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PREPARATION OF AMORPHOUS SILICA GLASS DOPED WITH IRON BY SPARK PLASMA SINTERING AND THE INVESTIGATION OF IT' S STRUCTURAL PROPERTIES

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ABSTRACT

In this project, silica glass doped with 1, 2 and 3 wt% iron was preparedby spark plasma sintering method. In this way, a solution with different percentages of trivalent iron chloride was prepared in water and Tetraethyl orthosilicate was added to it. After 1 hour, an integratedcell wasobtained thatwas converted to gelwith the addition of ammonia. After drying the gel at 70 ° C for 24 hours, Xerogel powder was sintered at the condition of 1200 ° C and pressure of 20 MPa by spark plasma method and silica glass was prepared. X-ray diffraction pattern of the sample is indicative of absence of crystalline phase in the samples. The results show that with the increase of iron percent, glass density decreases while grain size and porosity increase.

Keywords: Silica Glass, The Spark Plasma Sintering, Xerogel

INTRODUCTION

Transparent silica glass has characteristics such as low thermal expansion coefficient, low electrical conductivity, high chemical resistance and so on. Usually transparent silica glass is prepared by melting at high temperatures [1] For this purpose, various methods such as sol-gel process, vapor phase deposition, casting tape, etc. are used. Among the various compounds studied in the synthesis of sol-gel, silicate systems due to the availability of silicon with its medium reactivity have attracted the most attention. Hydrolysis and polycondensation of tetraethoxysilane leads to a silica gel, which can be converted into silica glass at fairly low temperatures without melting. The process is highly regarded to develop glass that their production through conventional vapor phase is difficult. Since the wet gel derived from a sol-gel process can be

broken easily during drying, the obtaining dried gel with proper integration as precursors of silica glass is difficult [2].

Gels made from organic alkoxysilane are soft and hydrophobic and may be used as precursors for integrated silica glass [3]. When alkoxy silicon is hydrolyzedin the presence of acidic catalysts, relatively flexible siloxane polymer with low fractal dimensions are formed,resulting in a compact and relatively transparent silica gel with low pore size that can be sintered at a temperature lower than the gel with larger pores .Usually slow drying is used to avoid shrinkage during drying and reducing stress fracture heterogeneous [4]. Since the sintering temperature of silica glass is relatively high, nanoparticle growth and their interactions with the host glass often increases and leads to the deterioration of transparency.Using glass with low melting temperatures can prevent this problem [5].

EXPERIMENTAL METHOD

The aim of this project is the preparation of the silica glass doped with iron by spark plasma sintering method. Therefore, the raw material composition and the glass powder are prepared using the sol-gel method.

Materials

Tetraethyl ortho silicate (Si (C2H5O) 4), iron chloride III (FeCl3), an aqueous solution of ammonia (NH4OH), nitric acid (HNO3) from Merck, Germany

Test Description

In this project a strategy is used to phase separation at the macroscopic scale. The method involves two-stage mixing alkoxide and water. According to the values in Table 1, in the first stage, tetraethyl Ortho silicate is partially hydrolyzed in the presence of a small amount of acid catalyst (nitric acid). Addition of iron chloride is helpful because of its acidic nature. In order to prevent further alkoxide hydrolysis, pH of the solution was increased by adding an aqueous solution of ammonia. pH control to neutralize the solution with an aqueous solution of ammonia (which has less basity) is more easier compared with a strong base. Increasing pH facilitates the polycondensation of Silica Oligomer that will lead to a macroscopic phase separation and gelation process. In this time, iron hydrate is precipitated and is trapped inside the gel network. Finally the aqueous gel (hydrogel) was obtained at 80 ° C and dried for 3 h and xerogel silica powder containing iron was prepared.

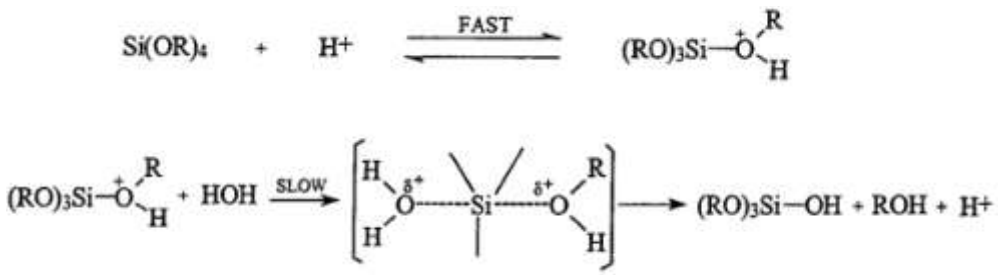
Table 1: The composition of samples containing different percentages of Fe (mole)

Component	Solution 1				Solution 2	
	Tetraethyl ortho silicate	Iron chloride	Nitric acid	Water	Ammonium	Water
0% Fe	1	0	0.002	5	0.02	5
1 % Fe	1	0.018	0.002	5	0.02	5
2% Fe	1	0.036	0.002	5	0.02	5
3% Fe	1	0.054	0.002	5	0.02	5

To prepare silica glass doped with iron, first a sufficient temperature and required time must be determined for this process. Therefore, obtained powder Xerogel was sintered by the process of the spark plasma. In this way, the graphite bar was filled with 6 grams of Xerogel. After manual pressing and placing the rods, the device was putted into the device. By turning on the machine, a pressure of 10 MPa is applied to the powder. Then the device was vacuumed. Temperature device can be controlled by changing the amperage of the device .

RESULTS AND DISCUSSION

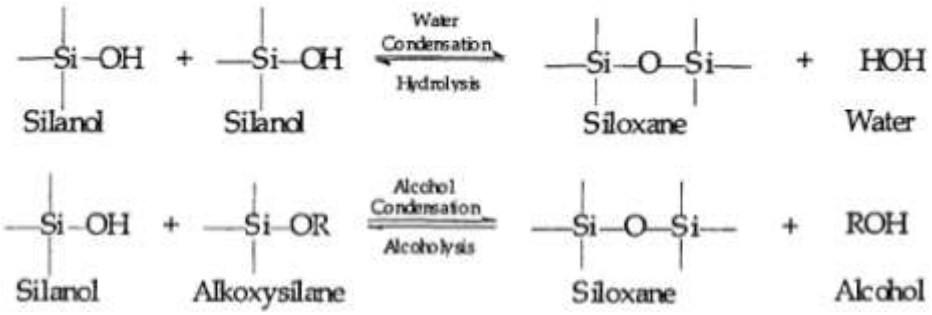
The reactions during the process of hydrolysis and polymerization of Tetraethyl orthosilicate schematically was shown in **Equation 1**.



(1)

As can be seen in the **Figure 1**, the hydrolysis reaction in the presence of positive protons (H +) is due to the acid dissolution in water and the replacement of ethyl (OR-) groups attached to silicon with hydroxide (OH-) of water. This process occurs for all ethyl groups. The rate of the reaction increases with acid increase. Since Tetraethyl orthosilicate is insoluble in water (a mixture of non-emulsified form) (**Figure 1**), when a homogeneous solution is obtained, it means that the hydrolysis reaction is completed. In order to perform the polymerization, reaction of 2 and 3must occurs by adding an alkali solution (ammonia).

Figure 1: (left) non-dissolving (right) Tetraethyl orthosilicate in water containing iron chloride



(2)

(3)

Figure 3 shows Tetraethyl orthosilicate polymerization process in the presence of water (a) and alcohol (b). Adding an alkali solution increase the polymerization rate. As can be seen, this process leads to the formation of silica gel network (**Figure 2**), which xerogel silica powder can be produced after drying.

Figure 2: wet silica gel containing 3-valent iron

(4)

The process of adding iron chloride in water is anexothermic decomposition reaction of acid salt and 3-valent iron ions will created in the solution.

According Lopez et al studies, when the primary cell comprising a transition metal, the final structural and electronic properties will change due to the reorganization of the network of silica gel around the transition metal.Previous studies suggest that a part of the metal is connected to the silica network until saturation and forms the network structure of Si-O-Fe-O-Si and is maintained at temperatures up to 1000°C. The rest is deposited on a solid surface where heavily involved with the hydroxyl groups (**Figure 3**). In addition, the metal has a catalytic effect on the compression stroke which is obvious in the rate of polymerization.Gelation time also decreases compared to pureTetra-ortho-silicate [6]. The required time for hydrolysis and gelation of samples with different iron percentages isshown in **Table 2**.

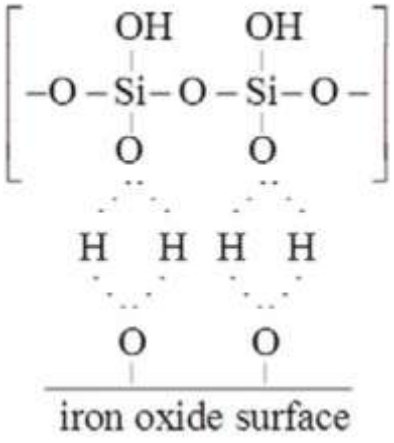


Figure 3: Reaction ofdeposited iron in silica gel structure [7]

With increasing pH, 3-valent iron converts to ferric hydroxide particles according to equation

$$Fe^{3+}_{(aq)} + 3OH^{-}_{(aq)} \rightarrow Fe(OH)_{3(s)} \downarrow (5)$$

This compound reacts with the iron in the silica network at high temperatures and forms magnetite [8].

$$3Fe(OH)_3 + e^- \xrightarrow{O_2} Fe_3O_4 + H_2O + OH^- \quad (6)$$

Table 2: hydrolysis and gelation times for different compound of prepared glass

Wt% of Iron oxide	Hydrolysis time (min)	Gelation time (min)
0	**75**	**27**
1	**68**	**35**
2	**64**	**33**
3	**60**	**32**

As can be seen, hydrolysis time is reduced with increasing iron content in Tetraethyl orthosilicate in water solution.This is because the solution is more acidic.Since the acidic facilitates and accelerates hydrolysis process, the increase of iron means increasing chloride salts and the reduction of pH of the solution and also an increase in the gelation time and thereafter its reduction. This can be attributed to the conflict between alkali property of solution and the structure of the catalytic effect of iron ions.Due to the constant addition of ammonia solution (0.02% molar), sodium chloride added to supply iron, reduces the alkali property of solution that this issue has less impact compared to the catalytic effect of iron ions in the following.

X-ray diffraction analysis

Figure 4 shows the powder X-ray diffraction analysis of Xerogel silica before heat treatment. As can be seen in the figure, a broad peak in the range of 20-30 degrees is clear that is related to the amorphous silica.

Figure 5 shows X-ray diffraction of the silica glass samples.As can be seen in the figure ,a broad peak in the range of 17-27 °

C is obvious that is related to the amorphous silica. Fused quartz sample does not show any other characteristic peakthat is due to the lack of silicon crystallization in glass making and cooling temperatures.

Figure 6 shows X-ray diffraction analysis of silica glass samples containing 1 (a), 2 (b) and 3 (c) percentage of iron. As seen in the figure, the samples did not show the characteristic peak as silica glass. This can be attributed to the weakness of the X-ray machine that despite the low scan rate has not the ability to identify compounds with low percentages.

Microstructural study

Scanning electron micrograph of dried silica gel is shown in **Figure 7 .**

As can be seen in the images, the average grain size is about 200-300 nm. Scanning electron microscope images of fracture surfaces of glass samples are shown in **Figures 7 to 11**.

As can be seen in the images, adding iron (**Figure 8**) to Fused quartz (**Figure 7**) causes the smaller grain size. Due to the lack of microscope systems investigations in the literature, it can be contributedto the place of germination phase in the presence of the iron. But with increasing iron content, grain size for the silica glass containing 3% iron (**Figure 11**) has grown compared with silica glass containing 2% iron (**Figure 10**) that this can be attributed to increased acidity in primary cell in respect to increased percent of iron.

Simultaneous thermal analysis

To study the thermal behavior of the gel at different temperatures and also the conversion temperature of the glass, Simultaneous thermal analysis was performed on Xerogel silica powder samples containing 1 wt% Fe for temperature up to 1200 ° C (**Figure 12**). Because of the low doped element, no need was felt to check other compounds. As seen in the **Figure 12**, an endothermic peak is observed at around 100-200 ° C with severe weight loss in the structure of the sample that could be related to the release of water.

In the following, the obvious change was not observed until about 1000 ° C and at that temperature, an exothermic peak can be seen which is likely related to the glass conversion process. Gradual weight loss of samples at temperatures more than 200 ° C is due to internal changes and emersion of bands that are not hydrolyzed.This temperature is considered as the first criterion for the plasma sintering process.

The spark plasma sintering process

The most important part of the study is the glass preparation using the spark plasma sintering method. Finding the right temperature and holding time on the critical temperatures are the requirements for this process. The critical temperatures are in the

range of 200°C i.e. temperature of the water emission and the critical temperature of glass conversion. To avoid stress in these two parts, the temperature is changed with controlled rate. Length Change insintered xerogel powder containing 0% Fe in respect to a temperature up to 1200°C is shown in **Figure 13**.

As can be seen in **Figure 3**, three ranges are in a recognizable form. The first zone is below 100 C. In this range due to the removal of structural water and the pressure at the same time reduces the height reduction of the segment (increasing the height) is observed. Gas emersion from the sample is traceable with vacuum break. So that the change in temperature of about 100 ° C for 7 min, height powder decreases about 4 mm. The other range is related to the relatively stable situation of the powder. In the range of 200-800 ° C, the powder does not actually changes while at 600 ° C for 1 min, only about 2 mm reduction in height is observed. After this process, we entered the final stage. According to test results the powder was heated up to temperatures of 1035 ° C and was maintained at this temperature for about 8 minutes. As can be seen in the figure,no change in the height is observed at 1000ºC with a constant temperature. By shutting down and cooling the sample, no change in state transformation was observed.

With respect to failure in glass making before, some change including changes in the applied pressure to the sample, the maximum temperature and shelf-life were applied to improve conditions and process according to following diagram in **Figure 14**.

As seen in the **Figure 14**, arrangements required for the passage of the gas already has been done as past sample . Changes in this sample compared with the previous sample can be seen in the temperature range of 950 ° C . At this temperature, the applied pressure was increased from 10 to 20 MPa, which is a breakthrough moment in the record chart. Next, the sample was heated to a temperature of 1200 ° C . Another important point in this process is the height change of the sample at a temperature of 1200°C without increasing temperature. This phenomenon can be attributed to glassy statetransition that leads to rearrangement of the particles and reduction of the height of the sample without increasing the temperature. According to this chart, the transformation temperature was determined 1200 ° C and at a maximum shelf life was considered 15 minutes .

Density and Porosity

Glass density curve in terms of the amount of containing iron is plotted in **Figure 15**. As seen in the figure, the density not

follows a clear trend in respect to Fe. To examine the case, open porosity were also checked and its graph is plotted in **Figure 16**.

As the **Figure 16** shows, the open porosity of the samples is in the range 6.5-7.5. Therefore, the density reduction can be attributed to impurities added to the glass during the process.Due to extensive use of Graphite, some of it was likely poured into the sample that is observable as small black spots in the samples.

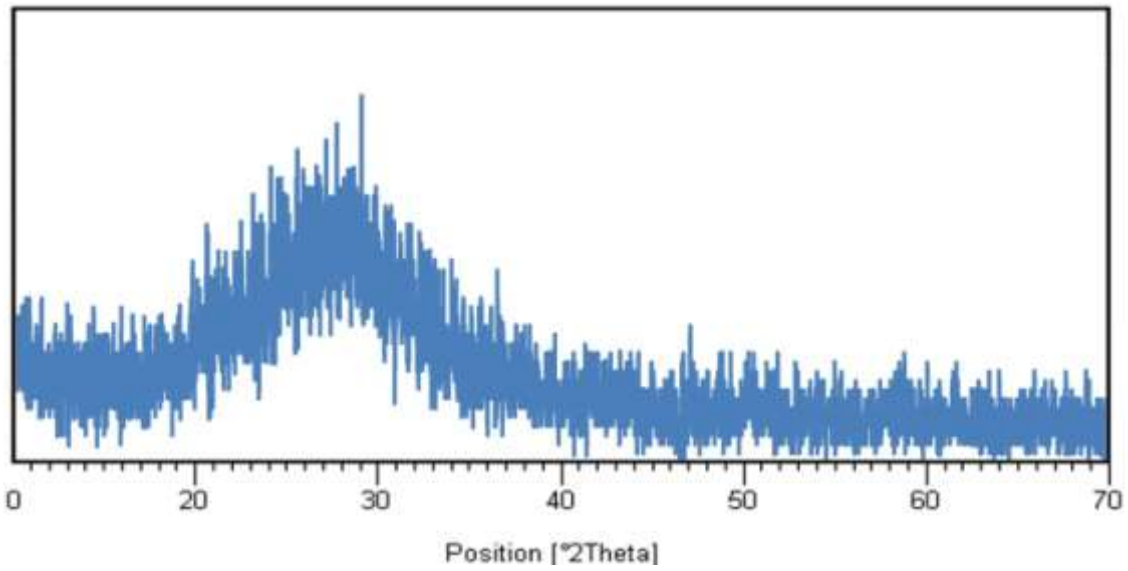


Figure 4: X-ray diffraction analysis of xerogel silica before heat treatment

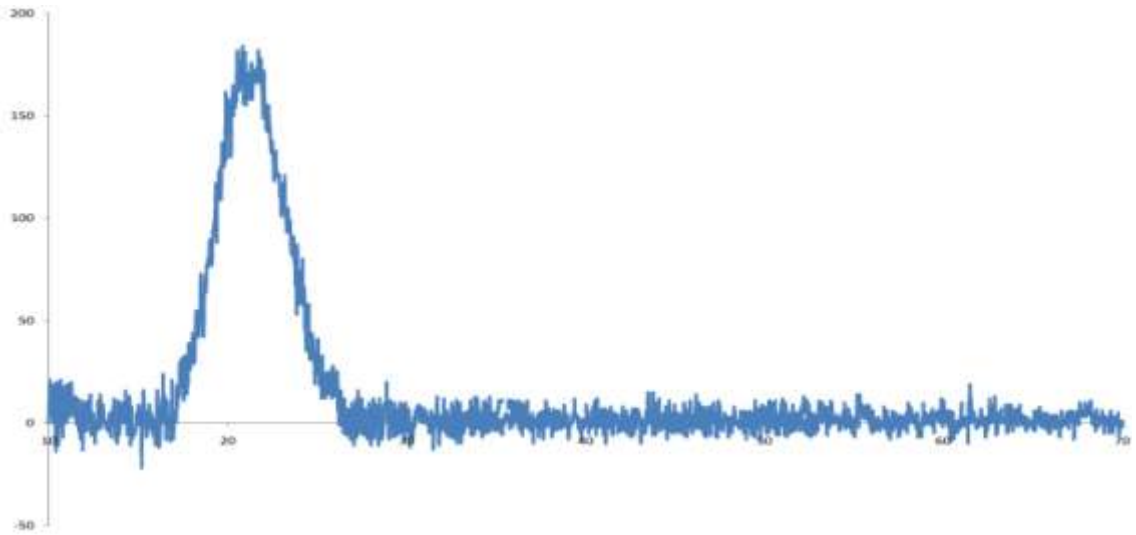


Figure 5: X-ray diffraction analysis of silica glass

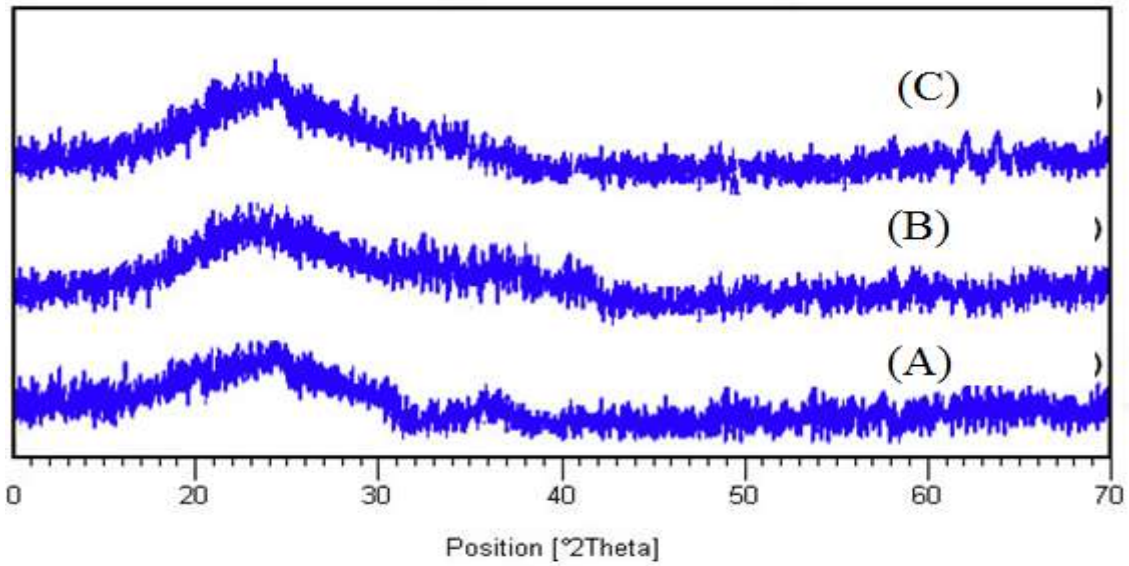


Figure 6: X-ray diffraction analysis of melted silica glass containing (a) 1, (b) 2 (c) 3 wt% iron

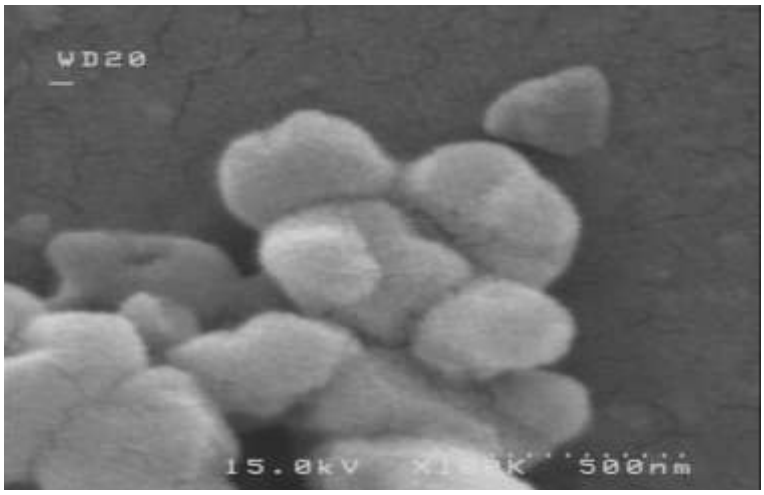


Figure 7: Scanning electron microscope image of silica powder Xerogel.

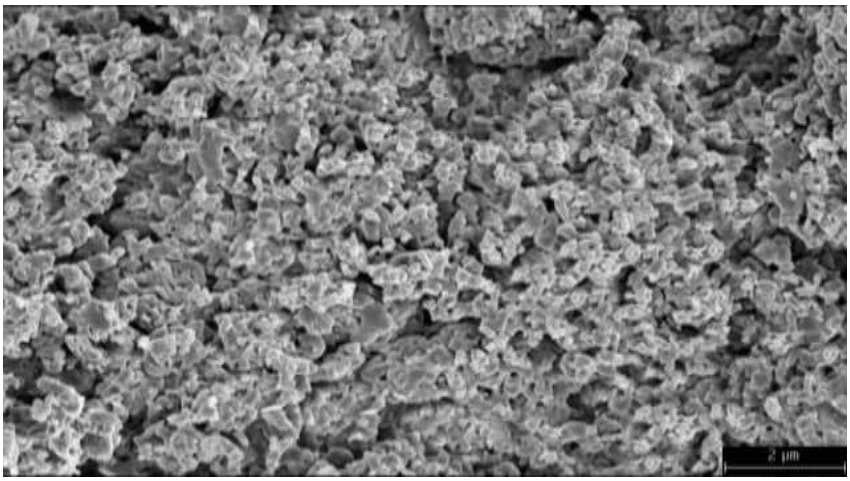


Figure 8: Scanning electron microscope image of silica glass

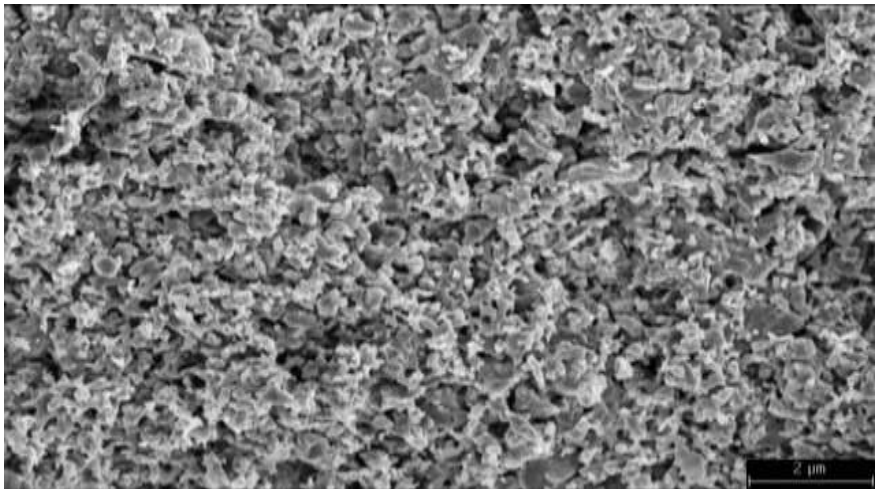


Figure 9: Scanning electron microscope image of silica glass containing 1% iron

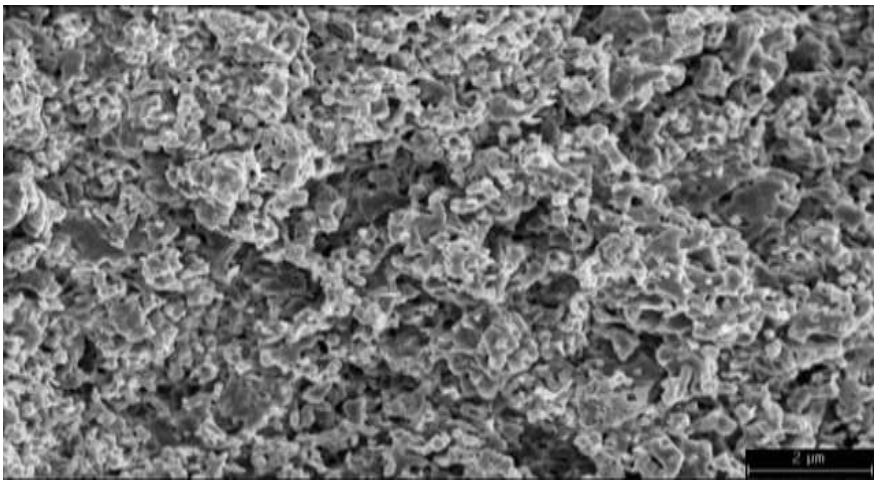


Figure 10: Scanning electron microscope image of silica glass containing 2% iron

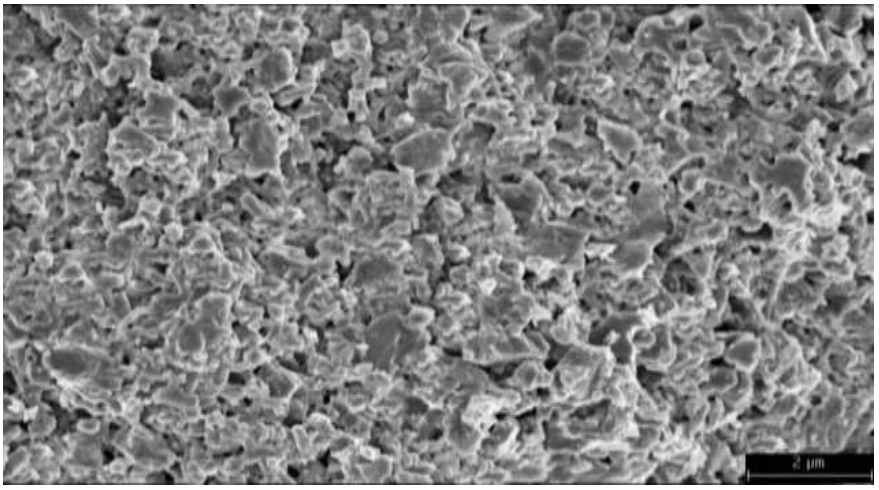


Figure 11: Scanning electron microscope image of silica glass containing 3% iron

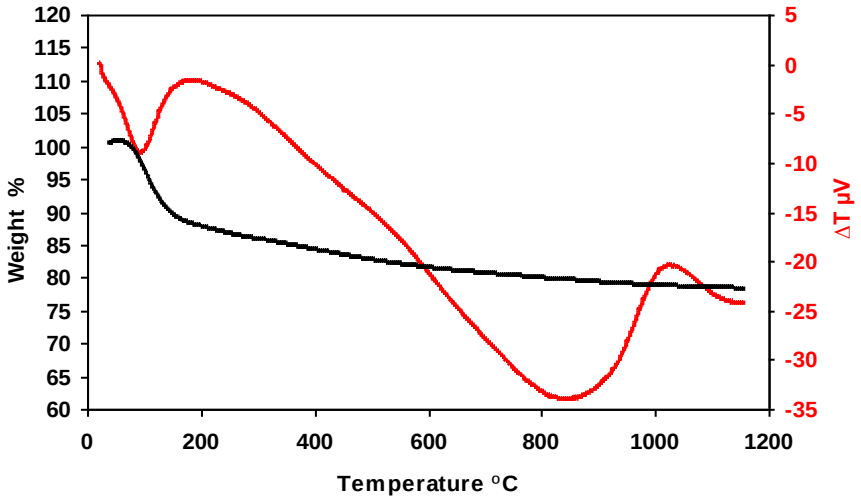


Figure 12: Simultaneous Thermal Analysis of xerogel powder containing 1% iron

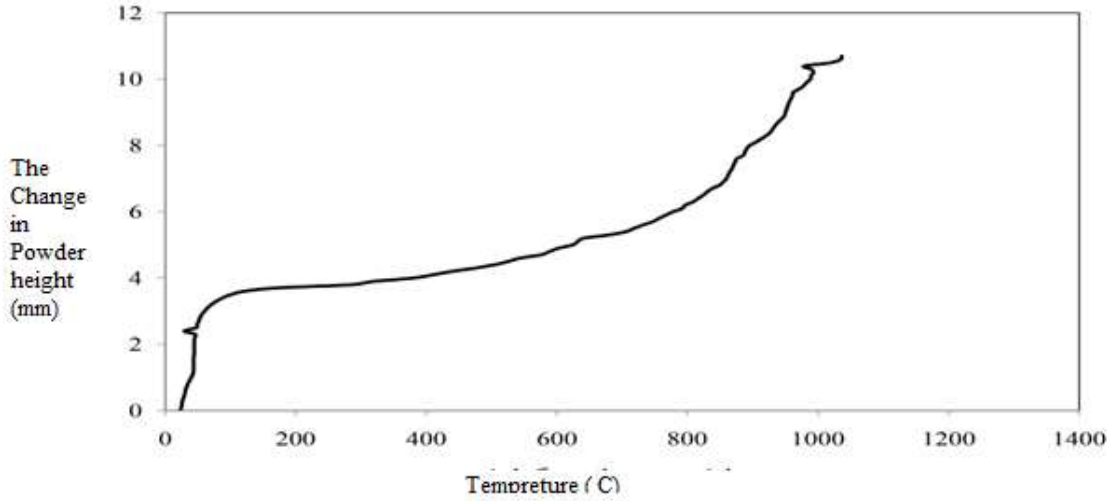


Figure 13: Changes in the height of the powder for powder containing 0% iron temperature up to 1000 °C

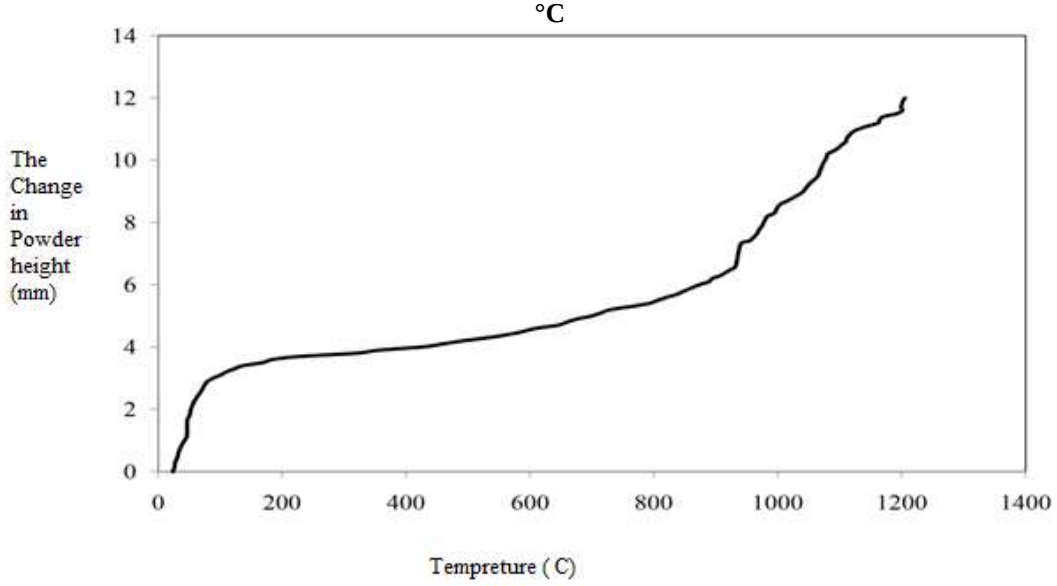


Figure 14: Changes in the height of the powder temperature up to 1200 ° Cfor powder containing 0% iron

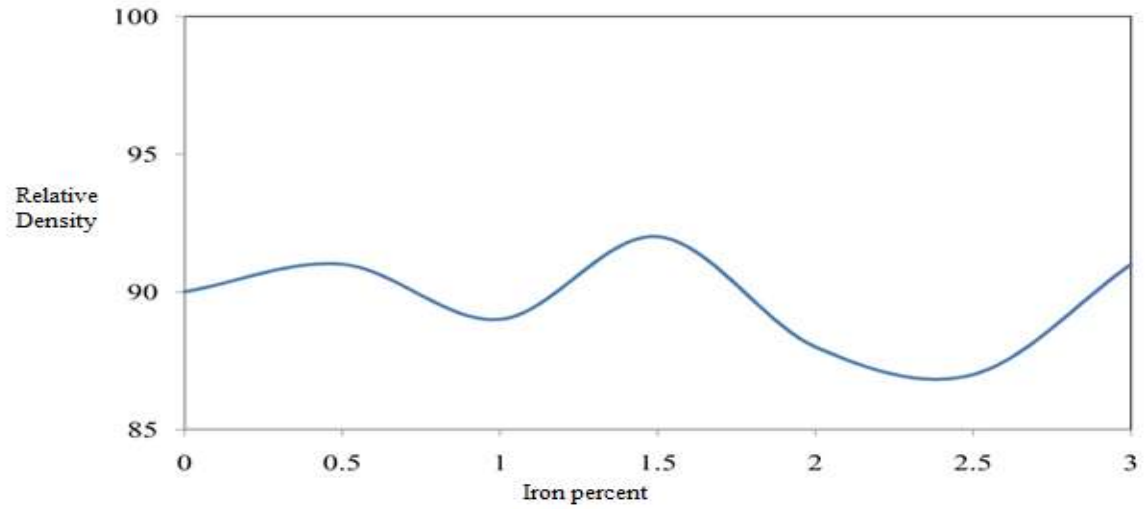


Figure 15: relative density of glass in respect to the iron content

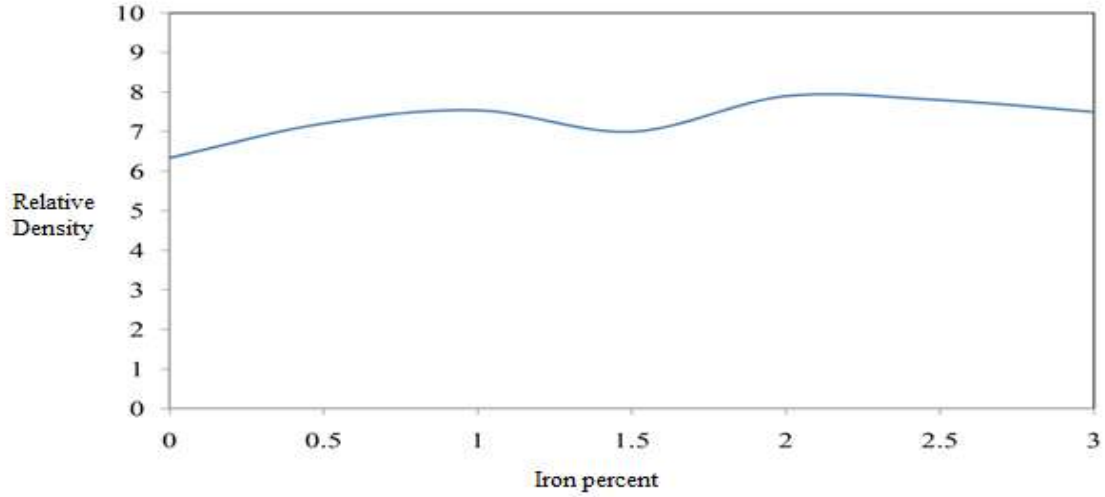


Figure 16: The percentage of open porosity glass in respect to the iron content

CONCLUSION

In this project, silica glass doped with 1, 2 and 3 wt% iron, was prepared by spark plasma sintering method. Iron chloride addition to Tetraethyl orthosilicate accelerates the hydrolysis process and delays the process of gelation. In X-ray diffraction spectrum, a broad peak was observed that is related the amorphous silica and silica glass sample does not show any other characteristic peak that is due to the lack of silicon crystallization in glass temperature and cooling time. With the addition of iron, the grain size is increased that is shown in the electron micrograph. It also reduces the density of glass and increases the percentage of open porosity.

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