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THE INFLUENCE OF pH AND UV VISIBLE ABSORBTION ON HYDROLYSIS STAGE AND GEL BEHAVIOR OF GLASSES SYNTHESIZED BY SOL-GEL

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Abstract: *Lead-containing glass borosilicate was synthesized by Sol-gel technique using metalalkoxids such as tetraethyleorthosilicate (TEOS), Al-sec-butoxide and trimethyl borate. The sol containing TEOS converts to gel during drop wise addition of Al-alkoxide while inorganic lead salt was added in the last stage of gelation to prepare the alcogels. The specimens were dried at room temperature to set then heated at 600°C quickly to avoid crystallization preparing a glass containing 63 wt% lead oxide. The influence of pH on absorption behavior of the sols studied by UV visible technique so the characteristic of the gel, alcogel and xerogel were studied in the different acidic concentrations. The UV spectrums show that the higher the acidity of the hydrolysis stages, the higher the absorbance. The results showed the sample with 63 wt% lead was found fully amorphous. Microstructure and phase analysis of the glass powders were investigated by X-ray diffraction (XRD), X-ray fluorescence (XRF) and scanning electron microscopy (SEM) equipped with EDS analysis.*

Keywords: *Sol Gel, Lead Glass, Uv-Vis.*

1. INTRODUCTION

Production of a new generation of materials calls for the development of new technologies that would make it possible to manufacture high-quality materials with decreased energy consumption. The properties of ceramic and glass materials can not be improved significantly by using traditional methods. The reason is that material properties are determined by heterogeneities of their structure and chemical composition and the content of undesirable impurities. In this context researchers in all leading industrial countries have tried to develop new methods making it possible to produce single-fraction glasses and ceramics that are homogeneous in chemical, phase composition and structure with sub-micron particles. One of these methods is sol -gel[1]. Sol -gel processing, which is a wet chemical route for preparing glass and ceramic compositions, in different synthesis conditions has been used to obtain compounds from amorphous precursors. This approach led to good results in terms of lower grain size, higher reaction yield and a reduction in the sintering temperature of the resulting glasses and ceramics. The results were mainly due to the fact that, for the sol_ gel processes, the chemical reactions take place in solution, which offers mixing at the molecular level [2].

This process constitutes an important part of so-called "soft chemistry" [3] and produces a variety of inorganic networks from silicon or metal alkoxide monomer precursors [4]. The history of that dates back to the 1950s is being actively studied in leading laboratories all over the world; in the last decade the number of scientific publications in this field shows an exponential increase. The emergence of the sol-gel science was at first very progressive, and curiously enough, the different initial motivations were of a practical, if not technical, nature [5]. Also sol-gel chemistry has recently evolved in a general and powerful approach for preparing inorganic materials. This method typically entails hydrolysis of a solution of a precursor's molecule to obtain first a suspension of colloidal particles (the sol) and then a gel composed of aggregated sol particles. The gel is then thermally treated to yield the desired material [6]. The sol-gel technique is attractive because it can provide high purity, compositional homogeneity, low- temperature processing, and ease of formation for monoliths and coatings. The products of these studies were mostly powders or monoliths pressed from the sol-gel dried powders [7]. As it was mentioned in sol-gel method, which is based on the hydrolysis and condensation of molecular precursors, such as metal alkoxides, the major problem is to control the reaction rates which are generally too fast, resulting in loss of microstructural control over the final oxidematerial [8]. So the present work is mainly discussing on the preparation of the lead and alumino-brosilicate glass and the main advantage of the target is low temperature glass production. Also the behavior of sol with the different absorbance, effect of pH condition on gel behavior and the microstructural analysis are investigated.

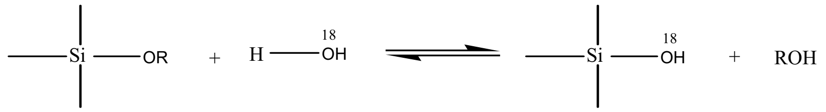
2. EXPERIMENTAL

Silicon tetraethylorthosilicate (TEOS $Si(OC_2H_5)_4$ (98%Aldrich) as SiO_2 source, aluminum tri-sec-butylate Al $(OC_2H_9)_3$ (97%Aldrich) as Al_2O_3 source and trimethyl borate B $(OCH_3)_3$ (98%Aldrich) as BO_3 source were used as the precursors. solvents and catalyst for preparing the sols were absolute ethanol (EtOH), water and HCl 0.1 molar (Merck) respectively. Aluminum alkoxide is very reactive, so special care was paid to prepare the ternary gel [9]. First an alumino-borosilicate (ABS) glass was made by sol-gel process during the experiments. The hydrolysis stage contains addition of: 36.6 ml ethyl alcohol, 24.2 ml TEOS, 2.5 ml H_2O, and 0.1 ml HCl (as the catalyst). Then 5.3 gr. Al-sec-butoxide was solved in 5.52 ml propanol separately. It should be considered that propanol was added to the Al-sec-butoxide rapidly to prevent the Al-sec-butoxide gel from drying; otherwise the clear solution would not appear. After a 15-minute stirring, the clear solution containing Al-sec-butoxide was added drop wise and slowly into the beaker containing hydrolysis solution. The mixture was stirred vigorously to prevent alumina gel formation in the mixture. Then 1.3 ml H_2O, 10.4 ml $B(OR)_3$, 7.7 ml H_2O, 2.4 ml CH_3COOH, 14.75 ml $Na(CH_3COO)(2M)$, 7.7 ml H_2O, and 3.2 ml $Ba(CH_3COO)_2(1M)$ were added to the solution. After adding the last component, condensation started and a colloidal mixture was formed that needed to be stirred for one hour. The alcogel was aged for one week with a cover. Lead acetate was used in preparation of the lead containing samples. Different concentrations of inorganic lead salt solutions were added into the network by removing partial amounts of other components. Also a high lead content (63 wt %) glass sample (LG63) was prepared, the alcogels were kept in the ordinary stages to dry, and the xerogel was heated at 600°C (12°C/min). Heating and cooling should be fast (about 10°C per minute) to prevent crystallization. The Uv _Vis spectrums were taken by Camspec-M330 spectrometer using biradiation technique in this work. The pH meter for adjusting acidity was Parking Elmer 744. Blank samples were prepared using water, alcohol and acid in different acidic concentrations and were adjusted with instrument and then the absorbance of TEOS containing sol was measured after adding that to the blank for each sample. This stage was carried out for the pH: 1.5, 2, 3, and 4. Phase analysis of the samples was carried out using X-ray diffraction, Jeol JDX_8030 X-Ray diffractometer (Cu -K_α radiation) in the range of 5 to 80° with step size of 0.02. Also quantitative analysis of the samples was carried out using XRF technique by PM 1480 Philips.

Microstructural analysis was done using scanning electron microscopy, Cam Scan MV 2300, coupled with energy dispersive spectroscopy (SEM-EDS). For (SEM-EDS) analyses the samples were coated with gold.

3. RESULTS AND DISCUSSION

Three reactions are generally used to describe the sol-gel process at the functional group level: hydrolysis, alcohol and water condensation. The hydrolysis stage is similar in all of the samples which transparent and colorless solutions were formed. The hydrolysis occurs by the nucleophilic attack of the oxygen atom of water into the silicon atom as evidenced by the reaction of isotopically labeled water with TEOS. (reaction1) It causes producing of unlabelled oxygen atom in alcohol molecule; so, in the reaction of isotopic water with TEOS it was noticed that the alcohol atom in the reaction with acidic catalysts was nonisotopic [4]. This fact means that only water molecule reacts with TEOS.



(1)

Absorbance study related to the hydrolysis reactions was carried out for acidic samples with different acid concentrations. The effect of pH on UV-absorbance of the TEOS sol was shown in Fig. 1. Decreasing pH leads to increase in absorbance.

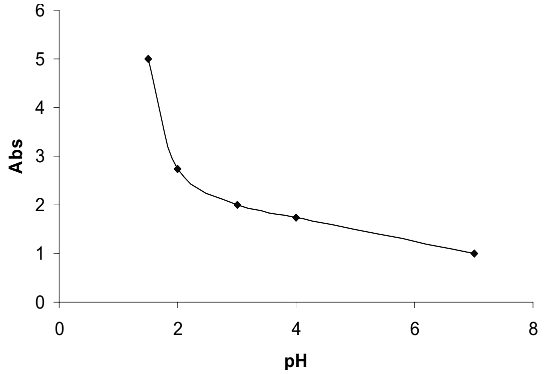
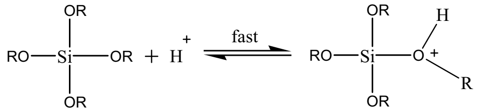
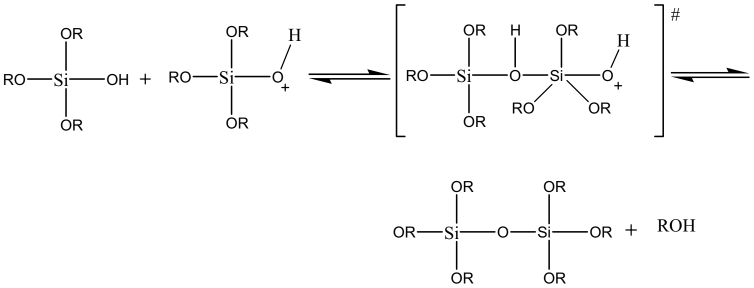


Fig. 1. The absorbance vs pH.

Due to the fact that the blank sample was separately adjusted with the spectrophotometer in any measurement of the pH, so the observed increasing of that absorbance that UV-Vis determinates is related to producing of more products on the right side of the reaction.1. On the other hand in higher acidic states the reaction leads to the right side so the higher absorbance can be related to the larger amount of the product containing Si and it means that the hydrolysis has completely taken place. As it noticed the introduction of water to the system initiates hydrolysis. In acidic solution the mechanism is nucleophilic substitution (SN_2) reaction, characterized by the pentacoordinate transition state of Si. Then the relatively high electro negativity of Si weakens the O-H bonds to the extent and condensation can occur (reactions 2a and 2b) [10].



(2 a)



(2 b)

By adding the other materials, the gelatin started and it was done until the completion of the process cycle. However, the characteristics and properties of a particular sol-gel inorganic network are_related to a number of factors that affect the rate of hydrolysis and condensation reactions, such as pH, temperature and time of reaction, reagent concentrations, catalyst nature and concentration, H_2O/Si molar ratio(R), aging temperature and time of drying [11]. Although sol-gel can occur without addition of any external catalyst, the reactions are most rapid and complete when the catalyst is employed. Mineral acids (HCl) and ammonia are most generally used, however; other catalysts are acetic acid, KOH, amines, KF, and HF. Additionally, it has been observed that the rate and the extent of the hydrolysis reaction is most influenced by the strength and concentration of the acid or base catalyst [3]. So the prepared gels have different appearances in the higher or lower acidic conditions. The influence of pH on the gelation time is given in Fig. 2. As it is shown, by increasing HCl, the pH of the solution decreased, leading to longer gelation time while the lowest gelation time (t=10 min) occurred at pH 6.5. The shrinkage was occurred after ageing for one week then the shrink xerogel was made.

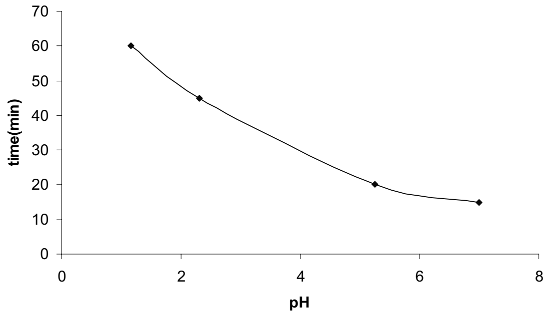


Fig. 2. Gelation time (min) as a function of pH during sol-gel process.

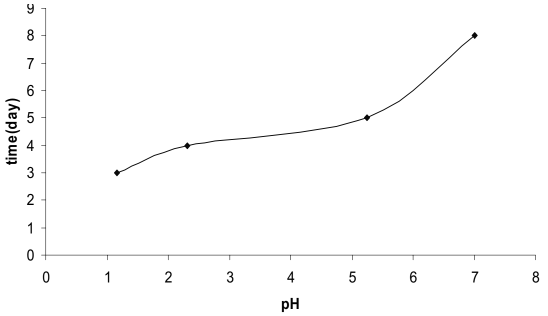


Fig. 3. Transformation of alcogel to xerogel, the shrinkage time (day) as a function of pH for a series of ABS glasses prepared under similar gelation conditions (temperature and H_2O content) by the sol-gel process.

Fig. 3. shows the shrinkage time due to pH which depends on the environmental pH in such a way that adding more acid lowers the shrinkage time to the minimum (3 days). Also, the higher rate of shrinkage time can be observed in less than pH 6. Shrinkage generally is dependent on both thermodynamic and kinetic of the gelling process while it is relatively independent of oxide composition. Subsequently the final xerogels have different morphologies in the different acidic conditions. In lower amount of acid concentration the resulted xerogel was chalk like and in higher amount of acid it was puffy and with lower density. In the neutral condition the structure of xerogel is between chalklike and puffy. (Fig. 4) Phase analysis of the samples heated at 600 ºC was investigated by XRD. Patterns of the samples are presented in Figs. 5 and 6. (corresponding to the ABS glass and LG63 respectively). XRD patterns of ABS and Lead glass exhibit the characteristics of the amorphous state. Chemical composition of the ABS and LG63 samples by X-ray fluorescence (XRF), are presented in Table 1 and 2 respectively.

Fig. 4. The xerogel morphology in different acid concentrations. Higher amount (right side) neutral condition (center), and lower amount of acid (left side).

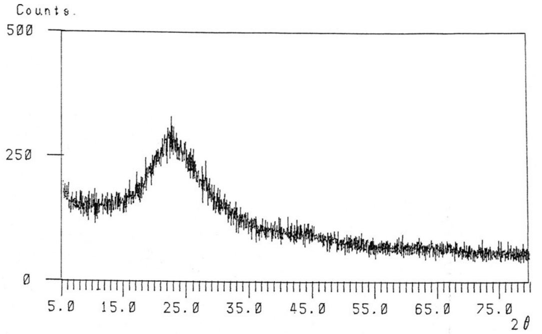


Fig. 5. XRD pattern of ABS sample heated at 600°C.

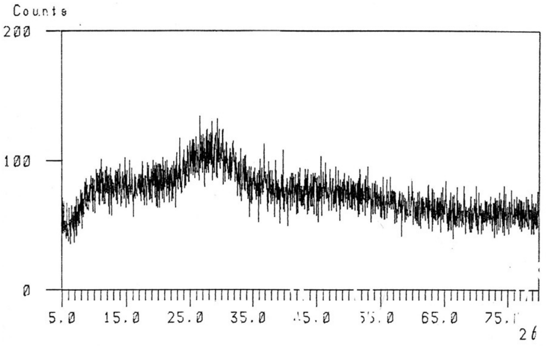


Fig. 6. XRD pattern of sample LG63.

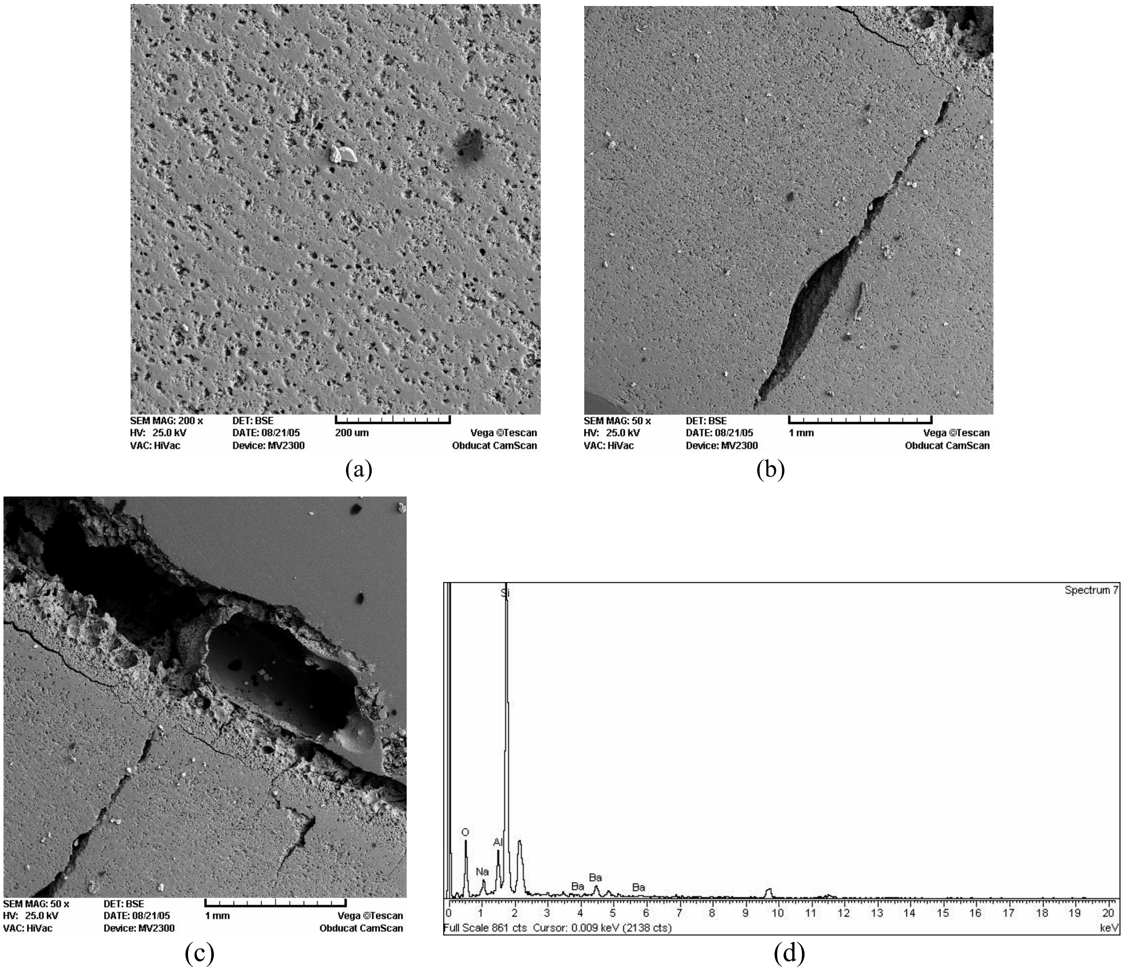
Table 1. Chemical composition of ABS Glass by XRF.

Composition	wt %
SiO_2	55.8
Al_2O_3	8.0
Na_2O	4.02
MgO	0.087
CaO	0.050
PbO	0.015
K_2O	0.0014
V_2O_5	0.0013
Co_3O_4	0.0088
Fe_2O_3	0.0064
P_2O_5	0.0036
CuO	0.0026
SrO	0.0020
ZrO	0.0011

Table 2. Chemical composition of LG63 by XRF.

Composition wt%	
PbO	63.1
SiO_2	33.7
Al_2O_3	0.92
Na_2O	0.68
MgO	0.30
MoO_3	0.14
CaO	0.106
CuO	0.037
Y_2O_3	0.021
Fe_2O_3	0.017
K_2O	0.009

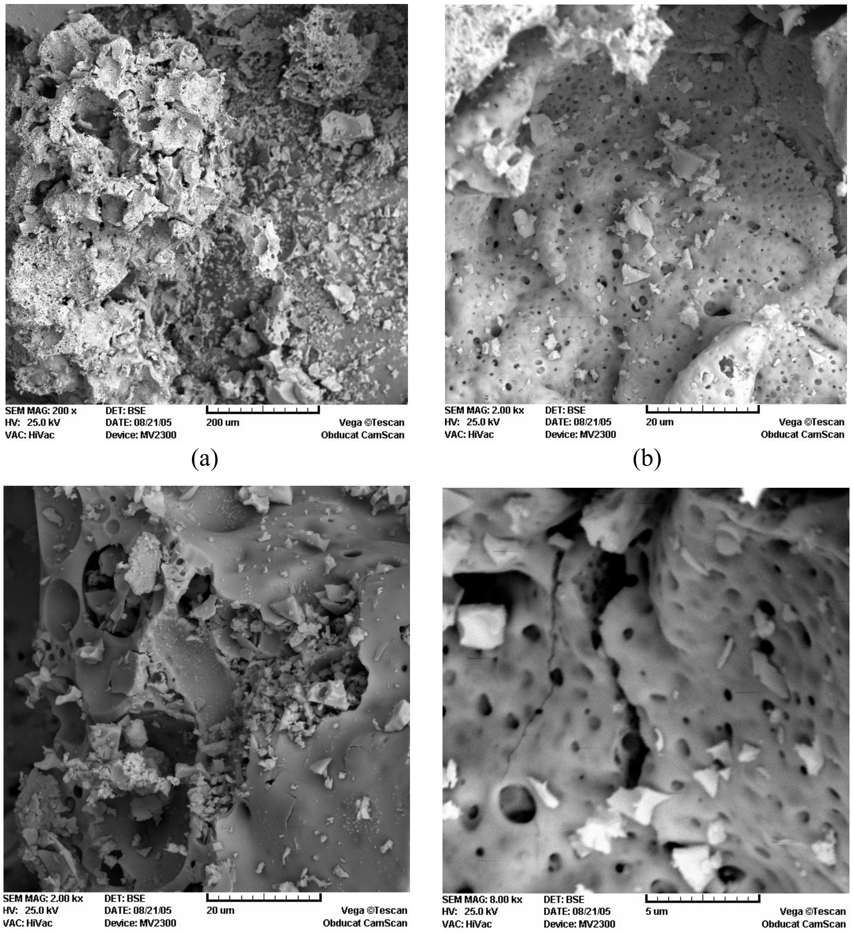
As it is shown the LG63 contains 63.1% PbO and 33.7% SiO_2 and bore is not detected by the instrument. Back scattered image of scanning electron microscopy(SEM) of the samples after heating at 600 ºC are presented in Figs. 7, 8. A porous microstructure of the ABS glass is shown in Figs. 7a, b and c. Most pores are isolated in the matrix with sizes of less than 15 μm. EDS analysis of the aluminoborosilicate sample is shown in Fig. 7d in which small amount of barium is related to the barium salt used in the sol gel process. Generally, the use of amorphous aluminosilicates in glasses necessitates the preparation of gels with narrow pore size distributions, centered on sufficiently small pore radii, and with a controlled surface charge. In addition, the gels have to be processed in a defect-free manner, with a controlled morphology. Sol-gel synthesis procedures have been claimed to produce highly uniform solids with well-defined properties as well as to allow for an easy modeling of the products, going from monoliths to glasses. On the other hand, the acid sol-gel synthesis, starting from organic and silicon and/or aluminum precursors has been widely approved in the field of glasses [12].



(a) (b)

(c) (d)

Fig. 7. SEM-images of ABS glass (a, b and c) in different magnifications and d) EDS analysis of the matrix.



(a) (b) (c) (d)

Fig. 8. SEM images of LG63 showing sponge-like microstructure with small pores.

The SEM investigations of the lead glass sample (LG63) in different magnifications showed that they are sponge-like and hollow, containing larger amount of pores (Fig. 8.). This behavior is in agreement with the absence of crystals observed in SEM images. Indeed it could be conformed to the XRD result too that LG63 is completely amorphous.

4. CONCLUSIONS

1. The samples get more colloidal and have more gelation ability at higher pH.
2. The least possible gelation time occurred in an almost neutral pH.
3. The results made by the impact of pH on shrinkage were quite opposite to that of the gelation time. More HC1 (less pH) results in a decrease in the shrinkage time.
4. The effect of pH on the absorbance showed decrease in the pH leading to increase the absorbance in the Uv_Vis spectrums.
5. The graph corresponding to the borosilicate glass showed that the X-ray pattern was completely amorphous.
6. The sample with the maximum lead content, (LG63), was fully amorphous.
7. The microstructure of the samples showed a flat porous surface in ABS glass and microstructure of the highest lead containing glass was found sponge-like containing large amount of pores.

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