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The devitrification kinetics of transparent silica glass prepared by gel-casting method

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ABSTRACT

The kinetics of the crystallization of cristobalite in the amorphous silica glass were studied for samples prepared by gel-casting and sintering in air. Avrami and rate equations were used to calculate the rate constants and the activation energy. The results showed that the crystallization obeys the first order and occurs mainly on the surface with activation energy of 543-546kJ/mol. The fewer amounts of OH-groups and the high amount of oxygen vacancies are expected to stand behind the increase in the activation energy as compared with that reported in literatures.

Keywords: Devitrification, Gel-Casting, Silica Glass, Cristobalite, Crystallization.

1. INTRODUCTION

Transparent silica glass is widely used in many applications due to its unique electronic characteristics such as low dielectric constant, low dielectric loss, high melting point, high thermal shock resistance, and high transparency for wide range of light spectrum [1]. However, thermodynamically, silica glass is unstable; it can be devitrified through the transformation from the amorphous structure to another crystalline phase during the manufacturing processes or when it is used at high temperatures [2].

Many techniques have been used to prepare transparent silica glass; these include spark plasma sintering (SPS) [3-5], pressure less sintering [4], vapor-phase axial deposition [6,7], solid phase sintering [8, 9], slip casting [10], and sol gel method [11-16]. It is well reported that the rate and mechanism of devitrification of the glasses vary with the chemical composition of the glass, temperature, ambient atmosphere, and impurities [17]. Thus, it is expected that devitrification of the glass produced by each technique is differ from that produced by the others.

In our previous work, transparent silica glass was successfully prepared by gel casting method followed by sintering in air [18]. It has been noticed that surface devitrification occurs at 1100ºC which is well below that reported by LI, *et al*. [2], they clearly reported that silica glass crystallizes heterogeneously to form cristobalite when the temperature approaches 1300ºC and the crystallization is controlled by nucleation and diffusion at the same time.

The current work has been established to study the devitrification kinetics of the silica glass prepared by gel-casting method. The ordinary rate and Avrami equations were used to calculate the activation energy and the rate constants of the crystallization process.

2. MATERIALS AND METHODS

Transparent silica glass was prepared from fumed silica nanoparticles and agar as described in details in our previous work [18]. Briefly, a silica suspension was prepared by mixing 3g of fumed silica (Guangzhou GBS High-Tech.& Industry Co. Ltd, Guangzhou, China, surface area 380m^2.g^{-1}), 78ml distilled water, and 0.15g of agar (Hi-Media Laboratories Pvt. Ltd.). The mixture was magnetic stirred at room temperature and dispersed with sonication for 3h. The mixture then subjected to microwave treatment for 150sec with power of 650W and frequency of 2450MHz. The resulting slurry was magnetically stirred for about 10min to get homogeneous gel at 50°C. The gel was casted into PVC mold placed on the plaster substrate and then left to dry in air. After drying, the green bodies were heat treated to 600°C for 2h at rate of 5°C.min^{-1} and then sintered at (1100, 1150, 1200, 1250°C) with different reaction times (60-240min). The sintered samples were

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grinded and sieved with standard sieve No (200).

XRD pattern of the samples was recorded using X-ray diffractometer (XRD 6000, Shimadzo, Japan) over 2θ range of 15-80° using scan speed of 2° per second. Fourier transformed infrared (FTIR) spectra of the samples were recorded using (Shimadzu 1800, Japan) to monitor the presence of OH groups in the samples, the analysis was performed over wavenumber range of 400-4000cm^{-1} with resolution of 2cm^{-1}.

3. RESULTS AND DISCUSSION

Figure 1 shows the XRD pattern of the fumed silica powder. The pattern confirms the amorphous structure of the fumed silica as it does not contain the diffraction peaks of any recorded silica phase. The broad peak at 22.3º is the characteristic peak observed for amorphous silica with nanosize. Similar patterns are reported in literatures for nano-size fumed silica and silica nanoparticles prepared by sol-gel method [19-22].

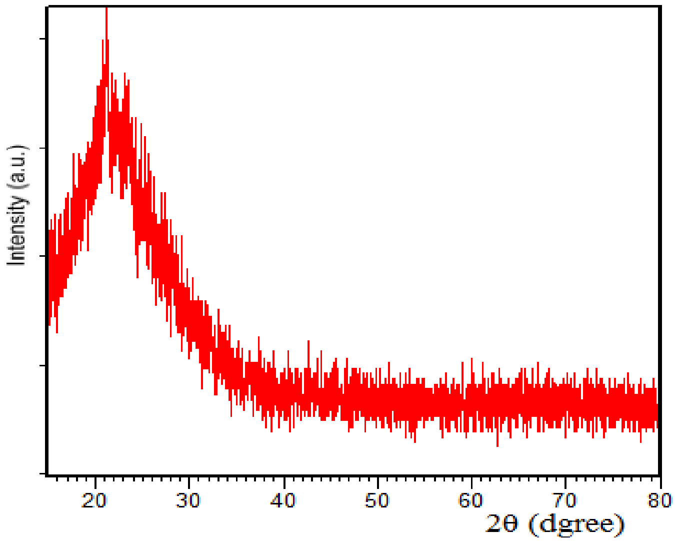

Figure 1: X-ray diffraction pattern of the fumed silica powder.

Figure 2 shows the FT-IR spectra of sample sintering at 1100°C. The peak near to 462cm^{-1} characterizes the bending vibration of Si-O-Si bond [3]. The band about 794cm^{-1} is related to the Si-O-Si symmetric stretching vibration mode of bridging oxygen between tetrahedra [1]. The peak around 1099cm^{-1} was corresponding to Si–O–Si asymmetric stretching of bridging oxygen between tetrahedral of bridging oxygen within the tetrahedra [3]. The peak of the silanol (Si-OH) group at 956cm^{-1} and the peaks of hydroxyl group peak for H_2O at 3440 and 1630cm^{-1} were not observed.

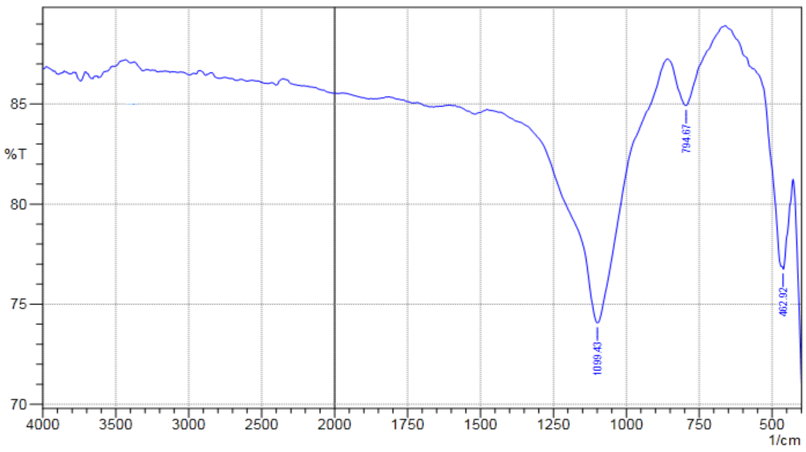

Figure 2: FTIR spectra of transparent silica glass sintering at 1100ºC.

It has been noticed that the samples are subjected to surface devitrification when sintering is achieved at temperature of or above 1100°C as shown in Figure 3. This layer could be eliminated by grinding and even manually.

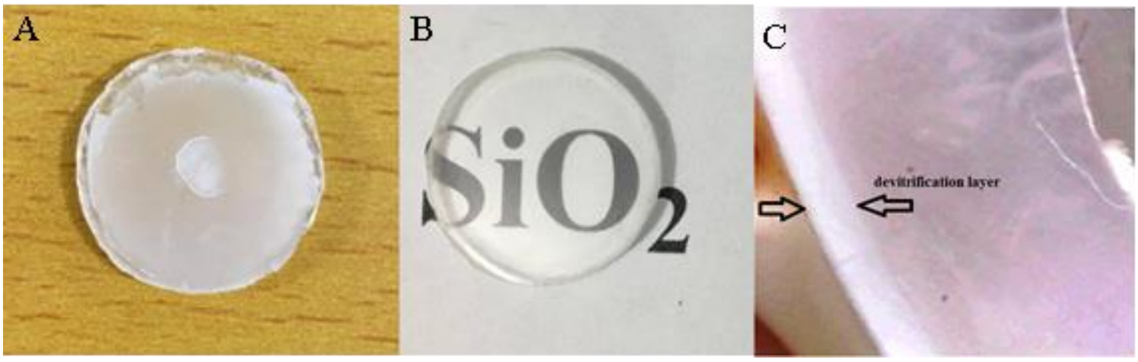

Figure 3: photographs of the A) unpolished sample, B) polished sample, and C) cross section for sample showing the devitrified layer.

The XRD analysis gives the evidence that the devitrified layer is formed by the transformation of the amorphous silica phase into cristobalite. The diffraction data of the devitrified layer are in full agreement with JCPDS (00-011-0695) as shown in Figure 4.

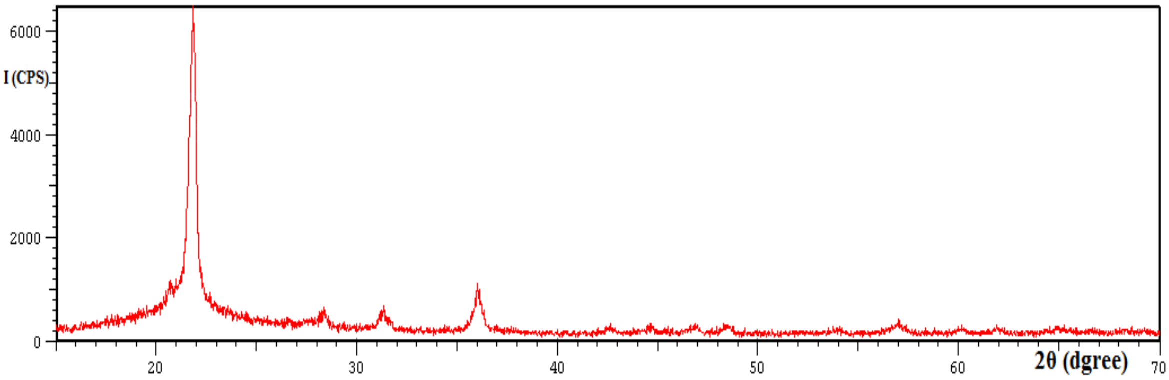

Figure 4: XRD diffraction of silica glass sample sintered at 1100ºC for 60min.

The formation of the new phase may attributed to many reasons including the finger prints on samples surface, the contamination on samples surface, the cooling time and rate, the OH-group, the ambient atmosphere and temperature, and the impurities [17,23,24].

The relative amount of cristobalite phase was calculated based on the peak intensity using the following equation [2]:

$$Y = 18532C + 810 \tag{1}$$

where Y is the peak value of (101) plane and C is content of cristobalite.

Figure 5 shows the XRD patterns, over 2θ range of 20-25°, for samples sintered at different temperatures and reaction times in order to calculate the amount of the cristobalite according to Equation 1.

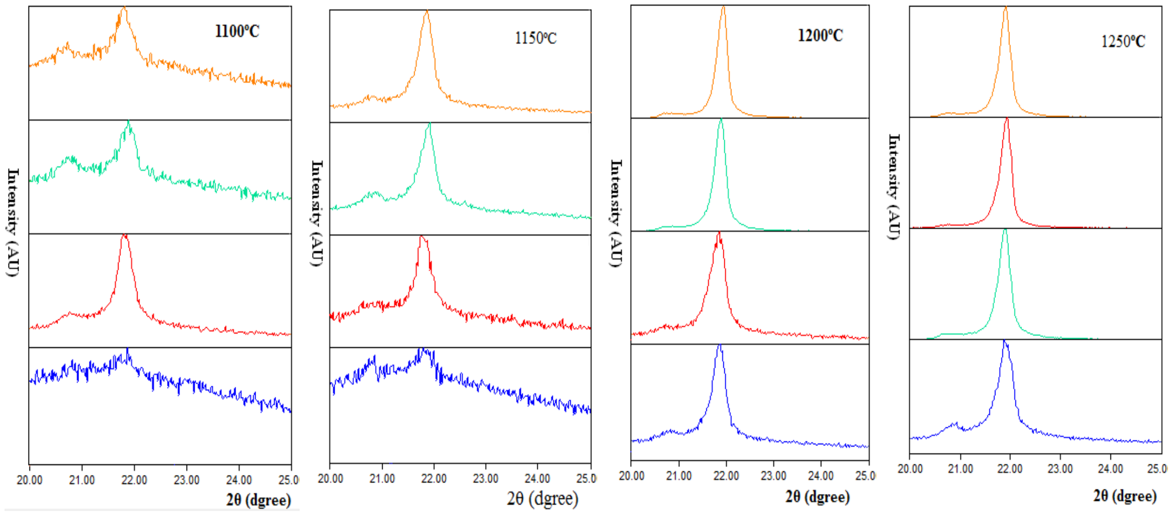

Figure 5: XRD diffraction of silica glass sample prepared by gel-casting sintered at (a) 1100°C (b) 1150ºC (c) 1200°C (d) 1250ºC with different soaking time (60-240min).

Figure 6 shows the relation of the amount of the cristobalite formed during the devitrification process with the soaking time and the sintering temperature. As expected, the rate of transformation was found to increase with increasing the reaction time, as the transformation is time dependant process, and sintering temperature due to the higher energy of the atoms at the higher temperatures.

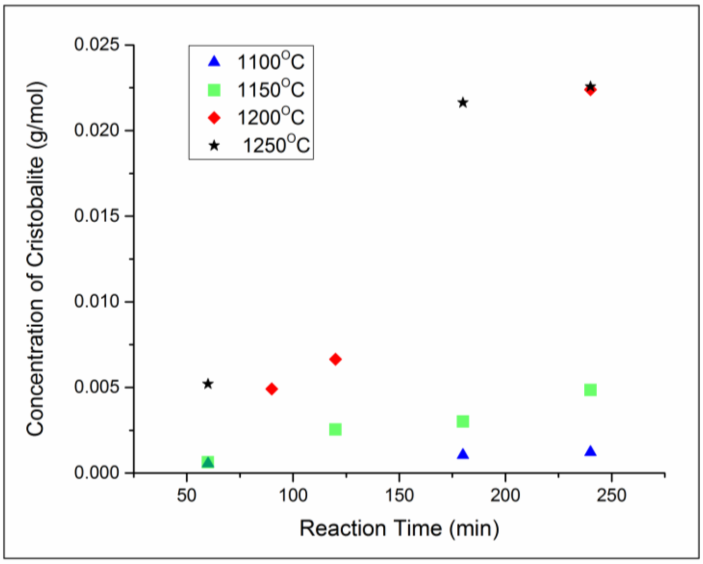

Figure 6: Concentration of cristobalite for samples sintered in air at different temperature with different reaction time.

The kinetics of silica glass transformation, from amorphous glassy state to cristobalite, was studied using two methods as follow:

3.1 Avrami Equations

The kinetic transformation of silica glass was investigated using Avrami equation [25]:

$$\ln\ln(1-C)^{-1} = \ln k + n\ln t \tag{2}$$

where C is the concentration of cristobalite (wt %), t heating time (min), k the overall rate constant, and n is a constant associated with growth dimension, nucleation position, and crystallization mechanism. Figure 7 shows least square fitting acquired from the relation between the [lnln $(1\text{-}C)^{-1}$] vs [ln t] for silica glass samples sintered at different temperatures. The value of n and k were obtained from slope and intercept of fitted lines, respectively, as given in Table 1.

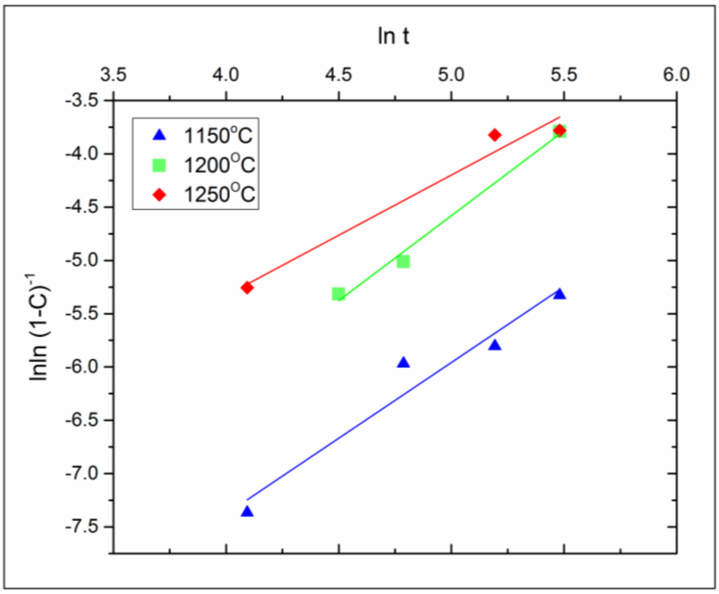

Figure 7: [lnln $(1\text{-}C)^{-1}$] vs [ln t] for different sintering temperature.

Table 1: The equations and the values of R^2, n and k of silica glass sintering at different temperature.

TEMP (°C)	EQUATION	R^2	n = SLOPE	K = INTERCEPT
1150	Y = -13.07+ 1.42 X	0.95	1.42	-13.07
1200	Y = -12.54+ 1.59 X	0.99	1.59	-12.54
1250	Y = -9.85+ 1.13 X	0.97	1.13	-9.85

The average value of n was found to be 1.34, this indicates that the distribution of nucleation sites is non-amorphous; the growth may be restricted to 1 or 2-dimensions, and site saturation for surface only [26]. The value of k as expected was found to be increased as sintering temperature increases. The value of activation energy was obtained from best fit line for the relation between [ln k] and [1000/T] as shown in Figure 8. It was equal to 543kJ/mol.

3.2 Rate Equation

The transformation of silica glass into cristobalite was found to follow first order reaction as the relation between the concentrations of cristobalite was found to fit the following equation:

$$\ln C = -kt + \ln A_o \tag{3}$$

where C is the weight percent of the untransformed silica glass, t is the reaction time (min), k is the rate constant and A_o is the initial silica weight percent (100%). The rate constant for each temperature was calculated from the slope of the straight line, according to Equation 3, as shown in Figure 9. The linear dependence of the [ln C] vs [t] for the results confirms the first order reaction for silica glass transformation. The results of the fitting process are given in Table 2. The relation between temperature and rate constant is given by the following equation:

$$\ln k = \ln d - \left(\frac{Ea}{RT}\right) \tag{4}$$

where d is a constant, R is the general gases constant, Ea is the activation energy and T is the absolute temperature. The activation energy was calculated from the slope of the line between [ln k] vs [1/T] as shown in Figure 10. The activation energy was found to be 546kJ/mol.

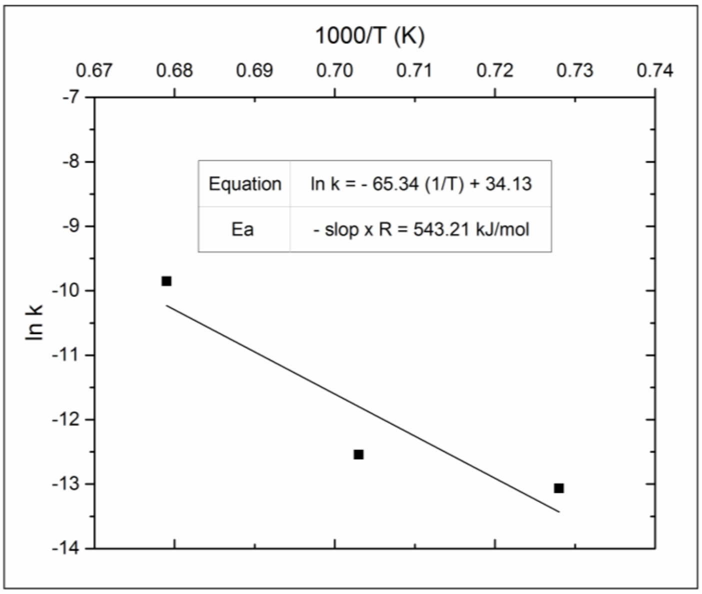

Figure 8: The relation between [ln k] and [1/T] for Avrami equation.

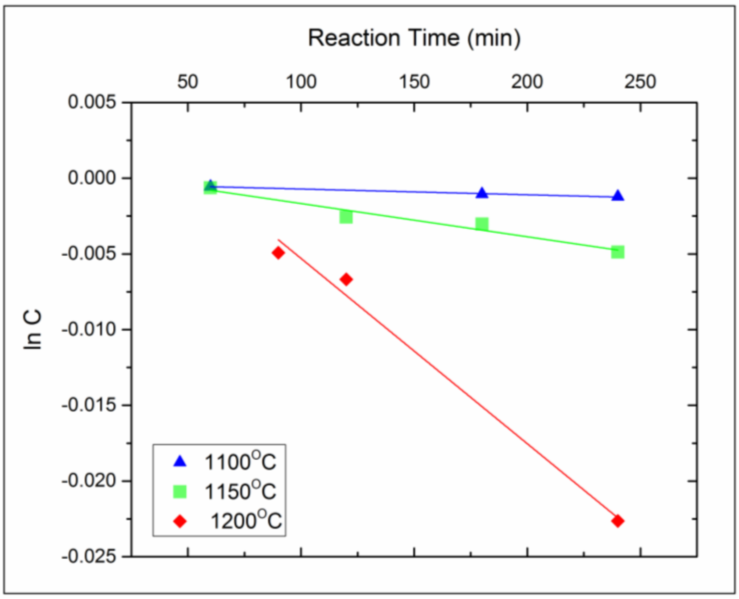

Figure 9: The relation between ln C and reaction time for different sintering temperature.

Table 2: The equations and the values of R^2 and k of silica glass sintering at different temperature.

TEMP (°C)	EQUATION	R^2	K = - SLOPE
1100	Y = -0.0003- 4E-6X	0.99	4E-6
1150	Y = 0.0005- 2E-5X	0.95	2E-5
1200	Y = 0.0069- 1E-4X	0.99	1E-4

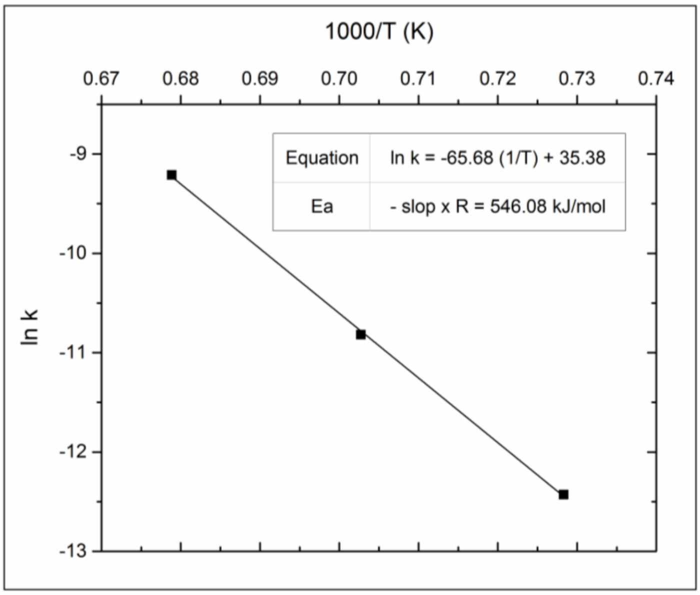

Figure 10: The relation between [ln k] and [1/T] for first order reaction.

The activation energies (543 and 546kJ/mol) obtained from both equations are nearly the same. They are little bit higher than that reported in the literature. Li et al. [2] calculated activation energy for silica glass that it has been sintered in air and in nitrogen with the sintering temperatures of 1300ºC up to 1500ºC, was 408kJ/mol and 529kJ/mol, respectively.

Similar to any type of glass, the crystallization in silica glass occurs in two stage, nucleation and growth. As mentioned previously, the samples showed surface crystallization at 1100ºC. The most factors that determine the crystallization rate are the surface defects and crystal growth rate. The OH-group and oxygen vacancies are the most important defects in the silica glass. The higher amount of oxygen vacancies leads to restrain the crystallization of silica, which leads to increases the activation energy [2]. When the amount of oxygen vacancies are low and the sample is sintered in air, the water and oxygen molecules in air will react rapidly with oxygen vacancies on the surface of the silica which results in a decrease in the oxygen vacancies that leads to nucleation of cristobalite on the surface of silica.

The effect of OH-groups on crystallization is illustrated in the following reaction [2]:

$$\mathrm{Si-OH + SiOH \rightarrow Si-O-Si + H_2O} \qquad (5)$$

$$\mathrm{SiOH + SiH \rightarrow Si-O-Si + H_2} \qquad (6)$$

as shown in Equations 5 and 6, the result is Si-O-Si, which leads to increase the ratio of O and Si on the surface of silica particles that accelerate the crystallization. The results showed that the samples prepared by gel-casting are free from OH-groups, as shown in Figure (2), and this explains the reason for the higher value of activation energy obtained in the current study.

4. CONCLUSIONS

The kinetics of the phase transformation of silica glass samples, which were prepared by gel-casting, were studied using Avrami and rate equations. It has been found that the transformation occurs at temperature below that reported in literatures and obeys first order reaction with activation energy of 543-546kJ/mol which is higher than the reported values. The use of very fine silica nanoparticles, the removing of OH groups before the sintering, and the oxygen vacancies are expected reasons behind these values.

5. ACKNOWLEDGMENTS

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