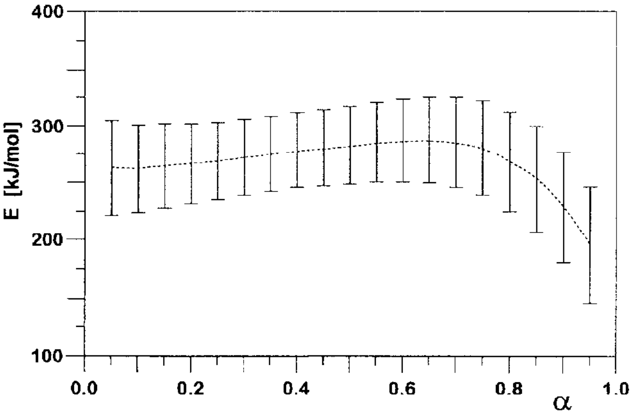

Fig. 3 Values of activation energy *E* obtained for different degrees of crystallization α calculated by the Friedmann method for the powder sample of $Ca_{0.5}Mg_{0.5}(PO_3)_2$ glass

and 1.0. In Fig. 3, the values of E are shown for the composition $Ca_{0.5}Mg_{0.5}(PO_3)_2$. To calculate the mean activation energy for all the samples, we used only the interval $\alpha \in (0.3, 0.7)$, where the values of *E* are more reliable. The mean values obtained for *E* are given in Table 2. It can be seen that the Kissinger method gives values of *E* higher by about 10% than those found with the Friedmann method. The activation energy is also higher for powder samples than for bulk samples. For the mixed sample with x=0.5, the activation energy is at a minimum for both bulk and powder samples.

Table 2 Activation energy of the crystallization process in $Ca_{1-x}Mg_x(PO_3)_2$ glasses, calculated by the Friedman method and the Kissinger method for powder and bulk glassy samples

x	Powder sample		Bulk sample	
	Calculation method			
	Friedman	Kissinger	Friedman	Kissinger
	E/kJ mol^{-1}			
0	295±19	315±17	185±16	237±16
0.5	281±35	287±8	138±23	191±6
1	314±10	323±14	202±23	246±11

Perng *et al.* [15] studied the crystallization kinetics of pure $Ca(PO_3)_2$ glass. They obtained an activation energy of 402.8 kJ mol^{-1} for a fine powder glass (45 μm) obtained by quenching from the melt. Our values are lower, at 315 kJ mol^{-1} (Kissinger method) and 295 kJ mol^{-1} (Friedmann method), but our particles were coarser (85 μm). We observed a similar trend to that reported by Perng *et al.* [15]: the values of *E* were lower for bulk glasses than for powder samples. This trend was valid for all samples of $Ca_{1-x}Mg_x(PO_3)_2$ glasses.

To evaluate the proper kinetic model, we applied functions $z(\alpha)$ and $y(\alpha)$ [5] suitable for differentiation between various kinetic models. The function $z(\alpha)$ is defined as

$$z(\alpha) = \pi(\varepsilon)\Phi T / \beta \tag{7}$$

where $\pi(\varepsilon)$ is an approximation of the temperature integral, introduced for the solution of Eq. (2), which can not be integrated analytically.

The function $y(\alpha)$ is defined [5] as

$$y(\alpha) = \Phi e^{\varepsilon} \tag{8}$$

where the maximum is confined to the interval $0 \le \alpha_M \le \alpha_p$. The value of α_M is important for calculation of the kinetic exponent in the corresponding kinetic model by plotting the $y(\alpha)$ dependence normalized in the interval <0.1>. The shape of $f(\alpha)$ obtained is characteristic of each kinetic model [5].

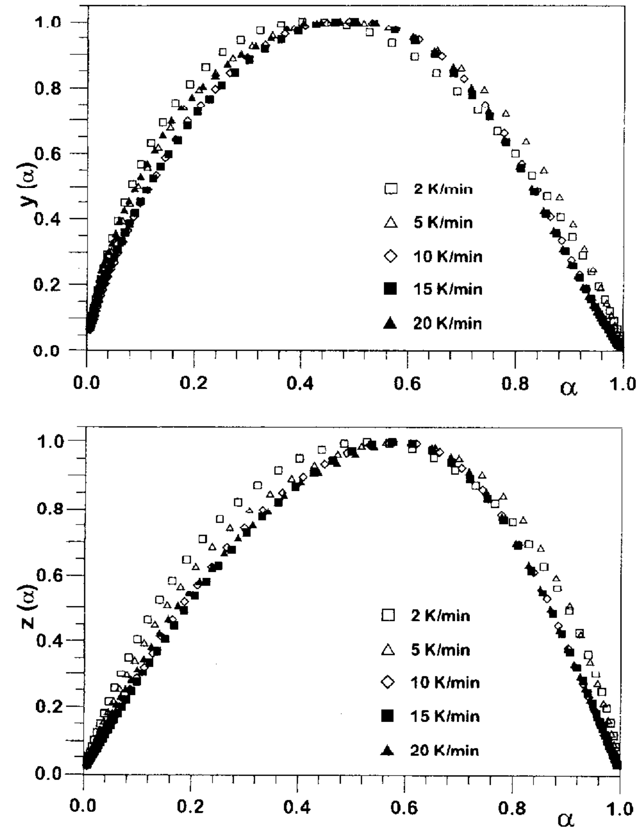

Fig. 4 Normalized function $y(\alpha)$ (a) and function $z(\alpha)$ (b) calculated for powder $Ca_{0.5}Mg_{0.5}(PO_3)_2$ glass. Measurements at different heating rates

The courses of the functions $y(\alpha)$ and $z(\alpha)$ for crystallization of a powder sample $Ca_{0.5}Mg_{0.5}(PO_3)_2$ glass are shown in Figs 4a and 4b, respectively. As the courses of the two functions for this composition do not display any systematic deviations with regard to the heating rate, we can say that neither function depends on the heating rate. In this case, we can determine with good precision the maxima of the functions $y(\alpha)$ and $z(\alpha)$: $\alpha_M=0.48\pm0.01$ and $\alpha_p^\infty=0.58\pm0.01$, respectively, for the powder glass of this composition. The corresponding maxima calculated for all the powder and bulk glass samples are given in Table 3. When the maximum of the function $y(\alpha)$ is at $\alpha_M \in (0, 1)$, the kinetic data can be dscribed by the SB(M, N) or JMA ($m>1$) model [5]. The values of the maxima of the function $z(\alpha)$ (α_p^∞) are used for the choice of either the SB or the JMA model. For the application of the JMA model, the maximum of the function $z(\alpha)$ should lie at 0.632 [9]; lower values of α_p^∞ correspond to the application of the SB model for a description of the crystallization process.

Table 3 reveals that for most of $Ca_{1-x}Mg_x(PO_3)_2$ glasses the calculated value of $\alpha_p^\infty < 0.63$, and thus the SB model probably holds for them. Only for the powder sample of $Ca(PO_3)_2$ and the bulk sample of $Mg(PO_3)_2$ is the value of $\alpha_p^\infty \cong 0.63$, which means that the JMA model should be valid for the kinetics of crystallization of these two glasses.

Table 3 Maxima of the functions $y(\alpha)$ and $z(\alpha)$ for powder and bulk samples of $Ca_{1-x}Mg_x(PO_3)_2$ glasses

x	Powder sample		Bulk sample	
	α_M	α_p^∞	α_M	α_p^∞
0	0.48±0.01	0.63±0.02	0.47±0.05	0.55±0.04
0.5	0.48±0.01	0.58±0.01	0.49±0.03	0.58±0.02
1	0.41±0.03	0.55±0.03	0.47±0.03	0.65±0.03

It is interesting that for the powder samples of $Ca_{1-x}Mg_x(PO_3)_2$ glasses the value of α_p^∞ decreases with increasing x, whereas for the bulk samples of $Ca_{1-x}Mg_x(PO_3)_2$ glasses the value of α_p^∞ increases with increasing x.

In Fig. 5, the fit of the kinetic data calculated according to the SB model for the $Ca_{0.5}Mg_{0.5}(PO_3)_2$ glass is compared with the experimental curves of crystallization obtained at various heating rates. It can be seen that the agreement of the data calculated with the SB model with the experimental data is very good. The difference observed between the experimental and theoretical values at higher heating rates can be ascribed to a lower coefficient of heat transmission of the silica crucibles used for the measurement.

Table 4 gives the calculated data on all the parameters for both the SB and JMA models. We have also verified the validity of the kinetic models by fitting the experimental data with the calculated curves, using the parameters obtained with the TAS software package [5] for the JMA and SB models. The best fit was

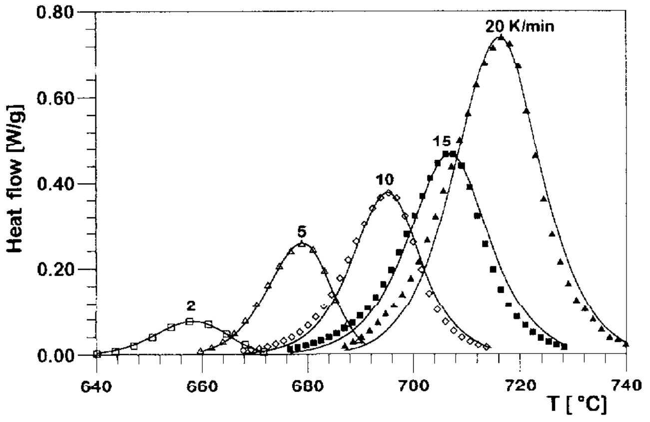

Fig. 5 Experimental points and calculated curves of DSC peaks obtained from the SB model for $Ca_{0.5}Mg_{0.5}(PO_3)_2$ glass

Table 4 Kinetic parameters of crystallization of powder and bulk samples of $Ca_{1-x}Mg_x(PO_3)_2$ glasses calculated for the SB(M,N) and JMA(m) kinetic models

Powder sample		Kinetic model				
		SB (M,N)			JMA (m)	
x	E(kJ mol^{-1})	M	N	ln$A$(s^{-1})	m	ln$A$(s^{-1})
0	295±19	0.84±0.03	0.75±0.06	33.10±0.26	2.96±0.10	31.62±0.07
0.5	281±35	0.97±0.03	1.04±0.03	31.41±0.16	2.46±0.20	30.16±0.16
1	314±10	0.78±0.10	1.10±0.05	34.03±0.16	1.84±0.16	33.08±0.14

Bulk sample		SB (M,N)			JMA (m)	
x	E(kJ mol^{-1})	M	N	ln$A$(s^{-1})	m	ln$A$(s^{-1})
0	185±16	0.95±0.05	1.21±0.26	19.59±0.13	1.80±0.20	18.14±0.36
0.5	138±23	0.86±0.09	0.92±0.14	12.52±0.10	2.70±0.11	11.33±0.22
1	202±23	0.52±0.09	0.63±0.07	18.17±0.31	2.83±0.51	16.99±0.32

obtained with the SB model for all samples, with the exception of the powder sample of $Ca(PO_3)_2$ and the bulk sample of $Mg(PO_3)_2$, where the JMA fit was better than that with SB.

Conclusions

To summarize our results, the activation energy for the mixed $Ca_{0.5}Mg_{0.5}(PO_3)_2$ glass is lower than those for pure calcium metaphosphate or magnesium metaphosphate. A shift in the crystallization peak to higher temperatures with increasing content of magnesium corresponds to a higher degree of covalency of the chemical bonds between the cationic and anionic parts of the compound. The higher degree of covalency is also reflected in an increased melting point of the crystalline phase with higher Mg content. The shape of the crystallization peak for the $Ca_{1-x}Mg_x(PO_3)_2$ glasses changes differently with composition for the powder and bulk glasses. For the bulk glasses, the crystallization process increases in rate with increasing Mg content, whereas for the bulk glasses, the opposite behaviour was observed. We assume that these differences are associated with the kinetics of the crystallization process, because the slow crystallization processes for the powder $Ca(PO_3)_2$ glass and the bulk $Mg(PO_3)_2$ glass give a better fit for the JMA model than for the SB model, the latter model being preferable for all the other studied samples. We believe that these differences are associated with the different rates of nucleation and crystallization processes in the $Ca_{1-x}Mg_x(PO_3)_2$ glasses.

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