

Preparation of Alkali Lead Glass and Glass – Ceramic Compositions as Electrical Insulators

Shukur Majid M., Kadhim. F. Al-Sultani and Hassan Mohammed N.
College of Materials Engineering, University of Babylon, IRAQ

Available online at: www.isca.in

(Received 19th September 2011, revised 7th October 2011, accepted 26th January 2012)

Abstract

Lead silicate glasses with three composition ratio B1, B2, and B3 of (SiO₂, Al₂O₃, Na₂O, K₂O, and PbO) were prepared in this study by conventional melt quenching technique. K₂O percentage increases in compositions B2 and B3 to improve physical and electrical properties. Also glass – ceramic of lead silicate with three composition ratio C1, C2, and C3 of (SiO₂, Al₂O₃, Na₂O, K₂O, PbO, and TiO₂) were prepared by conventional melt quenching technique as a first stage, and then converted to glass – ceramic by heat treatments of the parent glass as a first step and render nucleation and crystallization as a second step. 5 wt.% of TiO₂ is used as a nucleation agent in preparing of glass – ceramic. Physical and electrical properties for all prepared specimens were investigated; we have noted increasing of dielectric strength with increasing of sintering temperatures for glass samples, where they have maximum value at 600°C. Whereas the glass – ceramics samples have a maximum value at C3 composition. Dissipation factor for glass and glass-ceramic samples have been decreased with increasing of K₂O content at all sintering temperatures. Dielectric constant (ϵ_r) for glass samples at low frequencies has a maximum value at B1 composition and for sintering temperatures of 525 and 550 °C. At high frequencies, it has maximum value at B3 composition and for sintering temperature of 550°C. Dielectric constant (ϵ_r) for glass-ceramic samples at low frequencies has a maximum value at C1 composition, and at high frequencies it has maximum value at C3 composition.

Keywords: Glass-ceramic, electrical insulators, sintering temperatures.

Introduction

Glass-ceramics are polycrystalline materials formed by the controlled nucleation and crystallization of special formulated glasses¹. The amorphous glass article is initially formed and then thermally converted via heat treatment to a crystalline material, called a “glass-ceramic”. These glass-ceramic materials go back to their discovery by S.D. Stookey in the 1950's². Glass-ceramics are an important class of materials that have been commercially quite successful, which is characterized by the lack of porosity and ease of forming³. Alkali-lead silicate glasses are an important source of glass ceramics. Such glasses typically contain over 10% lead oxide PbO. Lead glasses containing 20-30% PbO, 54-58% SiO₂ and about 14% alkalis are highly insulating and therefore of great importance in electrical engineering⁴. The glass-ceramic of lead glasses possesses increased impact strength, hardness and thermal shock resistance compared with conventional non-crystalline glasses⁵. Glass – ceramic can also be formed by powder processing methods in which glass frits are sintered and crystallized. This procedure somewhat extends to the range of possible glass-ceramics composition. It allows for surface as well as internal nucleation⁶.

The wide variety of applications include electric range tops, wood stove windows, telescope mirrors, cooking utensils, dinner ware, building facing materials, radomes, precision

electronic ports, fluid amplifiers, ink jet printer heads, and dental prostheses. Also a new high temperature resistant glass–ceramic coating used for gas turbine engine components⁷. The production of glass ceramic type of alkali–lead silicate glasses has been attempted using various approaches. These approaches were often simple additions of different alkali oxides K₂O percentages to produce macroscopically homogeneous ceramic material which has a specific application in electrical equipments.

Material and Methods

Experimental procedure of glass samples: Three batches of lead silicate glass composition have been prepared. Table 1 shows the compositions of these batches.

Table-1
Composition of lead- silicate glasses

Oxide	B1 %wt	B2 %wt	B3 %wt
SiO ₂	63	59	55
Al ₂ O ₃	1	1	1
Na ₂ O	8	8	8
K ₂ O	6	10	14
PbO	22	22	22

The amount 300 g of batch has been selected of the compositions (B1, B2, B3) and was calculated on the basis of its percentage components. Table 1 shows that the percentage of K_2O has been changed increasingly from composition of batch B1 to composition of batch B3 to determine the extent of its impact on the melting temperature and electrical properties.

Potassium and sodium carbonates are used instead of K_2O and Na_2O respectively because they act as fluxes better than their oxides. Weight ratio was calculated by the equation of combustion of both Na_2CO_3 and K_2CO_3 , as a liberated gas of CO_2 during the melting process. Each batch according to percentage in table 1 was prepared by mixing and milling of raw materials using a ball mill. The main purpose of this step was to get a homogeneous distribution of oxides within the mixture, since uniform mixing of the batch materials is very important to facilitate the melting process and to ensure more homogeneity in any glass preparation process, where time of the mixing was 1 hr at 400 rev / min for each batch. Then the batch powder was heated in a crucible made of silicon carbide (SiC) by electrical furnace to a temperature about $1200^\circ C$ for 2 hours. It may be noted that the powder begins agglomerate and then softening at $650^\circ C$. Viscous mass of glass was obtained at $1000^\circ C$ and elevated temperature to $1200^\circ C$ was achieved to reduce viscosity of the batch. Occasionally, stirring of molten glass was done to complete homogeneity by using graphite stick and then quenched the molten glass in distilled water bath (melt - quench technique) to get the cullet of glass, The cullet was dried at $110^\circ C$ for a period of 24 hours. The quenched glass fragment are milled by electrical mill to a fine powder and then sieved to less than $45 \mu m$. Then the glass powders are analyzed using x-ray diffraction to confirm their amorphous nature. All samples are formulated by cold pressure shaping technique/cold die compacting (uniaxial pressing), using a hydraulic pressing device. The prepared powder was placed in steel die of 13 mm diameter and thickness of 4 mm, with applied pressure of 150 MPa. Every sample treated with polyvinyl alcohol (PVA) binder was heated at $350^\circ C$ for a minimum of one hour to complete the burn-off the binder. The samples were heat treated at different temperatures 450, 500, 525, 550, 575, 600, 650, and $750^\circ C$, for 1hr with a heating rate of $5^\circ C/min$. The better thermal extent of sintering temperature for all batches to obtain glass samples without any distortion was 525, 550, 575, and $600^\circ C$.

Experimental procedure of glass-ceramic samples: Glass-ceramic in this research was produced in heterogeneous nucleation. The compositions of the batches are shown in table 2. All batches are nucleated by TiO_2 agent of concentration 5 wt%. At first stage, we have manufactured glass samples for compositions C1, C2, and C3 with the same method which followed in manufacturing of glass samples for compositions B1, B2, and B3.

Table-2
Compositions of glass-ceramic samples

Oxide	C1 %wt	C2 %wt	C3 %wt
TiO_2	5	5	5
SiO_2	60	56	52
Al_2O_3	1	1	1
Na_2O	8	8	8
K_2O	6	10	14
PbO	20	20	20

The glass samples should be adjusted and controlled by heat treatment schedule in order to promote the process of crystallization and conversion to the glass-ceramic. This regime is first included the nucleation step, which was done for all the glass samples by conventional heating in an electric furnace. Crystallization step is followed by the conventional heating process. In such two-stages of heat-treatments, the low-and-high temperatures are designated as the nucleation and the crystallization treatments respectively. The glass samples were heated to the nucleation temperature of ($350^\circ C$, 3 hours ramp) in an electric furnace, and held for a certain period of time (3 hours). After such nucleation, the nucleated glass disk was crystallized by other stage, in which the nucleated glass samples were heated above to the crystallization temperature $550^\circ C$ and 3 hour ramp) in order to grow the formed nuclei as crystals and hence to convert the glass into glass – ceramic material.

Results and Discussion

Result of X-Ray Diffraction Analysis: Glass: Figure 1 shows the XRD patterns for lead silicate glasses of the batches B1, B2 and B3 respectively. This figure indicates that the prepared glasses were quenched successfully and an amorphous structures was achieved, where the glass powder (or samples) are basically composed of amorphous glassy phase and there are no crystalline phases. Such observation led to suggestion that these glasses are composed of assemblages of very small crystals, termed crystallite. It is well established that measurable broadening of X- ray diffraction peaks occurs for particle sizes or grain sizes smaller than 0.1 micron. So, the broadening increases linearly with decreasing particle size⁸.

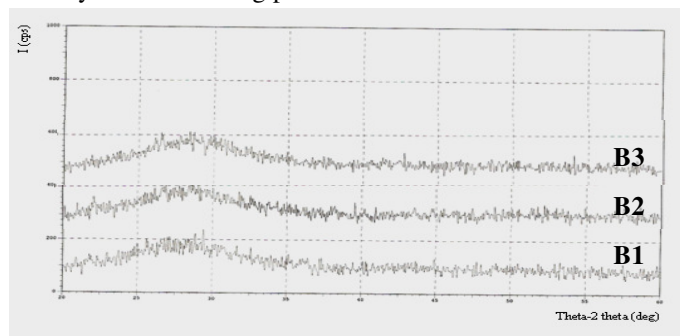


Figure-1
XRD Patterns of glass samples

Figure 2 displays XRD patterns for lead silicate glass-ceramic of the batches C1, C2 and C3 respectively. These batches are treated in two stage as 350°C for 3 hr. and 550°C for 3 hr. This figure shows that the heat treatment which used was successfully crystallized into glass-ceramic with its characteristic XRD peaks. The crystal phase identification and the crystallographic planes corresponding to the 2θ value for all the peaks were performed using the x-ray diffraction file index. XRD chart of batch C1 shows that the glass-ceramic samples is mainly composed of crystalline phases of Alumosite $PbSiO_3$ and plumalsite $Pb_4Al_2(SiO_3)_7$. Therefore, the samples are consist of two phases crystalline and amorphous, which characteristics of glass ceramic structure.

The main reason for appearing the crystalline phases (Alumosite and plumalsite) is the modifier adding K_2O to the primary lead glass, in which, a bond in the network is broken and the relatively mobile potassium ion becomes a part of the structure. With increase in the amount of modifier, the average number of oxygen-silicon bonds forming bridges between silicon atoms decreases and any further increase in modifier would reduce the length of the chain. So, the principal effect of a modifier is to lower the melting and working temperature by decreasing the viscosity. An excess of modifier as in C3 sample can make the structural units in the melt sufficiently simple and mobile that crystallization occurs in preference to the formation of a glass⁹.

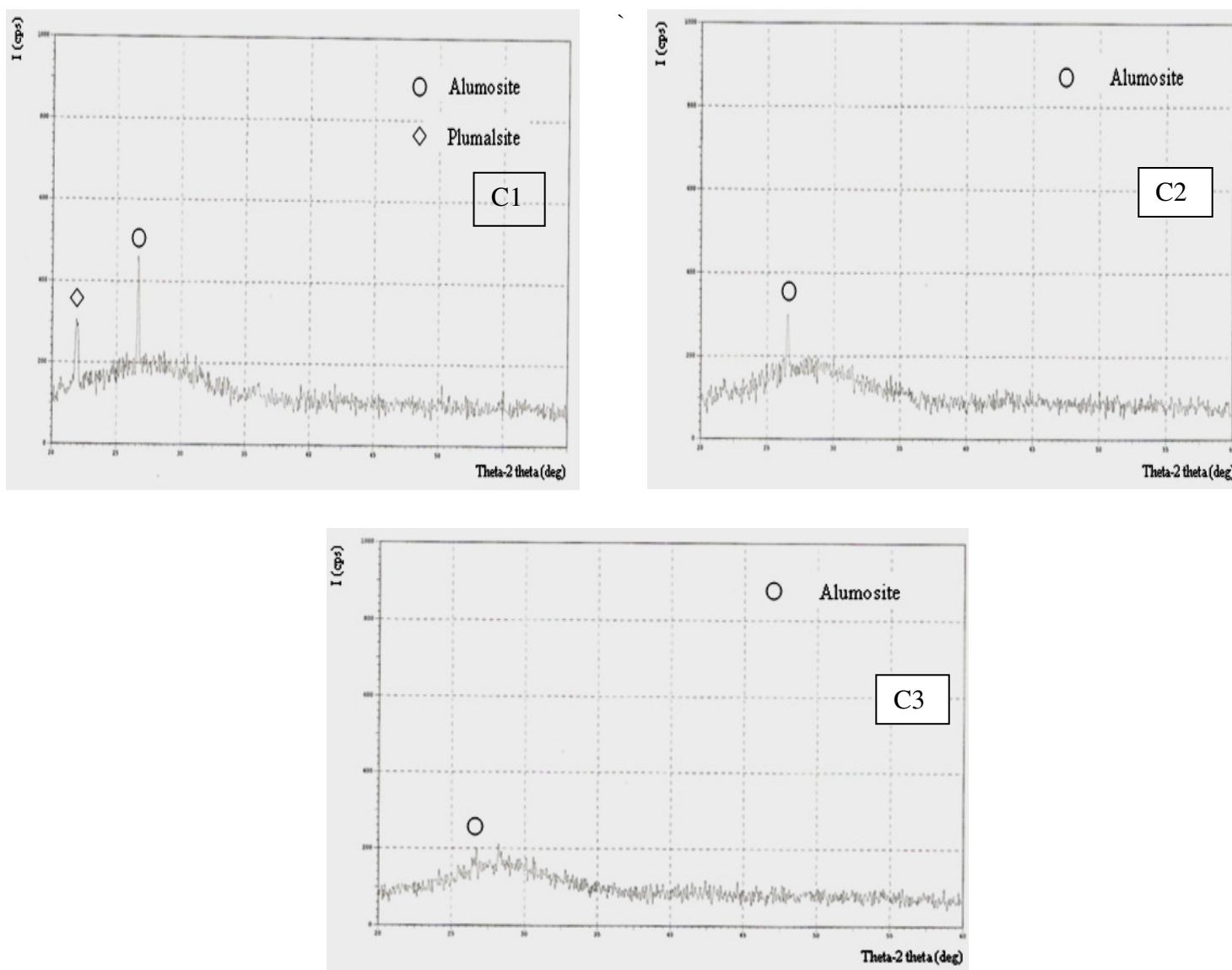


Figure-2
XRD patterns of glass ceramic samples C1, C2, and C3

Results and discussion of electrical properties: Dielectric strength: Figure 3 shows the effect of sintering temperatures on dielectric strength for glass samples, where the dielectric strength increases with raising of sintering temperature, because the raising in sintering temperature causes decreasing in porosity, since porosity is affected inversely on the dielectric strength (i.e. decreasing in the porosity values will increase the dielectric strength of glass samples). It will be interesting to know that the increasing in porosity will generate interior electrical fields and causes loss in dielectric strength¹⁰.

Figure 4 shows the effect of compositions on dielectric strength for glass-ceramic samples. Glass ceramic of the composition C1 has a lowest value of dielectric strength, whereas composition of the glass ceramic batches C2 and C3 have a higher values of dielectric strength. As a matter of fact, K₂O percentage is considered the main reason for increasing in the values of dielectric strength from batch C1 to batches C2 and C3, in which K₂O is acted as an active flux and in result the increasing in its percentage in the batch will reduce the porosity and in turn the dielectric strength is increasing.

Dielectric constant (ϵ_r): Glass: The dielectric constant of a glass results from electronic, ionic, dipole orientation and space charge contributions to the polarizability. It increases with the increase of total polarization rate. Only electronic (P_e) and ionic (P_i) polarization are taken into account when high frequency is applied. The electronic and ionic polarization are related to ion radius and its atomic weight, respectively. The larger radius of the ion results in the higher (P_e), whereas higher atomic weight results in the lower (P_i). The dielectric constant of sample B3 is totally attributed to contributed by K⁺ polarization created by presence of K⁺ ion. Since K⁺ ion has a large atomic radius 1.33 Å, and their percentage 14 % in the batch B3 should gain high electronic polarization^{11,12}. Figure 5 shows the relationship between frequency (f) and every of dielectric constant (ϵ_r) and dissipation factor for prepared glass samples B1, B2, and B3 respectively. These batches are sintered at different temperatures and the frequency applied was in the range (40 Hz – 5 MHz).

It may be noted from previous figure 5, at low frequencies, the maximum values of dielectric constant were at sintering temperature 525°C, and the minimum values at sintering temperature 600°C for all compositions B1, B2, and B3. This behavior is related to the porosity of the sample, where it is high at low sintering temperature, and then causes increasing in polarization which results from interstitial shipments at low frequencies¹³.

Figure 6 make clear the relationship of polarization and dielectric constant (ϵ_r) with frequency. It may be noted from

that figure the polarization is high at low frequencies due to space charge contributions resulting from high porosity^{7,14}.

In figure (5) the samples which have the same sintering temperature, show the same behavior in which the dielectric constant (at low frequencies) be as follow:

$$(\epsilon_r B1) > (\epsilon_r B2) > (\epsilon_r B3)$$

It has been observed that the batch composition B3 has lower value of dielectric constant. This batch as mentioned before has 14% K₂O in its composition and acts as a flux when the sample is heat treated, so the result becomes lower porosity and hence acquires lower dielectric constant. On the other hand, the batch B1, in which K₂O % equal to 6 %, shows dielectric constant (ϵ_r) for sintered samples (B1-525, B1-550) a maximum value at low frequencies result of high porosity which increases the effect of space charge polarization contribution. Whereas, the dielectric constant (ϵ_r) decreases with increasing the frequency to reach minimum value at frequency range (1-2) MHz. The reasons of that are: i. the absence of space charge polarization effect at high frequencies, ii. the effect of ionic and electronic polarization on dielectric constant (ϵ_r) for composition B1 was less than its effect on compositions B2 and B3, because there is low percentage of K₂O in composition B1 relative to B2 and B3 compositions.

It may be noted that the batch B2, in which K₂O % equal to 10% and the sintered samples (B2-525 and B2-550) has a dielectric constant (ϵ_r) less than that of the samples with composition B1 at low frequencies, because low effect of space charge polarization occurred (due to low porosity content) which results from the acquiring large K₂O % on comparison with composition B1. Also, it was observed from figure 5 that the dielectric constant (ϵ_r) value decreases with increasing the frequency to reach minimum values at frequency range (2.5-3) MHz. The reasons of that are: i. The absence of space charge polarization effect at high frequencies, ii. the low effect of ionic and electronic polarization on dielectric constant (ϵ_r) (due to low percentage of K₂O) relative to composition B3. The dielectric constant (ϵ_r) value at high frequency for B2 samples is higher than that of B1 samples due to increase in K₂O percentage, and in-turn stepping up the effect of electronic polarization at high frequency, because the (P_e) and (P_i) are related to ion radius and atomic weight. In other words, K⁺ has large in size and contributes high (P_e), as we previously explained.

The of batch B3, in which K₂O % equal to 14 % and the sintered samples (B3-525 , B3-550) has the lowest value of dielectric constant (ϵ_r) at low frequencies in comparison with compositions B1 and B2. The reason is the low effect of space charge polarization at low frequencies (due to low porosity), as a result to more active flux of K₂O % content in the samples of batch B3 than that of the samples of batches B1 and B2.

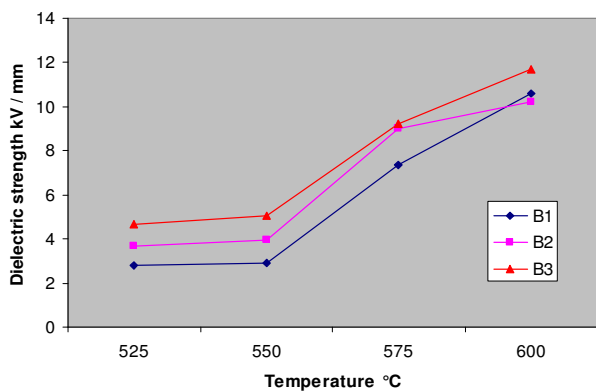


Figure-3
 Effect of sintering temperatures on dielectric strength for glass samples

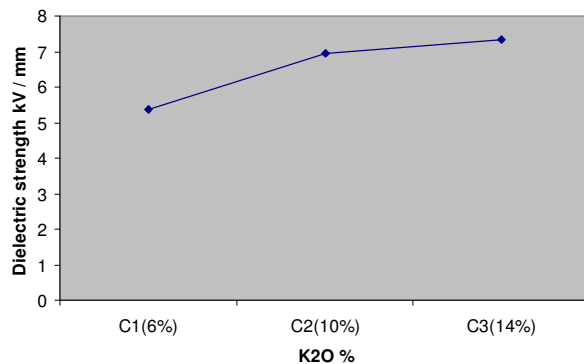


Figure-4
 Effect of compositions on dielectric strength for glass-ceramic samples

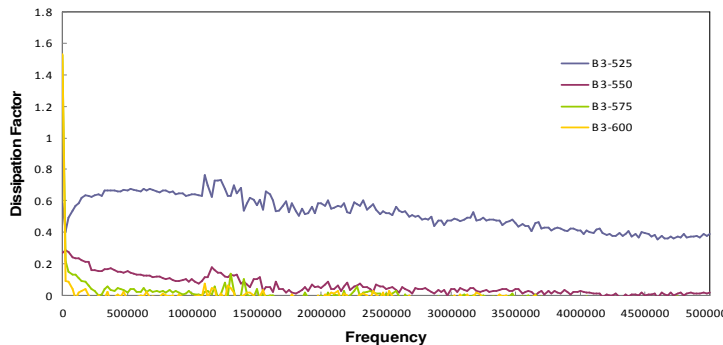
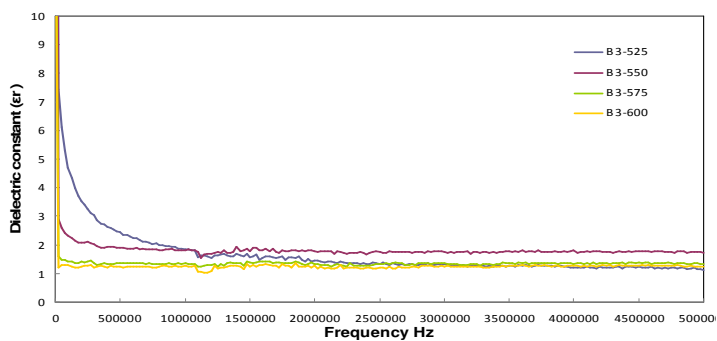
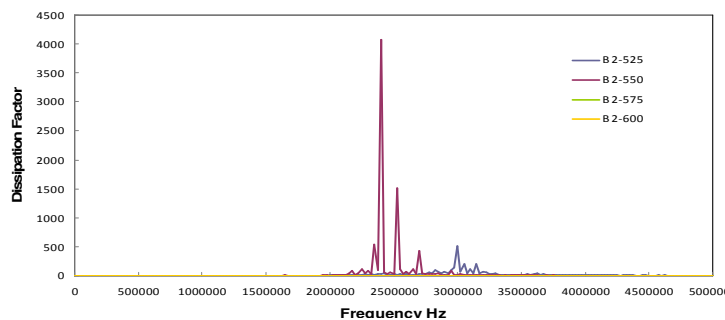
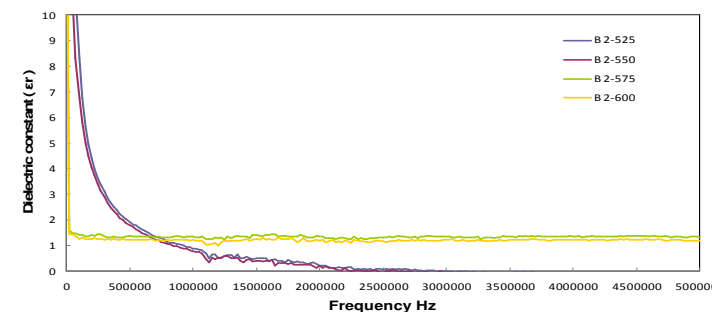
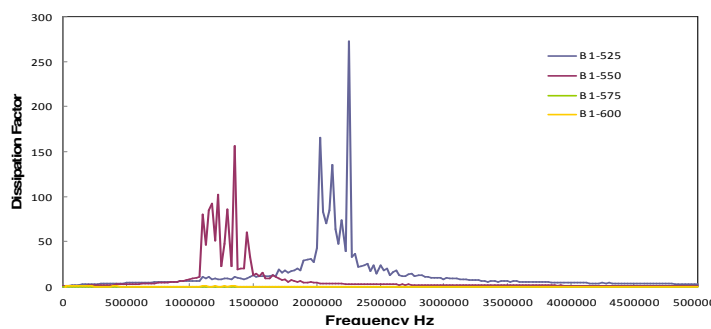
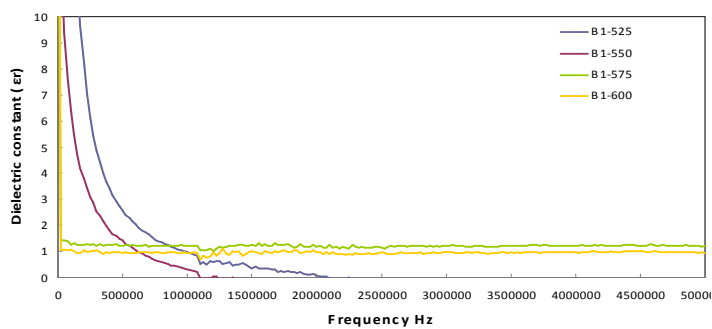


Figure-5
 The relationship between frequency and both of dielectric strength and dissipation factor for glass samples B1, B2, and B3

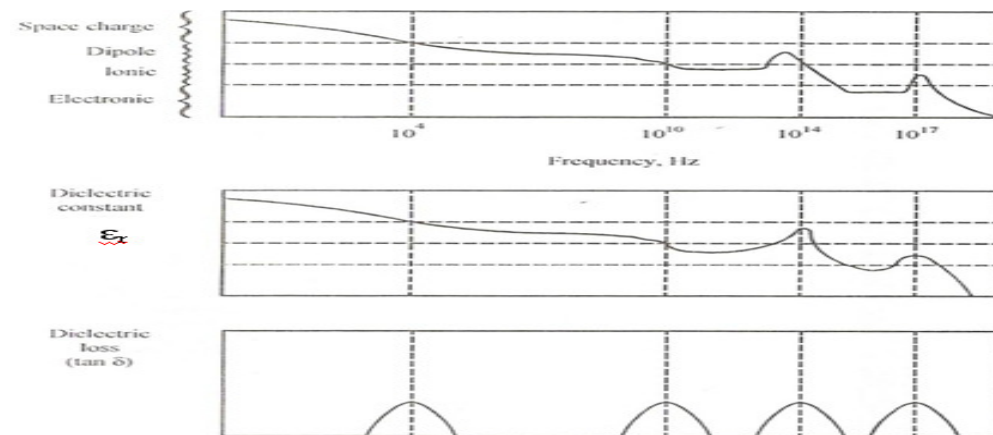


Figure-6
 Frequency effects on dielectric material [7]

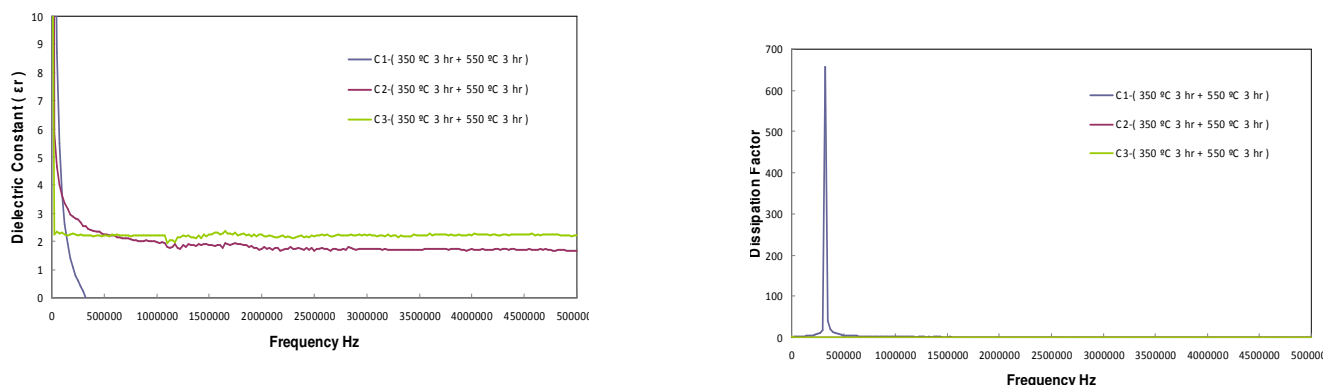


Figure-7

Relationship between frequency (f) and both of dielectric constant $f(\epsilon_r)$ and dissipation factor for glass - ceramic samples at different compositions and have the same heat treatment

Glass-Ceramic: Figure 7 shows the effect of frequency on dielectric constant (ϵ_r) for glass-ceramic samples of three compositions C1, C2 and C3.

It may be noted from figure 7, (at low frequency) that: ϵ_r C1 > ϵ_r C2 > ϵ_r C3. The main reason of that be high contribution of space charge polarization $P_s(C1) > P_s(C2) > P_s(C3)$. This is a result of high porosity for C1 composition relative to C2 and C3 compositions. Where, the porosity is gradually raised from C1 composition to C2 and finally reached to more porosity of C3 composition. This behavior is related to the densification rates of glass ceramic compositions in which the increment of $K_2O\%$ will cause increasing in densification and results of decreasing porosity. Also we shall explain the behavior of dielectric constant of these compositions at high frequency as below: for samples in composition C1 in which $K_2O=6\%$, the dielectric constant (ϵ_r) value is decreased by increasing frequency to minimum value at (3 MHz). The reasons of that are: i. the absence of

space charge polarization effect at high frequencies, ii. the low effect of ionic and electronic polarization on dielectric constant (ϵ_r) for composition C1 relative to compositions of C2 and C3, because there is low percentage of $K_2O\%$ in composition C1 in comparison with C2 and C3 compositions. For samples in composition C2 in which $K_2O=10\%$, the dielectric constant (ϵ_r) value is decreased by increasing frequency to reach stable value at high frequency due to the effect of high ionic and electronic polarization at high frequency. For samples in composition C3 in which $K_2O=14\%$, the dielectric constant (ϵ_r) value is decreased by increasing frequency to reach stable value at high frequency due to the effect of high ionic and electronic polarization at high frequency. As a matter of fact that the composition C3 has stable dielectric constant (ϵ_r) value at high frequency more than dielectric constant (ϵ_r) value at high frequency for composition C2.

Dissipation factor (Dielectric loss): As a result of comparison figure 6 with figures 5 and 7 which describe the relationship between dissipation factor and dielectric constant with frequency. It will be interesting to know that there are many effects of polarization on dielectric constant and dissipation factor. The figure 6 shows the maximum value of polarization and dielectric constant at low frequencies, where all types of polarizations in material (space charge, dipolar, ionic, and electronic) exist at low frequencies.

It may be noted from above figures that the dielectric constant at sintering temperatures (525 and 550)°C decreases with increasing frequency to become minimum value at low frequencies, because of losses space charge polarization effect (as we previously explained), therefore the dissipation factor has a maximum value at losses of space charge polarization.

Energy losses in dielectrics result from three primary processes: ion migration losses, ion vibration and deformation losses, and electron polarization losses. The major factor affecting the usage of ceramic materials is the ion migration losses¹⁵. Modifying cations have a significant effect on the dielectric loss of the glasses, for example, the order of mobility of alkali ions $Li^+ > Na^+ > K^+$, therefore the dielectric losses of glass contains Li^+ is more than glass of Na^+ content and consequently the glass of K^+ content has less dielectric losses^{11,15}.

Conclusion

Lead silicate glasses are characterized by good dielectric properties. Also, The increasing of K_2O percentage in this type of glasses will increasing the dielectric properties, and reduces the dissipation factor for all samples. The percentage of K_2O effects on crystallization of this glass, where the maximum percentage may cause the crystallization and the optimum percentage was 6%. The increasing of $K_2O\%$ reduce the melting point and facility of glass production, and the temperature of 1200°C is enough to convert the raw materials of three compositions B1, B2, and B3 to amorphous structures. Adding 5% of the crystallization agent TiO_2 in this type of glass may cause a crystallization in the glassy matrix. The optimum range to sinter the glass samples was (525- 600)°C, and the optimum heat treatment to deduce a crystallization in glassy phase was (350 for 3 hr and 550 for 3 hr). The decreasing in porosity will increase the dielectric strength. Glass sample B3 has a maximum dielectric strength at sintering temperature 600°C. Whereas in glass-ceramic samples C3 has a maximum dielectric strength. The maximum value of dielectric constant at low frequencies for sintered glass sample was 525°C, while the maximum value of dielectric constant at high frequencies was 575°C. For glass–ceramic sample of C1 composition has a maximum value of dielectric constant at low frequencies,

while glass–ceramic sample of C3 has a maximum value of dielectric constant at high frequencies.

References

1. Bereznoi A.I., Glass-ceramic and photosittals, New York Plenum Press, (1970)
2. McMillan P.W., Glass-ceramics, London: Academic press, 2nd edition, 1 (1979)
3. Allen M.A., High Temperature Oxides, part iv, Academic press New York and London (1971)
4. Wolfram H. and George B., *Glass-Ceramic Technology*, The American Ceramic Society, www.ceramicbulletin.org (2002)
5. Morsi M.M., Crystallization of Lithium Disilicate Glass Using Variable Frequency Microwave Processing, Blacksburg, Virginia Copyright (2007)
6. Guy A.J., Essentials of Materials Science, McGraw-Hill, (1976)
7. Charles A.H., Hand book of Ceramics Glasses and Diamonds, McGraw-Hill Companies Inc. (2001)
8. Someswar D.S.D., A new high temperature resistant glass–ceramic coating for gas turbine engine components, Bull. Mater. Sci., Indian Academy of Sciences (2005)
9. Madhumita G., Sengupta P., Kuldeep S., Rakesh K., Shrikhande V.K. Ferreira J.M.F. and Kothiyal G.P., *Crystallization behaviour of $Li_2O-ZnO-SiO_2$ glass–ceramics system*, www.elsevier.com (2005)
10. Hill G.H. and Morse C.T., The Effect of Porosity on Electric Strength of Alumina, Dielectric Mat, Measure and APP. IEE, No. 67 (1970)
11. Zhongjian W., Yichen H., Hongkai L. and Fang Y., Dielectric properties and crystalline characteristics of borosilicate glasses, www.elsevier.com (2007)
12. Pampuch R., Ceramic Materials: an Introduction to their Properties, Elsevier Scientific Pub. Comp. Amsterdam, (1976)
13. Barsoum M.W., Fundamental of Ceramics, The McGraw-Hill companies Inc., (1997)
14. Kingery W.D., Bowen H.K. and Uhlmann D.R., Introduction to Ceramics, 2nd Edition Wiley New York, (1976)
15. Sharaf El-Deen L.M. and Elkholy M.M., The dielectric polarizability of amorphous $Cu_2O-Bi_2O_3$ glasses, <http://www.complexity.org.au/vol09/elkhol01/> (2002)