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Ministry of Higher Education
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Babylon University
College of Engineering

Preparation of Glass and Glass – Ceramic Compositions as Electrical Insulators

A Thesis

Submitted to the council of College of Engineering, Babylon University in Partial Fulfillment of the Requirements for the Award of Degree of Master of Science in Materials Engineering

(Ceramic Materials)

By

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(B. Sc. Mat. Eng. 2000)

Supervised by

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جامعة بابل - كلية الهندسة

تحضير مركبات زجاجية و زجاجية-سيراميكية كعوازل كهربائية

رسالة مقدمة إلى

كلية الهندسة – جامعة بابل

كجزء من متطلبات نيل درجة الماجستير

في علوم هندسة المواد/ (هندسة السيراميك)

أعدت من قبل

محمد ناجي حسن الأعرجي

بكالوريوس علوم في هندسة المواد - 2000

بإشراف

أ.م.د .ماجد محي شكر

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2009

﴿ الإهداء ﴾

إلى ..... سيد الخلق ، خاتم النبيين ، ناصر الإسلام

نبينا محمد عليه وعلى آله أفضل الصلاة والسلام

إلى ..... أئمة الهدى وأعلام التقى

آل بيت النبي (عليهم السلام)

إلى ..... القلبين اللذين احترقا لتضيئا طريق حياتي

أمي وأبي

إلى ..... ذخري في الحياة

أخوتي

إلى ..... توأم الروح

زوجتي

وإلى ..... كل من يحبون لي الخير

محمد

بسم الله الرحمن الرحيم

((يرفع الله الذين أمنوا منكم والذين
أُوتوا العلم درجاتٍ والله بما تعملون خبيرٌ .))

صدق الله العلي العظيم
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Mohammed

2009

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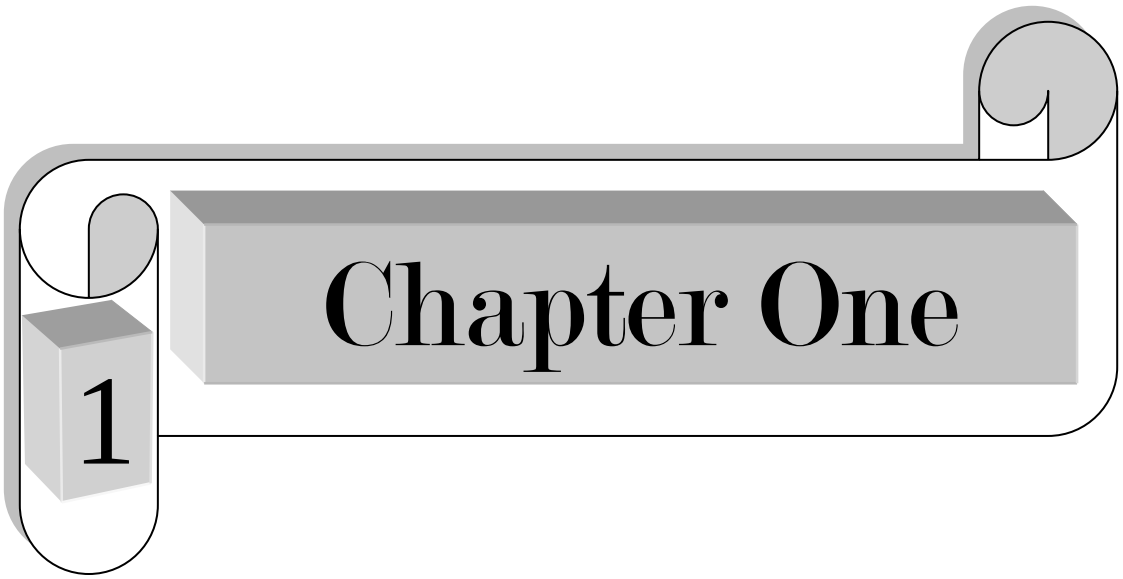

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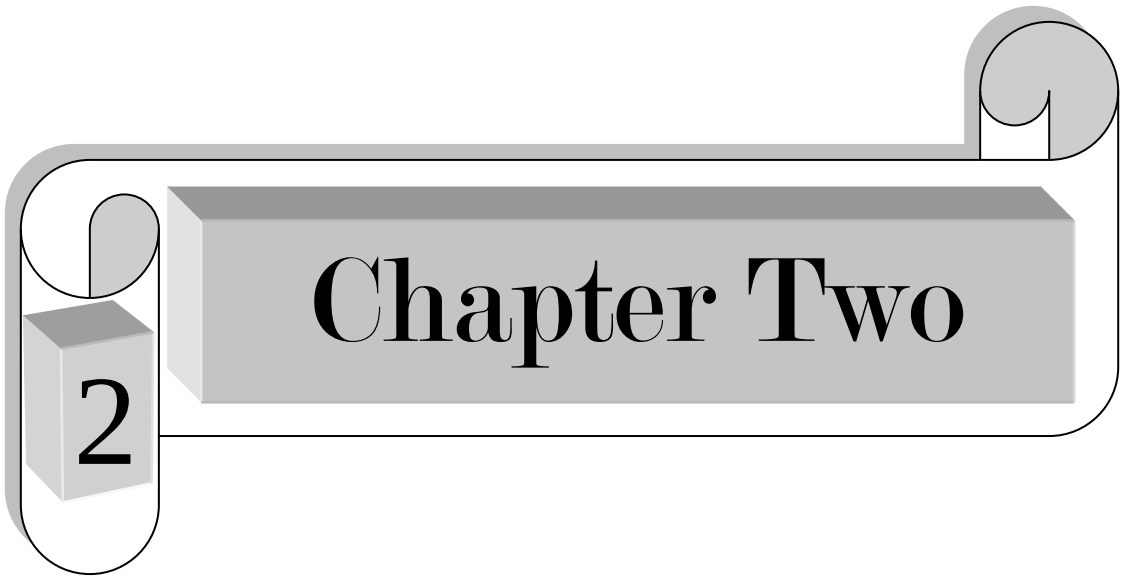

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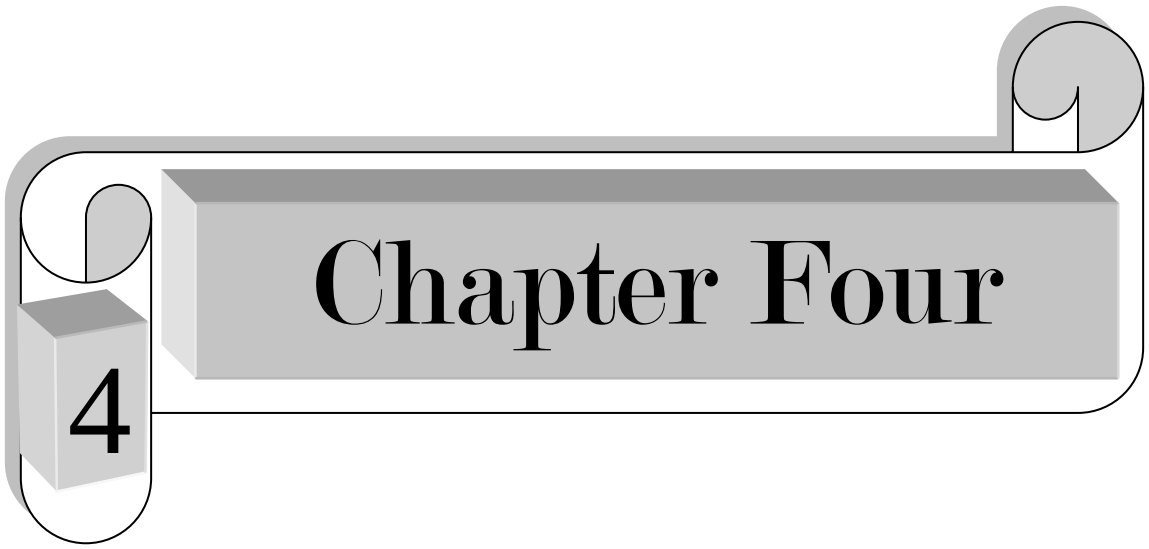

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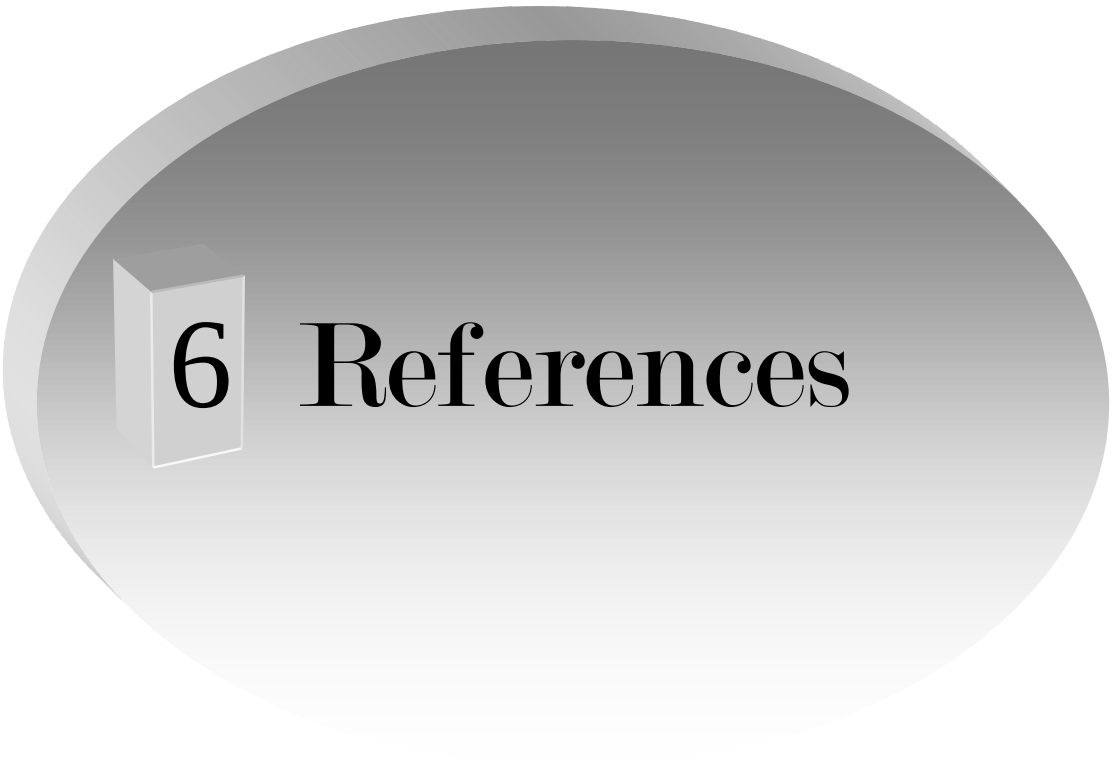

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Abstract

In this work , lead silicate glasses in three compositions :

B1-composition (wt.%): (63 SiO_2 , 1Al_2O_3 , 8 Na_2O , 6 K_2O , 22PbO),

B2-composition (wt.%): (59 SiO_2 , 1Al_2O_3 , 8 Na_2O , 10 K_2O, 22PbO),

B3-composition (wt.%): (55 SiO_2 , 1Al_2O_3 , 8 Na_2O , 14 K_2O, 22PbO),

were prepared by conventional melt quenching technique, as a first step. And subsequently converted this type of glass to glass – ceramic by carried out two – steps of heat treatments of the parent glass including nucleation and crystallization as a second step. The aim of this study was to use the glass and glass ceramic in electrical applications.

Approximately 300 g of glass powder for each composition was prepared, K_2O percentage increases in compositions (B2 , B3) to improve physical and electrical properties .

5 wt.% of (TiO_2) is used as a nucleation agent in preparing of glass – ceramic, as the following compositions :

C1-composition (wt.%): (60 SiO_2 , 1Al_2O_3 , 8 Na_2O , 6 K_2O , 20PbO , 5TiO_2),

C2-composition (wt.%): (56 SiO_2 , 1Al_2O_3 , 8 Na_2O , 10 K_2O, 20PbO , 5TiO_2),

C3-composition (wt.%): (52 SiO_2 , 1Al_2O_3 , 8 Na_2O , 14 K_2O, 20PbO , 5TiO_2),

Glass samples were prepared by melting and quenching of involving oxides and mill of resulting cullet to get glass powder, which pressed into disc forms. The prepared sample was sintered at (525,550,575,600) °C for (1 hr) to get glass samples, glass-ceramic samples prepared from heat treatment (350 ºC 3 hr + 550 ºC 3 hr) on glass samples for three compositions (C1 , C2 and C3).

Physical and electrical properties for all prepared specimens were investigated, where the apparent porosity and water absorption have a maximum value at lower sintering temperature for all compositions of glass and at (C1) composition for glass-ceramic samples. All specific

values are decreasing with increasing of sinter temperatures to minimum value at (575,600) °C for glass and at (C3) composition for glass-ceramic samples.

For electrical properties, we have noted increasing of dielectric strength with increasing of sintering temperatures for glass samples, where it has maximum value at (600) °C. Whereas it has maximum value at (C3) composition for glass-ceramic samples.

Dissipation factor for glass and glass-ceramic samples decreases with increasing of (K_2O) content at all sintering temperatures.

Dielectric constant (ε_r) for glass samples at low frequencies has a maximum value at (B1) composition and in sintering temperatures of (525 , 550) °C. At high frequencies it has maximum value at (B3) composition and in sintering temperatures of (550) °C.

Dielectric constant (ε_r) for glass-ceramic samples at low frequencies has a maximum value at (C1) composition, at high frequencies it has maximum value at (C3) composition .

الخلاصة

لقد تم في هذا البحث تحضير زجاج الرصاص (Lead - Silicate glass) بطريقة الصهر والإخماد (melt – quench tech .) كمرحلة أولى . ومن ثم إحداث تبلور في هذا النوع من الزجاج عن طريق إجراء معاملة حرارية خاصة للحصول على السيراميك الزجاجي كمرحلة ثانية لغرض استخدام الزجاج والسيراميك الزجاجي في التطبيقات الكهربائية.

حيث تم تحضير ثلاث تراكيب من زجاج الرصاص هي :-

B1-composition (wt.%): (63 SiO_2 ,1Al_2O_3 , 8 Na_2O , 6 K_2O , 22PbO)

B2-composition (wt.%): (59 SiO_2 ,1Al_2O_3 , 8 Na_2O , 10 K_2O, 22PbO)

B3-composition (wt.%): (55 SiO_2 ,1Al_2O_3 , 8 Na_2O , 14 K_2O, 22PbO)

حيث تم تحضير 300 g تقريبا من المسحوق الزجاجي لكل تركيب , وتم زيادة نسبة K_2O في التراكيب (B2 , B3) لتحسين الخواص الفيزيائية والكهربائية. وتم إعادة تحضير التراكيب أعلاه باستخدام عامل مساعد على التبلور (TiO_2) بنسبة (5 wt.%) لجميع التراكيب عند تحضير السيراميك الزجاجي, لتكون التراكيب كالأتي :

C1-composition (wt.%): (60 SiO_2 ,1Al_2O_3 , 8 Na_2O , 6 K_2O , 20 PbO , 5 TiO_2)

C2-composition (wt.%): (56 SiO_2 ,1Al_2O_3 , 8 Na_2O , 10 K_2O, 20 PbO , 5 TiO_2)

C3-composition (wt.%): (52 SiO_2 ,1Al_2O_3 , 8 Na_2O , 14 K_2O, 20 PbO , 5 TiO_2)

تم تحضير العينات الزجاجية عن طريق الصهر والإخماد للمواد الأولية الداخلة في التركيب ومن ثم الطحن لكسارة الزجاج الناتجة للحصول على مسحوق زجاجي ومن ثم كبس المسحوق للحصول على عينات قرصية وتلبيدها بدرجات حرارة °C(525,550,575,600) , أما العينات السيراميكية الزجاجية فقد تم الحصول عليها عن طريق إجراء معاملة حرارية على العينات الزجاجية(C1,C2,C3), تتضمن مرحلتين (تنوية + نمو).

(350°C for 3 hr + 550°C for 3 hr)

تم دراسة الخواص الفيزيائية والكهربائية لجميع النماذج المحضرة , وقد لوحظ بان المسامية الظاهرية وامتصاصية الماء تمتلك أعلى قيمة لها عند درجات التلبيد المنخفضة لجميع الخلطات ولكلا المادتين (الزجاج والسيراميك الزجاجي) , بعد ذلك أخذت هذه القيم بالانخفاض مع

ارتفاع درجات حرارة التلبيد حتى بلغت أدنى قيمة لها عند درجات التلبيد °C (600 , 575) بالنسبة للزجاج, وعند تركيب (C3) بالنسبة للعينات السيراميكية الزجاجية.

أما بالنسبة للخواص الكهربائية , فقد لوحظ زيادة في متانة العزل الكهربائي بارتفاع درجة حرارة التلبيد للعينات الزجاجية حتى بلغت أعلى قيمة لها عند درجة حرارة تلبيد °C (600) وأعلى قيمة لها للسيراميك الزجاجي عند التركيب (C3).

أما عامل الفقد بالنسبة للعينات الزجاجية ينخفض مع زيادة نسبة (K_2O) وعند جميع درجات حرارة التلبيد. وكذلك الحال بالنسبة لعينات السيراميك الزجاجي فان زيادة نسبة (K_2O) تقلل من عامل الفقد.

أما ثابت العزل الكهربائي للعينات الزجاجية , فان أعلى قيمة له عند الترددات الواطئة تكون عند التركيب (B1) وبدرجات التلبيد المنخفضة °C (550 , 525) وعند الترددات العالية تكون أعلى قيمة له عند التركيب (B3) عند درجات حرارة التلبيد °C (550).
أما ثابت العزل الكهربائي للعينات السيراميكية الزجاجية , فان أعلى قيمة له عند الترددات الواطئة تكون عند التركيب (C1). وعند الترددات العالية تكون أعلى قيمة له عند التركيب (C3) بسبب زيادة نسبة (K_2O).

Certificate

We certify that we have read this thesis, titled ***"Preparation of Glass and Glass – Ceramic Compositions as Electrical Insulators"***, and as examining committee examined the student ***"Mohammed Naji Hassan Al-aaraji "*** in its contents and in what is connected with it, and that in our opinion it meets the standard of a thesis for the degree of Master of Science in Materials Engineering.

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Certification

We certify that, this thesis titled **"*Preparation of Glass and Glass – Ceramic Compositions as Electrical Insulators*",** was prepared by "***Mohammed Naji Hassan Al-aaraji***" under our supervision at Babylon University in partial fulfillment of the requirements for the degree of Master of Science in Materials Engineering.

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In view of the available recommendation, I forward this thesis for debate by the examination committee.

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Nomenclatureure

Symbol	Description	Unit
T_m	Melting temperature	^oC
T_g	Glass transformation temperture	^oC
T_c	Crystallization temperture	^oC
η	Viscosity	poise
V	Volume	cm^3
A	Area	mm^2
d	Distance	mm
Q	Charge stored	Coulumb
C	Capacitance	-
ε	Permittivity of dielectric material	farad / meter= $C^2/(J .m)$
ε_o	Permittivity of free space	farad / meter= $C^2/(J .m)$
ε_r	Relative dielectric constant	-
f	Frequency	Hz
P_t	Total polarization	C/m^2
P_e	Electronic polarization	C/m^2
P_m	Molecular polarization	C/m^2
P_i	Ionic polarization	C/m^2
P_s	Space charge polarization	C/m^2

r	distance	mm
d	Diameter	mm
D	Dry mass	g
S	Suspended mass	g
M	Saturated mass	g
h	Thickness	mm
V_{av}	Rate of breakdown voltage	kV

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Chapter One INTRODUCTION

1.1 Introduction

Glass-ceramics are polycrystalline materials formed by the controlled nucleation and crystallization of special formulated glasses[1]. The amorphous glass article is first 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 1950s [2].

The combination of crystalline properties, lack of porosity and ease of forming define glass-ceramics as unique materials [2,3].

Glass-ceramic are an important class of materials that have been commercially quite successful [1,4,5].

Glass-ceramic (Recrystallized glass), possesses increased impact strength, hardness and thermal shock resistance compared with conventional non-crystalline glasses [6].

The practical technique of forming a lead-silicate glass-ceramic follows this sequence:

1) The glass-forming batch, usually including a specific agent to promote nucleation, is melted to homogeneity

2) The melted glass is rapidly cooled and then formed to the desired shape.

3) The cold article is then reheated to a temperature that develops small dispersed crystalline nuclei in the glass.

4) The glass is further heated to allow its significant or complete crystallization [3].

Nucleation can occur heterogeneously (on a nucleation –catalyzing surface such as another previously precipitated crystalline phase), or homogeneously (spontaneously throughout the volume of the glass) [7].

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 nucleation [7].

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[7]. Also a new high temperature resistant glass–ceramic coating used for gas turbine engine components[8].

1.2 Literature Review

There are many studies and researches about the study of structural, physical, electrical properties of glass and glass- ceramic. Among these studies, I will report the important researches as follow:

1 - Kim S. J. and Yang Y. S. (2004) [9], have investigated the crystallization process and dielectric properties of $2SrTiO_3$-SiO_2 glass, where differential thermal analysis (DTA) measurements show two exothermic peaks with heating, and x-ray measurements reflect that the glass crystallizes into cubic $SrTiO_3$ and tetragonal $Sr_2TiSi_2O_8$.They are calculated activation energies by the modified Ozawa equation, for $SrTiO_3$ and $Sr_2TiSi_2O_8$ crystallization, are 4.99 ev and 5.68 ev, respectively. In electrical measurements, high temperature dielectric behavior is well explained by the conjunction of crystallization processes appearing in DTA results. They are found that oxygen vacancies produce a pronounced dielectric anomaly in the glass state.

2- Jun Du et al., (2005) [10], studied preparation and characterization of dielectric glass-ceramics in $Na_2O–PbO–Nb_2O_5–SiO_2$ system, where glass-ceramics in the $Na_2O–PbO–Nb_2O_5–SiO_2$ system have been synthesized to produce bulk materials with nanometer-sized crystals grown in a glass phase via roll-quenching followed by controlled crystallization. X-ray diffraction studies showed that $Pb_2Nb_2O_7$, $NaNbO_3$ and $PbNb_2O_6$ phases are formed from quenched glass in temperature range from 750 to 900 ºC. $Pb_2Nb_2O_7$ crystallizes at 750 ºC and disappears at 850 ºC, $NaNbO_3$ is the primary phase at 850 ºC, while $PbNb_2O_6$ is formed at a higher temperature of 900 ºC. The dielectric properties of the glass-ceramics formed through controlled crystallization have a strong dependence on the phase assemblages that are developed during heat

treatment. The highest dielectric constants (>600) were found in samples annealed at 850 ºC for 3 hr., and microstructural observation shows that randomly oriented, nanometer-sized crystalline are found with residual glass concentrated at crystallite boundaries. Further studies by scanning tunneling electron microscopy (STEM) in conjunction with energy dispersive spectroscopy (EDS) reveals inhomogeneous distribution of $NaNbO_3$ and $PbNb_2O_6$ in the sample annealed at 850 ºC for 3 h and these phases contribute to the high dielectric constant.

3- Eun-Sub Lim et al., (2005) [11], investigated the effect of BaO content on the sintering and physical properties of $BaO–B_2O_3–SiO_2$ glasses, where a ($BaO–B_2O_3–SiO_2$) glass system was chosen as a candidate composition for the application to Pb-free low temperature sinterable glass. Since BaO played the role of network modifier. They found both the glass transition temperature and crystallization temperature decreased as the BaO content increased. Crystallization easily occurred during sintering with a BaO content of more than 50 mol%, which effectively inhibited the over-firing phenomenon . This was probably due to the presence of crystallized particles. The dielectric constant and thermal expansion coefficient were in agreement with the theoretically expected values in the specimens of Ba35–Ba45, while differences were observed in the crystallized specimens of Ba50 and Ba55 due to the crystallization of the BaB_2O_4 phase.

4- Madhumita Goswami et al., (2005) [12], Studied the crystallization behavior in two types of lithium zinc silicate (LZS) glasses: (a) LZSL composition (wt.%): (Li_2O, 12.65; ZnO, 1.85; SiO_2, 74.4; Al_2O_3, 3.8; K_2O, 2.95; P_2O_5, 3.15; B_2O_3, 1.2) (low ZnO); and (b) LZSH composition (wt.%): (Li_2O, 8.9; ZnO, 24.03; SiO_2,53.7; Na_2O, 5.42;

P_2O_5, 2.95; B_2O_3, 5) (high ZnO). This glass has been prepared by usual melt–quenched technique. The crystallization route was following two different procedures: (i) cooling schedule (CS) and (ii) heating schedule (HS). The nucleation and crystallization temperatures were determined by DTA studies. In case of LZSL sample, the crystallization was carried out in the temperature range of 580–780 ºC, whereas in case of LZSH it was done in the temperature range of 570 and 720 ºC. Crystalline phases were identified using powder X-ray diffraction technique. Significant differences in the formation of crystalline phases and their relative ratios were observed between heating and cooling schedules. For LZSL, formation of Li_2SiO_3 phase along with small fraction of cristobalite phase was seen when CS was followed. On the other hand, mixed phase having small fraction of lithium zinc silicate in major cristobalite phase was obtained for heating schedule. However, in the case of LZSH, formation of lithium zinc silicate as major crystalline phase along with cristobalite phase is seen when HS was followed. For LZSL, the average thermal expansion coefficient (TEC) values were found to be around $178 * 10^{-7}$ and $114 * 10^{-7}$ $ºC^{-1}$, for CS and HS, respectively, and for LZSH, TEC was found out to be $\approx 185 * 10^{-7}$ $ºC^{-1}$ for HS.

5 - Hoi Kwan Lee et al., (2005) [13], investigated the effect of K_2O in glass– ceramics based on the $BaO–TiO_2–SiO_2$ glasses. The characterization of heat-treated glasses by using x-ray diffraction, fourier transform infrared spectroscopy and scanning electron microscope. The results showed that the K_2O has no effects with the formation of secondary crystal phase, while the lattice deformation and constant of crystal in $Ba_2TiSi_2O_8$ glass– ceramics increase with K_2O content due to the density and thermal expansion difference between the crystal and glass matrix. The FT-IR spectrum shows the glass–ceramics contained

K_2O possess similar structure of fresnoite ($Ba_2TiSi_2O_8$). The orientated crystal in a polar direction (c-axis) was observed for surface crystallization of BTS, 10 KBTS and 20KBTS. Especially, 20 KBTS glass–ceramics was prominent in surface crystallization, where the glass compositions studied were xK_2O–(33.3–x)BaO– 16.7 TiO_2–50 SiO_2 ($0 \leq x \leq 33.3$ mol%) (here after denoted BTS, 10 KBTS, 20 KBTS, 33.3 KTS) which modified from the stochiometric compositions corresponding to $Ba_2TiSi_2O_8$ crystals.

6- Esmat M.A. Hamzawy and Emad M. El-Meliegy (2005) [14], have studies the crystallization of the Na_2O–CaO–Al_2O_3–SiO_2–(LiF) glass compositions where spodumene-nepheline glass-ceramics was prepared from Na_2O–CaO–Al_2O_3–SiO_2 glass compositions. Additive of LiF changes the course of the reaction toward the formation of β-spodumene ($LiAl(SiO_3)_2$) together with nepheline ($NaAlSiO_4$). The crystallization of β-spodumene strongly reduced the thermal expansion coefficient from $70 * 10^{-7}$ $^oC^{-1}$ (20–700 ^{o}C), in the base sample, to $17 * 10^{-7}$ $^oC^{-1}$ (20–700 ^{o}C), in that containing 6 wt.% LiF. Additive of 3 wt% LiF is considered the best as it reduces the expansion coefficient and enhances the microstructure uniformity. Higher content of LiF results in impairing the machinability as the content of β-spodumene tends to exceed 50%. Li^+ substitute Na^+ cations resulting in the formation of β-spodumene solid solution (ss). However, shift in the nepheline *d*-spacing lines with the appearance of some unidentified ones may reflect a state of solid solution formation. The presence of fluorine in such glass structure is found to promote the nepheline growth. The transformation temperature (Tg) and the softening temperature (Ts) were reduced as a result to the addition of LiF.

7 - Graca M.P.F. et al., (2005) [15], studied the dielectric and structural properties of a (SiO_2–Li_2O–Nb_2O_5) glass (transparent) and glass-ceramic(translucent) prepared by the sol–gel method, where the glass composition $92SiO_2$–$4Li_2O$–$4Nb_2O_5$ (mol%), which is prepared by the sol–gel route gave the origin to a transparent and colorless gel. The dried gel was heat-treated at temperatures between 500 and 750 ºC, with and without the presence of an external electrical dc field, to characterize the glass samples by x-ray diffraction (XRD), scanning electron microscopy (SEM), Raman and dielectric spectroscopy. In the samples heat-treated at 650 ºC with 1000 kv/m and in the 700 and 750 ºC samples series, $LiNbO_3$ crystals, was an important ferroelectric material in the glass. The behavior of the dc conductivity and the dielectric constant, in the glass and glass-ceramic, reflects the important effect of the temperature and the applied electric field on the sample structure.

8- Haikui et al., (2006) [16], studied the properties of CaO–SiO_2–B_2O_3 system glass-ceramic , where low temperature Co-fired ceramic (LTCC) is prepared by sintering a glass selected from (30–50 CaO, 35–45 SiO_2 and 10–20 B_2O_3) wt%. and its sintered bodies are characterized by x-ray diffraction (XRD), scanning electron microscopy (SEM) and energy dispersive spectroscopy (EDS). They found that the optimal sintering temperature for this glass-ceramic is(820 ºC) for 15 min, and the major phases of this material are $CaSiO_3$, CaB_2O_4 and SiO_2. The glass-ceramic possesses excellent dielectric properties: ε_r = 6.5, tan $\delta < 2*10^{-3}$ at 10 MHz, temperature coefficient of dielectric constant about $51* 10^{-6}$ $ºC^{-1}$ and coefficient of thermal expansion about $8* 10^{-6}$ $ºC^{-1}$ at 20–400 ºC. Thus, this material is supposed to be suitable for the tape casting process and be compatible with Ag electrode, which could be used as the LTCC materials for the application in wireless communications.

9- Lu A.X. et al., (2006) [17], studied the effect of heat-treatment condition on crystallization behavior and thermal expansion coefficient of $Li_2O–ZnO–Al_2O_3–SiO_2–P_2O_5$ glass–ceramics, where utilizing P_2O_5 as nucleation agent. $Li_2O–ZnO–Al_2O_3–SiO_2$ glass was prepared by conventional melt quenching technique and subsequently converted to glass–ceramics with different crystal phases. During the processing, two-step heat-treatments including nucleation and crystallization were adopted. The effects of heat-treatment on the crystal type, the microstructure and the thermal expansion behavior of the glass–ceramics were studied by means of differential scanning calorimetry, x-ray powder diffraction analysis, scanning electron microscopy and thermal expansion coefficient tests. It was shown that the crystallization of $\beta'_{\parallel}$-Li_2ZnSiO_4 occurred after the glass was treated at 580 ºC. As the temperature increased from 580 ºC to 630 ºC, cristobalite and $\beta'_{\parallel}$-Li_2ZnSiO_4 were identified as main and second crystal phases, respectively. An increscent in the temperature to 700 ºC, the β-quartz solid solution in the glass–ceramic accompanied by a decrease in cristobalite content. The transformation from $\beta'_{\parallel}$-Li_2ZnSiO_4 to γ_o-Li_2ZnSiO_4 took place from 700 ºC to 750 ºC. The resulting crystallization phases in the glass–ceramics obtained at the temperature higher than 750 ºC were β-quartz solid solution and γ_o-Li_2ZnSiO_4. The glass–ceramics containing $\beta'_{\parallel}$ - Li_2ZnSiO_4 or β-quartz solid solution crystal phase possessed a microstructure formed by the development of dendritic crystals. The thermal expansion coefficient of the glass–ceramics varied from 36.7 to 123.8 * 10^{-7} $ºC^{-1}$ in the temperature range of 20–400 ºC, this precise value is dependent on the type and the proportion of the crystalline phases presented.

10- Chuang-Chung Chiang et al., (2007) [18], prepared in their study five glasses with different compositional ratios of $CaO–B_2O_3–SiO_2$ (CBS) system to investigate the effects of composition on the densification, thermal properties and dielectric properties of (CBS) glass-ceramic .
Among these glasses, ($8.6CaO–47.8B_2O_3–43.6SiO_2$) glass (CBS-10) can be densified at the sintering temperature below 850 °C through viscous sintering. It has a dielectric constant of 6 and a dielectric loss of 0.0014 at 4.3 GHz, which provide an attractive feature for microwave applications. Also, it possesses the highest thermal conductivity and reasonable electrical properties. Low sintering temperature of CBS-10 opens more room for adding fillers or additives to tailor its functional properties, which enable for use as substrate material for LTCC applications.

11- Jiangang Wang et al., (2007) [19], have studied the crystallization behavior and microwave dielectric property of ($MgO–Al_2O_3–SiO_2–TiO_2–CeO_2$) glass–ceramic. They prepared glass–ceramics with a molar composition of ($1.0MgO, 1.2Al_2O_3, 2.8SiO_2, 1.2TiO_2, 0.6CeO_2$), by one-step crystallization heat treatment of the parent glass at different temperatures for 2 h. The crystallization behavior and microwave dielectric properties of the materials were investigated by differential scanning calorimeter (DSC), X-ray diffraction (XRD), scanning electron microscope (SEM), energy dispersive spectroscopy (EDS) and network analyzer. The investigations show that the exothermic peaks in the range of (841–1220 ºC) are corresponding with perrierite ($Ce_2Ti_2Si_2O_{11}$), magnesium aluminotitanate ($Mg_2Al_6Ti_7O_{25}$, MAT), rutile (TiO_2), α-cordierite ($Mg_2Al_4Si_5O_{18}$) and ceria (CeO_2), respectively. Among the crystalline phases, the MAT was a metastable phase, which appeared at 925 ◦C, and then disappeared at higher temperature. Glass–ceramic heat-treated over 1150 °C consists of three main crystalline phases: the

perrierite, the rutile and α-cordierite. With heat-treatment from 1150 to 1250 ˚C, the perrierite phase increases while the rutile phase decreases. The microwave dielectric properties are correlated with the treatment conditions. With the heat-treatment of 1100–1250 ˚C, the dielectric constant (ε_r) of the material varies in the range of (10.99–11.73). When the heat-treatment temperature is increased, the dielectric constant increases first and then decreases, with its maximum value of 11.73 appearing at 1200 ºC.

12 - Graca M.P.F. et al., (2007) [20], studied the Influence of thermal and thermoelectric treatments on structure and electric properties of B_2O_3–Li_2O–Nb_2O_5 glasses by using of the melt quenching technique to prepare a transparent glass with the composition $60B_2O_3$–$30Li_2O$–$10Nb_2O_5$ (mol%). This glass was heat-treated with and without the application of an external electric field. The prepared sample was heat-treated (HT) at 450, 500 and 550 ºC and thermoelectric treated (TET) at 500 ºC. The following electric fields were used: 50 kv/m and 100 kv/m. Differential thermal analysis (DTA), x-ray diffraction (XRD), scanning electron microscopy (SEM), Raman, dc and ac conductivity, as a function of temperature, were used to investigate the glass and glass-ceramics properties. $LiNbO_3$ crystals were detected, by XRD, in the 500 ºC HT, 550 ºC HT and 500 ºC TET samples. The presence of an external electric field, during the heat-treatment process, improves the formation of $LiNbO_3$ nanocrystals at lower temperatures. However, in the 550 ºC HT and in the TET samples, $Li_2B_4O_7$ was also detected. The value of the σ_{dc} decreases with the rise of the applied field, during the heat-treatment. This behavior can indicate an increase in the fraction of the $LiNbO_3$ crystallites present in these glass samples. The dc and ac conduction processes show dependence on the number of the ions inserted in the

glass as network modifiers. The Raman analysis suggests that the niobium ions are, probably, inserted in the glass matrix as network formers. These results reflect the decisive effect of temperature and electric field applied during the thermoelectric treatment in the structure and electric properties of glass-ceramics.

1.3 Aim of the work

The present study will be concerned with preparing of glass and glass-ceramic compositions of lead silicate glasses, and specific the electrical properties of this glass and glass-ceramic to be useful as electrical insulators.

Chapter Two
THEORETICAL PART

2.1 Introduction

As the name implies, glass-ceramics combine the nature of crystalline traditional ceramics with glass. The result is a product with especially attractive properties[21]. Glass – ceramics are prepared by crystallization of special glasses or melts of various compositions throughout the bulk of the pre-shaped glass article. This is accomplished by initially forming a glass and then heat-treating applied at a certain temperature to encourage the nucleation of exceptionally small and numerous crystals. These crystals are then allowed to grow at high temperature until as much as 90% of the article has crystallized [22]. In many cases, special nucleating agents are introduced into the glass to enhance the nucleation process [5].

2.2 Fundamentals of glass – ceramic materials

2.2.1 Nature of glass

Certain liquids have the ability adjustment their structure upon cooling and continually stiffen to the solid state without crystallizing. These frozen liquids are called "glasses". Upon reheating, they slowly and continuously decrease in viscosity and revert to their former mobile state without any defined melting point. Thus they can be shaped in the plastic – state by high speed manufacturing techniques such as pressing, roll centrifugal spinning, blowing and drawing and can be reworked by traditional flame sagging and fire-polishing techniques.

Inorganic glasses can be made from many compositions in the broad areas of silicates, phosphates, aluminates, borates, halides and

chalcogenides. Silicate glasses are by far the most commercially important because they have excellent transparency and good chemical durability, and they can be made from inexpensive natural ingredients. However, the disadvantage of glass material is its brittleness, which makes it susceptible to mechanical failure[23].

The properties of glass, are mainly dependent on its structure. Thus, it is useful to consider briefly the glass structure. As in crystalline silicate, the SiO_4 tetrahedron is the basic unit in silicate glasses. The SiO_4 tetrahedra are irregularly linked together in a three dimensional network. Figure (2.1a) represents a random three-dimensional silica glass network, and figure (2.1b) shows the same composition after crystallization to the quartz structure[24].

The increased viscosity of glass forming melts on cooling can be attributed to the formation of such irregular infinite three-dimensional network.

According to their role in the glass structure, cations can be classified into three groups:

1- Network formers, such as Si, B, P, Ge, and As, having oxygen coordination number of 3 or 4 and tend to produce the basic cross-linked polymeric glass structure.

2- Network modifiers, such as Na, K, Ca, and Ba, having coordination number of 6 or more and generally tend to reduce the degree of polymerization and viscosity.

3- Intermediate oxides with cations, such as Al, Zn, Mg, Pb, and Be having intermediate coordination of 4 to 6 and act either as network formers or modifiers, depending upon the glass composition [5,25].

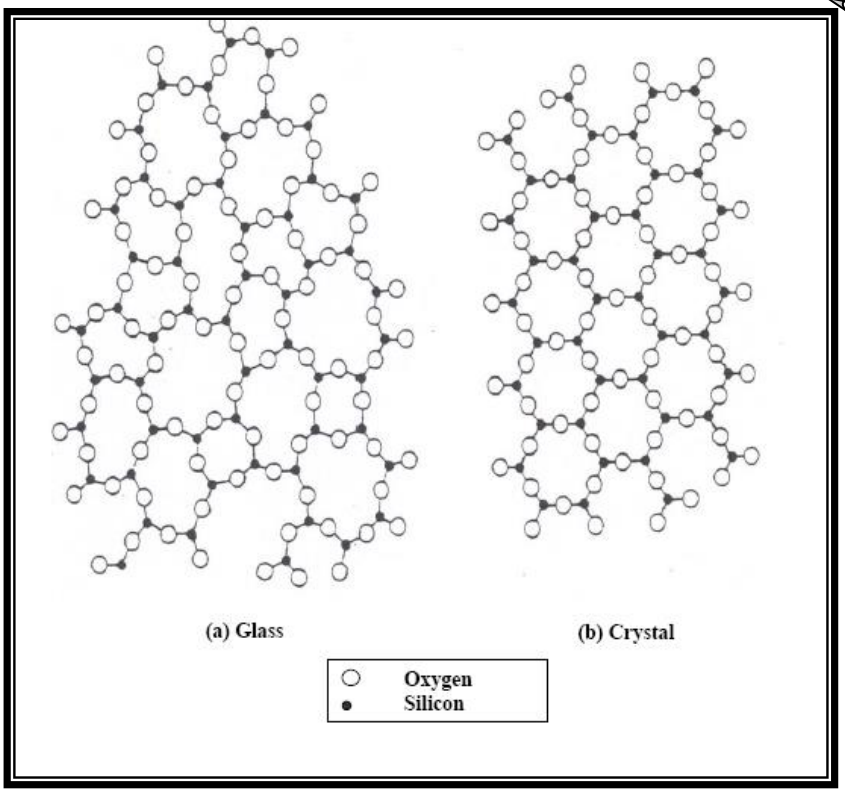


Fig. 2-1 : Schematic representation of

a. Irregular network structure of SiO_2 glass (amorphous)
b. Regular periodic crystalline structure of quartz [26].

2.2.2 Methods of Making Inorganic Glasses

The most common method for making glass is :

1. Fuse various raw materials in appropriate proportions together with the application of heat .

2.Gather and form into useful products .

3. Cool subsequently at a rate fast enough to avoid distortion of the shape and slow enough to avoid cracking .

Inorganic glasses may also be obtained by :

1. Hydrolyzing an alcoholic of an organ metallic compound .

2.Stirring the hydrolyzed product to allow rapid chelation to a gel state.

3.Drying the gel mass to drive off the organics .

4.Sintering at an elevated temperature to obtain a compact .

This method , called the sol-gel route to glassmaking , is often used to deposit thin films such as antireflection coatings [7].

2.2.3 Volume –Temperature Diagram

The behavior of glass under cooling can be explained by the relationship between volume and temperature as shown in figure (2-2). the glass melt start to cool from high temperature (a), the volume V typically shrinks along the line ab. Although b is the thermodynamic freezing point of the melt (or the thermodynamic melting point T_m of a crystal of the same composition). Crystallization may only occur if , and only if, (1) there is sufficient nucleation rate I followed by (2) a significant crystal growth rate u [7] .

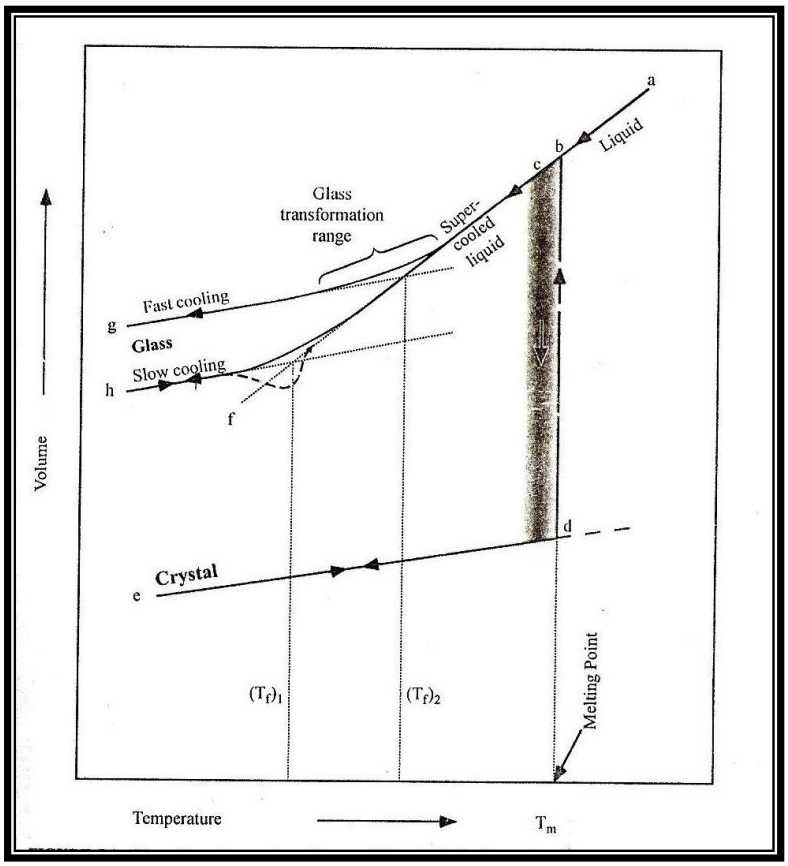


Fig. (2-2) Volume – Temperature Diagram .

The dependence of the nucleation rate I and the crystal growth rate u with temperature T is shown in figure (2.3). Note that both the rates are zero at T_m, hence no crystallization is expected at T_m, with increasing super cooling (also referred to as under cooling) the two rates begin to increase at varying rates. There is some overlap in the curves, shows hatched area in figure (2-3). leading to crystallization over a range of temperatures, which represented the shaded area in figure(2-2). Point c is being the location with the highest probability of crystallization

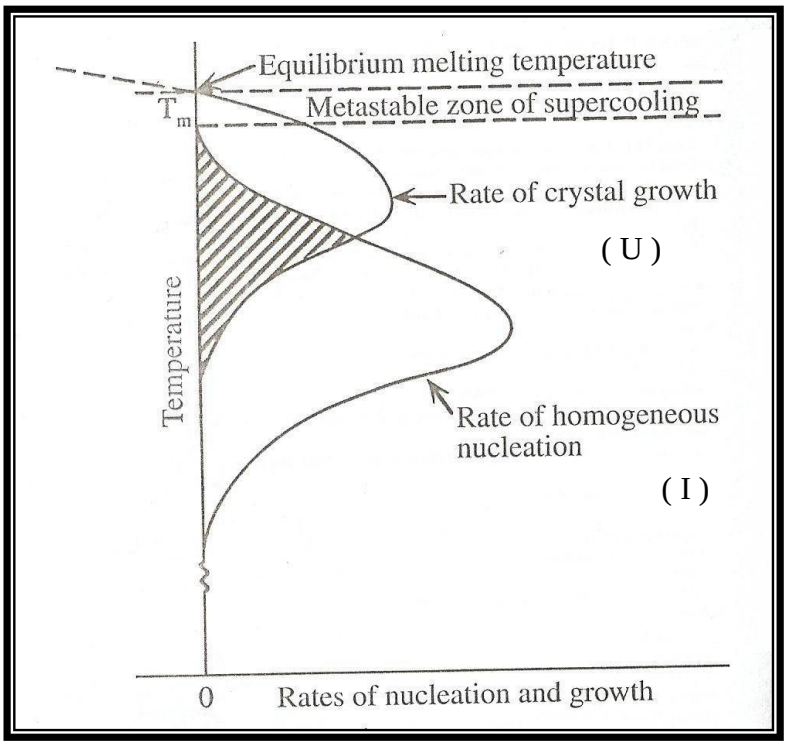


Fig. (2-3) Nucleation and crystal growth rates as a function of temperature [7,27].

The mass shrinks volume discontinuously without changing its temperature (a first –order thermodynamic transition) followed by shrinkage along the crystal state line *de* on further cooling, (there are some exceptions, for instance, water near the ice point where the liquid actually expands on cooling and on crystallization). In the absence of a significant overlap between the nucleation and the crystal growth rate

curves, the liquid at *b* passes monotones into a super cooled liquid state without the appearance of crystals. Further cooling brings about increases of viscosity at exponential rates such that the atomic configurations of the liquid are increasingly unable to redistribute themselves into a volume required by the equilibrium equation of state for the liquid. This implies that the state begins to depart from the extrapolated line *bcf*, and generates smooth curves of the type *bcg* or *bch*, depending on the cooling rate, The extent of departure per incremental cooling increases until the state line becomes nearly parallel to the crystal line [7,28].

2.2.4 Effect of Temperature on Glass Viscosity

The functional dependence of viscosity on temperature has been measured in a number of glass-forming liquids. It is generally accepted that the relationship between temperature (T) and viscosity (η) in a glass is reasonably represented by Vogel-Fulcher-Tammann (VFT) empirically derived equation, dating back to the 1920's [29,30,31]

$$\mathbf{Log_{10}\ \eta = -A + B/(T-T_o)} \text{ ---------- } (2\text{-}1)$$

Where: η = the viscosity in Pa.s ($N.s.m^{-2}$) or in poise.

A,B and T_o = constants

T = the temperature of interest (^oC)

Where base 10 logarithms are used because the large numbers are involved. The three constants A, B and T_o in above equation can be determined for a particular glass from three known temperature-viscosity points spanning at temperature rang. Glass manufacturers often tabulate the values of A, B and T_o for their products. The various steps of glass forming are determined by using the viscosity temperature (ηT) curves. Figure (2-4) shows the five viscosity reference temperatures :[29,31,32]

1. **The melting point**; corresponds to the temperature at which the viscosity is 10 Pa.s(100p); the glass is fluid enough to be considered as liquid.
2. **The working point**; represents the temperature at which the viscosity is 10^3 Pa.s(10^4 p), in the rang of this temperature the glass is readily drawn or pressed.
3. **The softening point**; the temperature at which the viscosity is $4x10^6$Pa.s ($4x10^7$ p), and is the maximum temperature at which a glass piece may be handled without causing significant dimensional alteration.
4. **The annealing point**; is the temperature at which the viscosity is 10^{12} Pa.s (10^{13}p). At this temperature, atomic diffusion is sufficiently rapid that any residual stresses may be removed within about 15 min..
5. **The strain point**; corresponds to the temperature at which the viscosity becomes $3x10^{13}$ pa.s ($3x10^{14}$ p). At a temperature below the strain point, fracture will occur before the onset of plastic deformation. The glass transition temperature will be above the strain point.

The temperature at which each these points occur depends on glass composition [33].

The relationship between viscosity of glass and its temperature is very important from the manufacturing point of view because it determines the melting conditions, the time and temperature required to homogenize a melt, the working and annealing temperatures, the rate of devitrification and the critical cooling rate, as well as the temperature of annealing of residual stresses.

2.2.5 Commercial Glass Families

Historically, development of glasses of many different compositions and properties was based on final product and manufacturing capabilities, This is still true today, but now employee safety and environmental concerns have considerable impact on development as well. Among other things, we must show how glass composition and manufacturing processes are chemically and physically interrelated[7].

Viscosity of glass is supreme. Character, every process step in glass manufacturing is performed most effectively within a certain range of melt viscosity. For example, melting of batch raw materials is generally performed best at a temperature where the melt has a viscosity of about 100 poises (p). On the other hand , pressing of molten glass into metal molds is most effective at viscosities in the range from 1000 to 10,000 P.

Another important factor is the viscosity of the melt at the liquidus temperature. The liquidus temperature of a melt is defined thermodynamically as the temperature above which the melt is stable as a liquid, Whether this liquid is very fluid or very viscous is not of thermodynamic importance. At temperature below the liquidus temperature , the melt begins to devitrify (i.e. develop crystals)[34,35].

It is customary in glass science and technology to refer to glasses as soft or hard , not in terms of physical hardness , but rather in terms of the temperatures required for soften the glass and make it flow. Soft and hard are relative terms. One glass is considered harder than another if flows easily at elevated temperatures. Glasses are called long or short depending on the slope of the viscosity-temperature curve. That's means the temperature interval between the softening and working points. The terms short and long thus refer to the relative amount of time available to

work the glass as it cools. The wide variety of viscosity - temperature relationships exhibited by commercial glasses is illustrated in figure (2-4)[7].

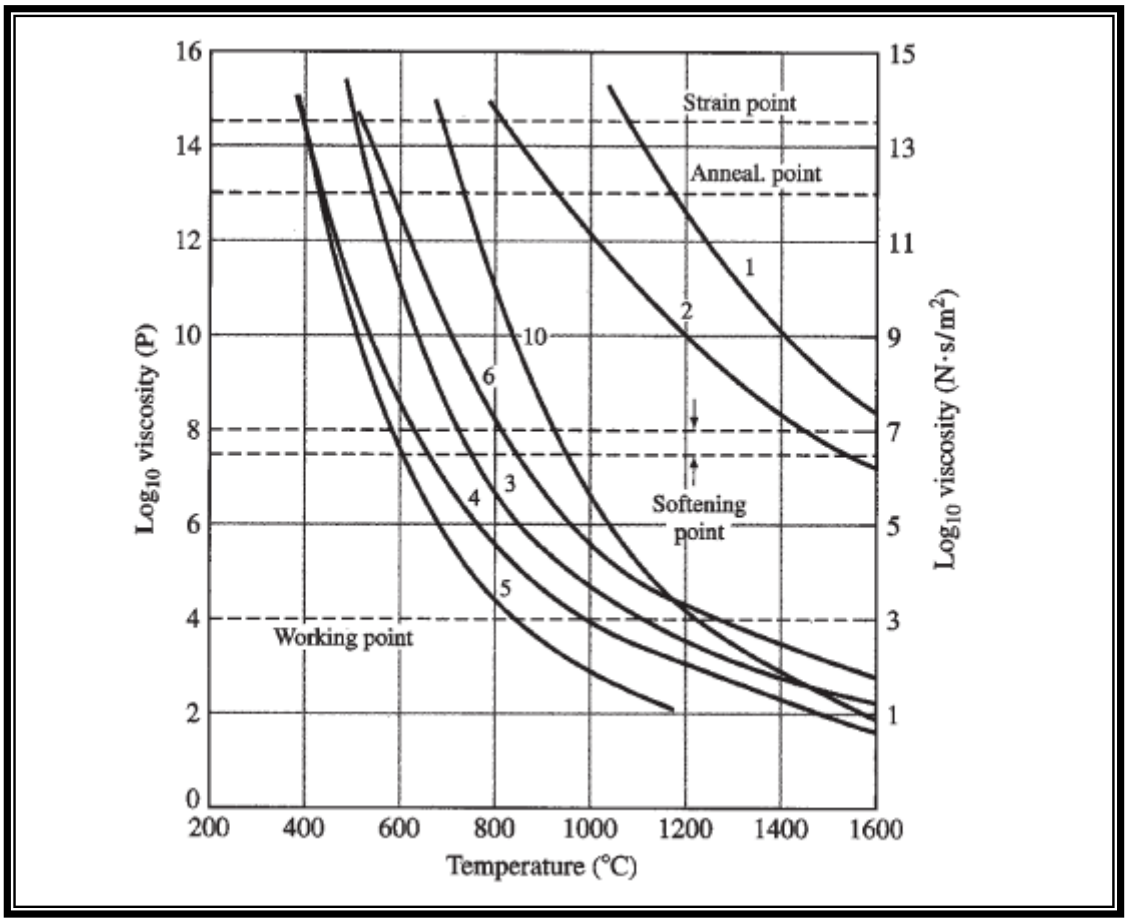


Fig. (2-4) Viscosity versus temperature characteristics for various glass compositions 1, fused silica ;2, 96% silica ; 3, soda lime (plate glass) ; 4, lead silicate (electrical) ; 5, high-lead ; 6, borosilicate (low expansion) ;10, aluminosilicate**[7,34,35].**

2.2.5.1. Soft glasses

2.2.5.1.1 Soda-Lime- silica Glasses(SLG)

Most commercial soda-lime glass compositions are based on a eutectic composition in the (Na_2O-CaO-SiO_2) phase diagram located at about 22wt%Na_2O, 5wt%CaO, and 73wt%SiO_2. A typical composition of soda-lime glass is (15Na_2O. 10CaO. 2Al_2O_3. 73SiO_2 wt%) [20]. Soda-lime glass is almost insoluble in water. Its density is about (2.3g/cm^3), hardness is about (5to7) on the Mohs scale, stiffness(E) is about 70GPa and design strength above 7MPa. It is transparent and electrical insulator with a good dielectric strength. It has a high thermal expansion (about 90x10^{-7}/^{o}C) [36,37]. It is used to make sheets for windows, bottles, jars and household lamps. After some treatments, this glass is used to manufacture safety glass, windshields and antiballistic sheets [7].

2.2.5.1.2 Lead Silicate Glass

When the lime (CaO) is substituted by lead oxide (PbO) in the soda-lime- glass mixture, the result is a glass with a higher refractive index. This glass is used for vases and other reflected uses. It absorbs gamma and x-rays, so it is used for shielding rays in technical equipments [7,36,38].

2.2.5.2. Hard glasses

2.2.5.2.1 Borosilicate Glass

This glass has a composition of (81 SiO_2. 13 B_2O_3. 4 Na_2O. 2 Al_2O_3 wt%). It has a low coefficient of thermal expansion (about 1.7x10^{-6}/^{o}C), high melting temperature (transformation rang), and excellent chemical durability. Therefore it is used for laboratories and chemical ware, but also for manufacturing of cooking ware like Pyrex and Kimax [7,39].

2.2.5.2.2 Aluminosilicate Glass

A typical composition of this glass is (58 SiO_2. 20 Al_2O_3. 16 CaO. 5 B_2O_3.1 Na_2O) wt%. This glass has a good electric properties, good resistance to chemical attack, and good use for high temperature applications. It is used for electrical and electronic applications [7].

2.2.5.2.3 Silica Glass

Silica glass is the glassy form of the chemical compound SiO_2. It has the highest refractoriness, lowest coefficient of thermal expansion among glasses ($5.5x10^{-7}/^oC$), very high chemical resistance, high optical transparency, and low dielectric constant. Major applications of this glass are lighting, semiconductor industry, optical use, high-energy laser optics, and spacecraft windows [7].

2.2.6 Lead compound applications .

Lead is one of the most widely used substance in the world, with applications as a pure metal, an alloying element in other metals, an additive in organic substances, and as an additive or primary material component in ceramics and glasses.

Table (2-1) shows the applications for lead and lead compounds in ceramic and glass technology [34].

Table(2-1) Applications for lead and lead compounds[34].

Glasses	Electronic ceramics
1. Leaded glass (“crystal”) for household products. 2. Glazes and enamels for ceramic whitewares. 3. High-index optical and ophthalmic glass. 4. Radiation shielding glass. 5. High electrical resistance glass for lamps and display technologies. 6. Glass solders and sealants for glass-to-glass joining and hermetic glass-to-metal sealing .	1. Capacitor dielectrics. 2. Piezoelectrics. 3. Electro optic devices.

Litharge (PbO) is the most important lead oxide which is used in glass and ceramic fabrication [34].

The primary reasons for adding lead to glass are to increase the refractive index of the glass, to decrease the viscosity of the glass, to increase the electrical resistivity of the glass, and to increase the x-ray absorption capability of the glass which is used for radiation shielding.

The primary reason for using lead-based in electronic ceramics is to modify the dielectric and piezoelectric properties, such as Curie point and piezoelectric coupling factor[34].

2.3 Glass- Ceramics

Glass ceramics can be described as polycrystalline materials formed , through the controlled nucleation and crystallization of glass. Glasses are melted, fabricated to shape and thermally converted to a predominantly crystalline ceramic. The glass ceramic process, therefore, is basically a simple thermal process [4,5].

Internally nucleated glass-ceramics were discovered at Corning Glass Works in the late 1950 by Stookey. The resulting product of glass-ceramic consists of a fully dense (no pores or voids) ceramic body, often of a shape that cannot be easily obtained by normal ceramic processing techniques. Some definitions of glass-ceramic require that the final product be at least 50 percent crystalline; often the percentage exceeds 90 percent. The overall glass composition is important for glass formation, workability, control of nucleation, and that of the residual glassy phase after processing is important for chemical durability[2].

Because of the requirements of various glass-forming processes that the molten glass be stable against crystallization during the forming steps, not every ceramic-composition can be formed as a glass. Perhaps the most notable example is alumina (Al_2O_3), which cannot be formed from the melt as a glass even under conditions of extremely rapid quenching.

Glass-ceramics can also be formed by powder processing methods in which glass frits are sintered and crystallized. This procedure somewhat extends the range of possible glass-ceramic compositions. It also allows for surface as well as internal nucleation. The devitrifying solder glasses are examples of powder-processed glass-ceramics[7].

In general, efficient bulk (internal) nucleation is necessary for fine uniform grain size in the final product. Nucleation can occur heterogeneously (on a nucleation-catalyzing surface as another previously precipitated crystalline phase) or homogeneously (spontaneously

throughout the volume of the glass).Homogeneous nucleation is sometimes preceded by a fine-scale glass-in-glass phase separation, in which one of the separated phases is more unstable with respect to nucleation and growth of the desired crystalline phase than was the parent glass [7].

2.3.1 Crystallization of glass

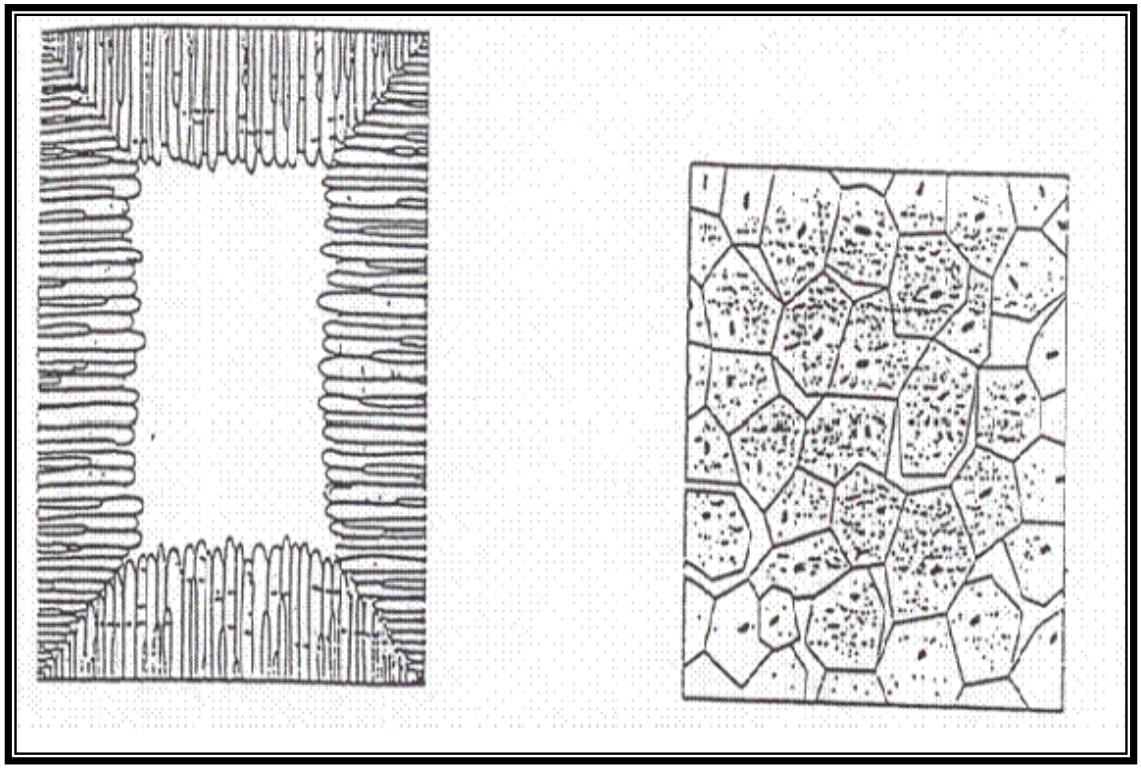
Crystallization is the process by which the well ordered or regular periodic crystalline structure is generated from the poorly ordered or random liquid structure of glass. It is generally considered as consisting of two independent processes[40]. These are the nucleation, formation of crystallization centers, and the growth of crystals on these formed centers, the steps of crystallization are: [5]

1. Nucleation

For crystallization to begin, crystal nuclei must be present. Nucleation involves the initiation of regions of longer-range atomic order, known as embryos. They are normally present in molten materials or in the super-cooled liquid [2]. When these embryos attain a critical minimum size capable of developing spontaneously into gross particles of the stable phase, they are known as nuclei. On heating a glass article, the main bulk of the material would crystallize internally and uniformly upon these tiny nuclei instead of crystallization from the surface (figure 2.5). Starting from these nuclei, the main crystalline phase would grow until it impinges on neighboring crystals, creating a crystalline material with small amounts of residual glass.

Without the internal nucleation process, as a precursor crystallization, devitrification is initiated at lower energy surface sites.

The result is a popsicle-like structure (Figure 2.5a), where the surface oriented crystals meet in a plane of weakness. Flow of the un-crystallized core glass in response to change in bulk density during crystallization commonly forces the original shape to undergo certain distortions. On the other hand, the efficient internal nucleation and growth in a viscous glassy medium characterize a fine randomly oriented crystals as shown in (figure 2.5b) with some residual glass matrix (up to 5%). Nucleation may take place either homogeneously, i.e., freely in the volume of the original



(a) (b)

Fig. (2-5) Schematic representation showing :

a. Crystallization of glass , without internal nucleation , from the surface .
b. Internal crystallization of glass showing a glass-ceramic microstructure [41].

glass phase, or heterogeneously on surfaces of the container, foreign particles or on the structural imperfection[42]. In homogeneous nucleation, the composition of the primary nuclei does not differ from

that of the main crystalline phase, whereas, in heterogeneous nucleation the crystallization of the glass is induced by introducing foreign nuclei. The nucleating agent, which is generally a metal, oxide or fluoride, is incorporated in the batch and becomes an integral part of the glass during melting.

A generalized mechanism by which nucleating agents induce crystallization can not be developed, since the role of the nucleating agents in catalyzing the formation of nuclei and the major crystalline phases undoubtedly differs from one nucleating agent to another. However, it is safe to say that the nucleating agent introduces sites of lower thermodynamic stability in the glass[43].

2. Crystal growth

After nucleation, the nucleated glasses must be heated to higher temperatures for crystal growth to proceed, in a reasonable time. This step also represents a complex process in which a number of phases may crystallize simultaneously. Commonly, the composition of the crystals differs from the composition of the original glass. This means that the crystal-glass interface is continuously changing in composition. In addition, portions of the primary crystal phase may start transformation by solid state reaction into a new structural type[44]. Some additives can markedly promote crystallization rates in glass, while others may inhibit crystal growth. This effect may be specific to particular crystal surfaces. For example, low concentrations of various transition metal ions such as iron, zinc and vanadium in alkaline earth aluminosilicate glasses, were found to increase the rate of crystal growth[45]. Chromium ions, on the other hand, were found to decrease the rate of crystal growth[46].

From a practical standpoint, it is important that the rate of crystal growth be "just right" [44]. If it is very slow, there is the danger of

deformation of the sample under its own weight before sufficient crystals form to retard flow. Conversely, if it is too fast, the heat evolved during crystallization may not be dissipated to the surroundings fast enough to avoid detrimental thermal gradients that may result in stresses sufficient to break the sample.

2.3.2 Processing

A typical temperature versus time cycle for the processing of a glass-ceramic is shown in figure (2-6), and it entails four steps:

1. *Mixing and melting*, in which raw materials such as quartz, feldspar, dolomite,and spodumene are mixed with the nucleating agents, usually TiO_2 or ZrO_2, and melted.

2. Forming, as noted below, one of the major advantages of glass-ceramics lies in the fact that they can be formed by using conventional glass forming techniques such as spinning, rolling, blowing, and casting. So complex-shaped and pore-free articles can be easily manufactured. The cooling rate during the formation process, however, has to be rapid enough to avoid crystallization or growth.

3. *Ceraming,* in which, the glass body is heated to a temperature high enough to obtain a very large nucleation rate. Efficient nucleation is the key to success of the process. The nucleation is heterogeneous, and the crystals grow on the particles of the nucleating agents, typically TiO_2 or ZrO_2, that are added to the melt.

4. *Growth*, following nucleation, the temperature is raised to a point where growth of the crystallites occurs readily. Once the desired microstructure is achieved. the parts are cooled. During this stage the body usually shrinks slightly by about 1 to 5 percent [29].

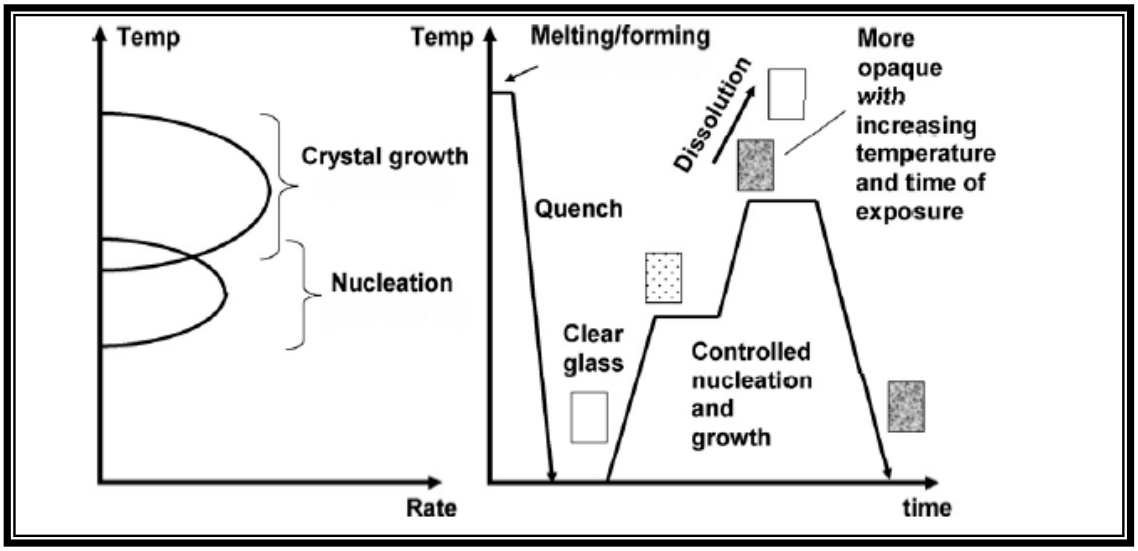


Fig. (2-6) Typical processing of glass – ceramic materials showing temperature dependence of transformation rates as well as temperature profile during processing[27,47,48].

2.3.3 Crystallization parameters

1. Base glass composition

Numerous researchers have showed that there are many thousands of chemical and mineral compositions that could be formed into glasses and subsequently crystallized. In spite of this proliferation of compositions, relatively few have appeared in marketable products[31].

2. Nucleating agents

Nucleating agents (i.e. heterogeneous nucleation) are widely used in most of glass-ceramic production processes. Their effect is so extensive that it could be safely said that a large number of glass-ceramic products is produced with nucleating agents. Changing the nucleating agents (its concentration and/or mixing it with another agent) greatly change the appearance, crystalline phases and crystal size in the resultant glass-ceramics[2,21,49].

The most commonly used nucleating agents are TiO_2 and $ZrO_2.P_2O_5$. the Pt group and noble metals, and fluorides are also used. TiO_2,is often used in concentrations of 4 to 12 wt%; ZrO_2 is used in concentrations near its solubility limit (4 to 5 wt% in most silicate melts) In some cases. ZrO_2 and TiO_2 are used in combination to obtain desired properties in the final crystallized bodies.

The Pt group and noble metal nucleating agents seem to function by directly forming a crystalline nucleating phase in a precipitation process The major crystalline phase or phases subsequently grow on particles of the nucleating phase. Such a process could also be operative in the case of oxide nucleating agents [41,50].

3. Heat-treatment

The nucleation and crystallization processes, which are necessary for the transformation of glass into glass-ceramic, are brought about by heat-treatment. The rates of nucleation and crystal growth can then be controlled during the heat treatment process. The rate of maximum nucleation is often important in the heat treatment process[40].

The nucleation and growth rate curves are not always completely separated, and the amount of overlap will depend upon the particular system concerned. If the curves are significantly overlapped, e.g. figure 2.7a, only partial control is possible. In this case, as soon as nuclei form

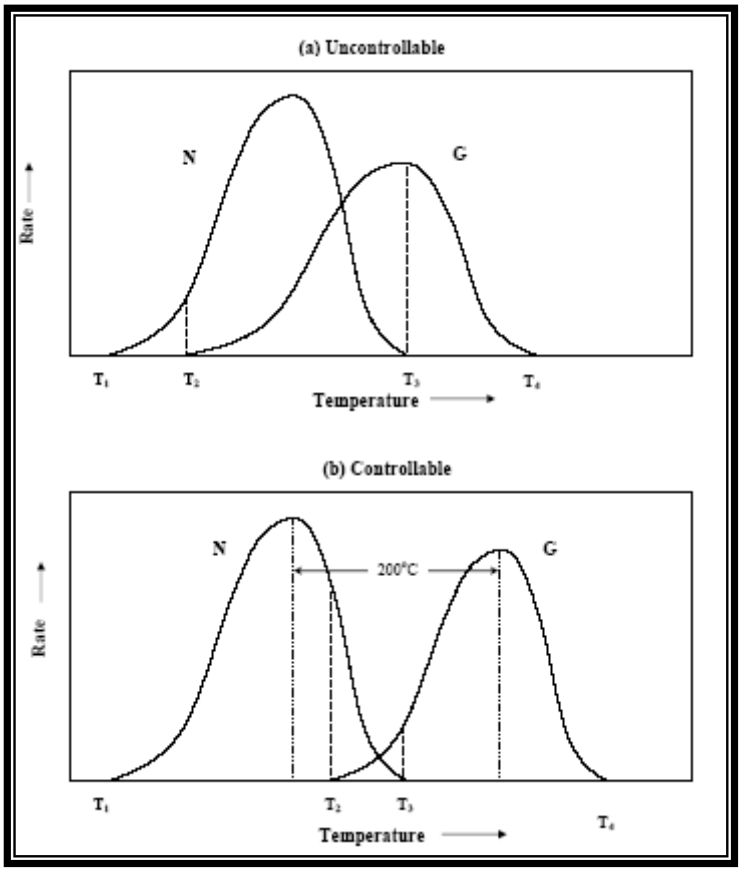


Fig.(2-7) Nucleation and crystallization rate curves [5,25]

between T2 and T3 comparatively few crystals can grow with a wide range of crystal size. On the other hand, when the overlap of the two curves is minimum, e.g. Fig. 2.7b, complete control is possible. Therefore, by holding the glass at a temperature between T1 and T2, it is possible to control the number of nuclei. After the required numbers of nuclei are formed, the glass is heated in the range T_3 to T_4 where crystal growth takes place.

In well controlled (good) glass-ceramic systems, there is generally considerable separation between the two curves, and it is obvious that the exact temperatures chosen for preparation will depend upon these requirements. For example, if a large crystal size is required, a moderate rate of nucleation combined with a high crystallization rate is necessary,

while for small crystal sizes the maximum nucleation rate combined with a moderate crystal growth rate should be chosen. If the shortest possible heat-treatment time is desired and no other conditions required, then maximum rates in both steps are suitable. Generally, a lower temperature holding stage is necessary in the heat-treatment cycle to serve to "nucleate" the glass after which crystals can grow during a subsequent higher temperature stage on the formed nuclei [5].

2.3.4 Properties and Advantages of Glass-Ceramics

Glass-ceramics have been shown the favorable thermal, chemical, biological and dielectric properties, generally superior to metals and organic polymers.

Glass-ceramics offer several advantages over both the glassy and crystalline phases, including :

1. the combination of easy fabrication and outstanding mechanical properties [7].

2. Usually the presence of the crystalline phase results in much higher deformation temperatures than the corresponding glasses of the same composition. For example, many oxides have *Tg* values of 400 to 450°C and soften readily at temperatures above 600°C. A glass-ceramic of the same composition, however, can retain its mechanical integrity and rigidity to temperatures as high as 1000 to 1200°C [29].

3. The strength and toughness of glass-ceramics are usually higher than those of glasses. For example, the strength of a typical glass plate is on the order of 100 MPa, while that of glass-ceramics can be several times higher. The reason, is that the crystals present in the glass-ceramics tend

to limit the size of the flaws present in the material, increasing its strength. Furthermore, the presence of the crystalline phase enhances toughness [29].

4. As with glasses, the properties (most notably the thermal expansion coefficients) of glass-ceramics can be controlled by adjusting the composition. In many applications, such as glass-metal seals and the joining of materials, it is very important to match the thermal expansion coefficients to avoid the generation of thermal stresses [29].

5. A uniform chemical composition of glass-ceramics can easily be achieved since the parent glass can be obtained in a homogeneous state. This process lends a very fine-grain microstructure with almost no porosity, so most glass-ceramics have high mechanical strength and good electrical insulation [5].

6. A wide practical application of glass-ceramics can be obtained by the variation of the chemical composition of the parent glass and the heat-treatment. Thus, the physical properties of glass-ceramics can be varied.

7. The control of the shape and dimensions of the glass-ceramics products can be achieved without too much difficulty. While in conventional ceramic materials, a relatively large shrinkage (by volume) occur during drying and firing processes and so this change in dimensions may be accompanied by distortion [5].

Glass-ceramics have many other advantages. Their uniform, fine-grain randomly oriented polycrystalline microstructures allow high reproducibility of properties. Usually the conversion of glass into a glass-

ceramic involves only minor overall changes in volume with low or zero porosity, which is important for high strength and good electrical properties . The small dimensional changes during the manufacturing process are also valuable for many applications. The constituents of most glass-ceramics are, generally, inexpensive, being derived from relatively low-cost batch materials. Processing temperatures (300-1000 ˚C) are usually lower than those needed to process engineering ceramics such as alumina or silicon carbide. Because a wide range of formulations can be used, physical properties can often be tailored to suit particular applications[51].

2.4 Electrical properties

The properties of ceramics, glasses, and glass - ceramics that are of most interest to the electrical or electronics design engineer include resistivity, dielectric constant, dielectric loss, dielectric strength, and magnetic permeability. The manner in which these properties vary as a function of temperature, frequency, and electric field determines the suitability of materials for specific applications [7].

2.4.1 Dielectric properties

Ceramic dielectrics materials will not conduct electricity and as such are of critical importance as capacitive elements in electronic applications and as insulators [29]. For these applications the properties of most concern are the dielectric constant, dielectric loss factor, and dielectric strength. New devices and new applications are continually increasing the frequency range and the range of environmental conditions, particularly temperature, that are of practical interest. Most of the high-frequency applications related to electrical properties are concerned with dielectrics [41].

For applications as capacitors and as electrical insulation, organic plastics are available; they are usually cheaper and can be fabricated with better dimensional accuracy than ceramics. The advantages of ceramics, which frequently indicate their use, are superior electrical properties, absence of creep or deformation under stresses at room temperature, greater resistance to environmental changes (particularly at high temperatures at which plastics frequently oxidize, gasify, or decompose), and the ability to form gas tight seals with metals and become an integral part of an electronic device. It should be noted that the selection of a particular dielectric frequently depends on its ability to

be formed as a gastight part to operate under unusual environmental conditions, on its suitable thermal-expansion characteristics, on its satisfactory thermal stress resistance and impact resistance, on its ability to be formed into complex shapes with good dimensional characteristics, and on other characteristics which are completely independent of the electrical behavior but are essential for the building of practical devices [41].

2.4.2 Electrical phenomena

In this section we wish to define the dielectric properties that are of interest for ceramic applications. These include the *dielectric constant, dielectric loss factor,* and *dielectric strength.* It is essential that ceramists understand why electrical engineers, their customers, find these particular sets of properties and formulations useful. This aspect is discussed here, but without going into the mathematical formulations required for actual application to circuit design. Because of space limitations, mathematical derivations are kept to those essential for understanding the phenomenological aspects [41].

2.4.2.1 Polarization

The application of an electric field to any solid will result in a separation of its charges, the charge of equal magnitude, but of opposite polarity, separated by some distance is called dipole. The product of magnitude of charge and the distance between them is called dipole moment. It is generally designed by the symbol (p) and is measured in terms of unit called (Coulumb . meter).

Let q = Magnitude of each charge , and

r = Distance between the charge.

Then the dipole moment,

$$p = q * r \quad \text{in (coulumb . meter)} \text{ ---------- (2-2)}$$

The dipole moment per unit volume is known as polarization. It is generally designated by letter (P) and is measured in terms of units called coulumb . meter per cubic meter.

Let P = Dipole moment in (coulumb . meter), and

V = Volume of dielectric in cubic meter.

Then the polarization

$$P = p / V \text{ in } (C.m/m^3) \text{ or } (C/m^2) [75] \text{ --------(2-3)}$$

The dielectric properties can vary widely among solids and are a function of temperature, frequency of applied field, humidity, crystal structure, and other external factors [29].

2.4.2.1.1 Basic Theory

Before discussion of polarization, it is imperative to understand how one measures polarization and to gain a qualitative understanding of how readily or not so readily polarizable a solid is. Consider two metal parallel plates of area *A* separated by a distance *d* in vacuum, and joint these plates to the simple electric circuit, as shown in (Fig. 2-8a), then closed the circuit to give an transient surge of current that rapidly decays to zero [29].

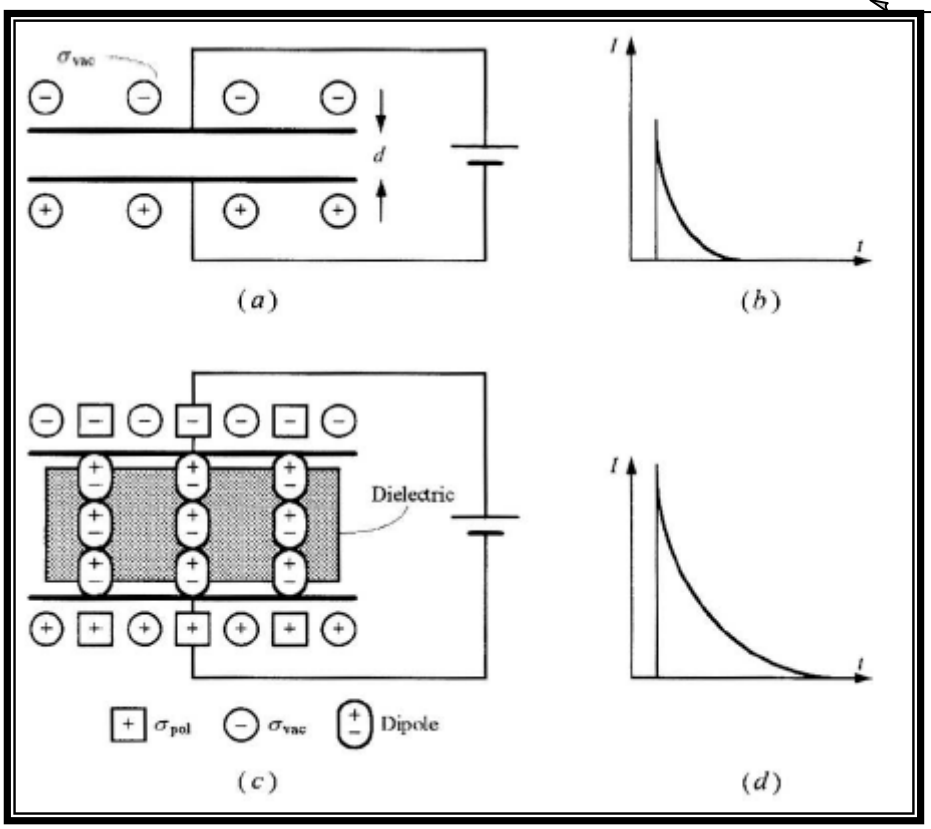


Fig. (2-8) *(a)* Parallel-plate capacitor of area *A* and separation *d* in vacuum attached to a voltage source. *(b)* Closing of the circuit causes a transient surge of current to flow through the circuit. Charge stored on the capacitor is equal to the area under the curve.*(c)* Same as *(a)* except that now a dielectric is placed between the plates. *(d)* Closing of the circuit results in a charge stored on the parallel plates that has to be greater than that stored in *(b)* [29].

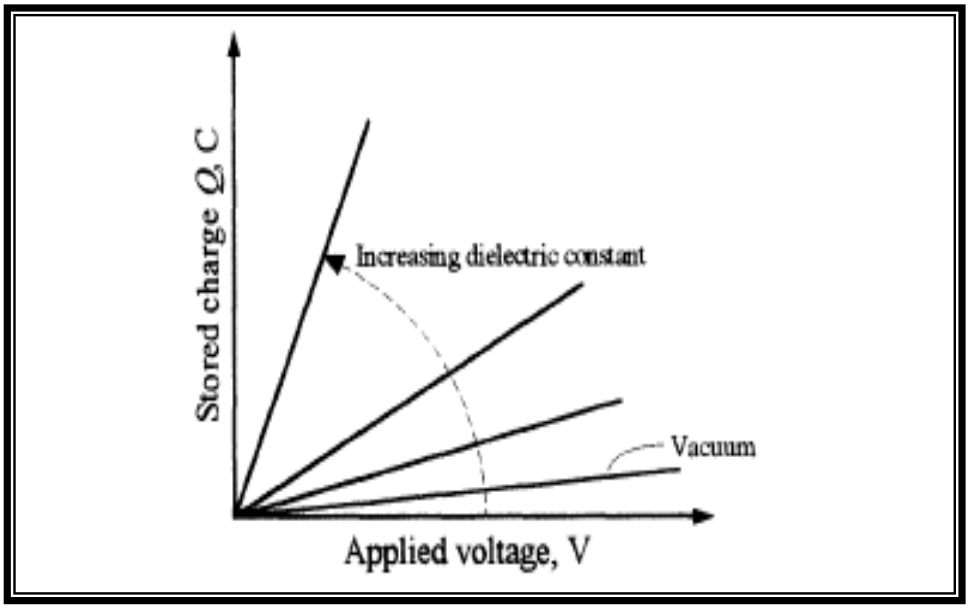


Fig. (2-9) Functional dependence of Q on applied voltage . slope of curve is related to the dielectric constant of the material [29].

As shown in figure 2-8 *b*.

$$Q = \int I\, dt \quad \text{---------- (2.4)}$$

Where Q is the stored charge between capacitors plates and represents the area under the *(I)* versus (*t*) curve.

Repeating the experiment at different voltages (*V)* and plotting (*Q)* versus *(V)* should yield a straight line, as shown in Fig. 2-9 . In other words, the well-known relationship:

$$Q = CV \quad \text{----------(2.5)}$$

The slope of the *Q* versus *V* curve is the **capacitance** C_o (free space)of the parallel plates in vacuum, given by

$$C_{vac} = \frac{\varepsilon_o A}{d} \quad \text{---------- (2.6)}$$

where ε_o is the permittivity of free space, which is a constant equal to

$\varepsilon_o = \frac{1}{36\pi} * 10^{-9} \frac{farads}{meter}$ [7] $= 8.85 * 10^{-12} C^2/(J .m)$. The units of capacitance are farads (F), where $1\ F = 1\ C/V = 1\ C^2/J$.[29]

If a dielectric (which can be a gas, solid, or liquid) is introduced between the plates of the capacitor (Fig. 2-8 c) and the aforementioned experiment is repeated, the current that flows through the external circuit and is stored on the capacitor plates will increase (Fig. 2-8d). Repeating the experiment at different voltages and plotting the total charge stored on the capacitor versus the voltage applied will again result in a straight line but with a larger slope than that for vacuum (Fig. 2-9). In other words, Eq. (2.6) is now modified to read

$$C = \frac{\varepsilon . A}{d} \quad \text{---------- (2.7)}$$

where ε is the *permittivity* of the material between the plates.

The *relative permittivity or dielectric constant* of a material (ε_r) is defined as

$$\varepsilon_r = \frac{\varepsilon}{\varepsilon_o} \quad \text{---------- (2.8)}$$

Since ε is always greater than ε_o , the minimum value for ε_r is (1). By combining Eqs. (2.7) and (2.8), the capacitance of the metal plates separated by the dielectric is

$$C = \frac{\varepsilon_r \varepsilon_o A}{d} = \varepsilon_r . Cvac \quad \text{--------- (2.9)}$$

Thus (ε_r) is a dimensionless parameter that compares the charge-storing capacity of a material to that of vacuum.

The foregoing discussion can be summarized as follows: when a voltage is applied to a parallel-plate capacitor in vacuum, the capacitor will store charge. In the presence of a dielectric, an additional polarization happens within that dielectric which allows the capacitor to store more charge [29].

2.4.2.1.2 Mechanisms of polarization

There are four basic mechanisms that contribute to polarization : [7]

1. *Electronic polarization* In the presence of an applied field, the cloud of electrons is displaced relative to the positive nucleus of the atom or molecule, creating an induced dipole moment. Electronic polarization is essentially independent of temperature and may occur very rapidly. The dielectric constant may therefore exist at very high frequencies, up to 10^{17} Hz, in ultraviolet range.

2. *Ionic polarization* Ionic polarization occurs in ionically bonded materials when the positive and negative ions undergo a relative displacement to each other in the presence of an applied electric field,

Ionic polarization is somewhat insensitive to temperature and occurs at high frequencies, up to 10^{13} Hz.

3. *Molecular(orientational) polarization*. Certain molecule structures create permanent dipoles that exist even in the absence of an electric field, These may be rotated by an applied electric field, generating a degree of polarization by orientation. Molecular polarization is inversely proportional to temperature and occurs only at low to moderate frequencies. Molecular polarization does not occur to a great extent in ceramics, and is more prevalent in organic materials and liquids, such as water.
4. *Space charge polarization*. Space charge polarization exists as a result of charges derived from contaminants or irregularities that exist within the dielectric. These charges exist to a greater or lesser degree in all crystal lattices and are partly mobile. Consequently, they will migrate in the presence of an applied electric field. Space charge polarization occurs only at very low frequencies.

In a given material. more than one type of polarization can exist and the net polarization is given by

$$P_t = P_e + P_m + P_i + P_s \text{ ---------- } (2 – 10)$$

Where :

P_t = Total polarization,

P_e = Electronic polarization,

P_m = Molecular polarization,

P_i = Ionic polarization, and

P_s = Space charge polarization.

Normally, the dipoles are randomly oriented in the material and the resulting internal electric field is zero. In the presence of an external

applied electric field, the dipoles become oriented as shown in figure (2-10). There are two common ways to categorize dielectric materials: as polar or nonpolar, and as paraelectric or ferroclectric. Polar materials include those that are primarily molecular in nature. such as water, and nonpolar materials include both electronically and ironically polarized materials. Paraelectric materials are polarized only in the presence of an applied electric field and lose their polarization when the field is removed. Ferroelectric materials retain a degree of polarization after the electric field is removed. Materials used as ceramic substrates are usually nonpolar, and paraelectric in nature. An exception is silicon carbide, which has a degree of molecular polarization [7,75].

In the presence of an electric field that is changing at a high frequency, the polarity of the dipoles must change at the same rate as the polarity of the signal in order to maintain the dielectric constant at the same level. Some materials are excellent dielectrics at low frequencies, but the dielectric qualities drop off rapidly as the frequency increases. Electronic polarization, which involves only displacement of free charge and not ions, responds more rapidly to the changes in the direction of the electric field, and remains viable up to about 10^{17} Hz the polarization effect of ionic displacement begins to fall off at about 10^{13} Hz, and molecular and space charge polarizations fall off at still lower frequencies. The frequency response of the different types is shown in figure(2-11), which also illustrates that the dielectric constant decreases with frequency. Changing the polarity of the dipoles requires a finite amount of energy and time. The energy is dissipated as internal heat, quantified by a parameter called the *loss tangent* or *dissipation factor* [7,75].

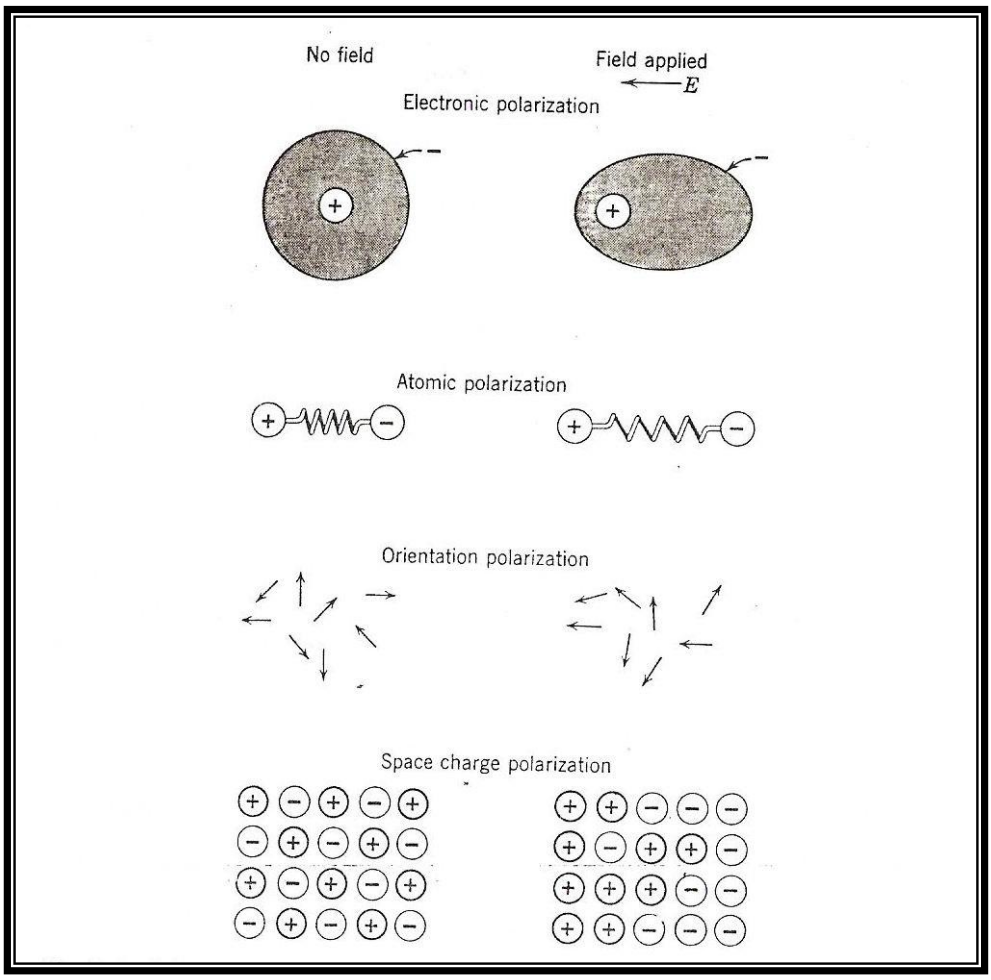


Fig. (2-10) Schematic representation of different mechanism of polarization.[41]

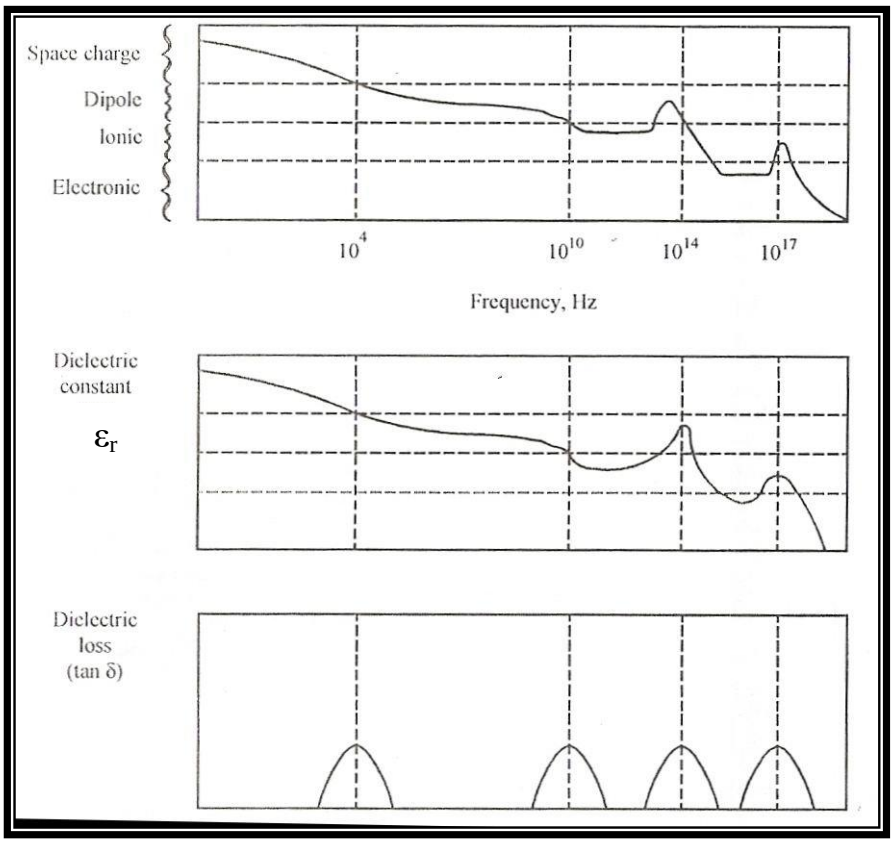


Fig. (2-11) Frequency effects on dielectric materials. [7,29]

2.4.2.2 Loss tangent , Dissipation Factor (DF).

It has been observed that when an alternating voltage is applied across a capacitor, having free space or vacuum as dielectric .The

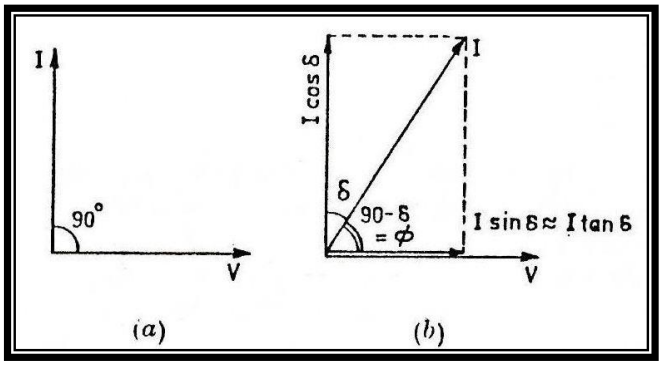


Fig. (2-12) Dielectric loss [75].

polarization of the dielectric is in phase with the voltage. In such a case, the resulting current leads the applied voltage by an angle of 90° as shown in figure (2-12)(a). A phase angle of 90° indicates that there is an electrical energy in the free space during the charging of the capacitor [7,75,29,57,52].

Now consider a capacitor with a real dielectric inside it. When the alternating voltage is applied to such a capacitor, the polarization is no longer in phase with the applied voltage. In such a case, the resulting current leads the applied voltage by an angle, Ø = 90° - δ as shown in figure (2-12)(b), where δ is known as loss angle. The current can be factorized into the following two components:

1- A component of current leading the applied voltage by an angle of 90°. This component is denoted by (I cos δ) and is called imaginary component of current. It is similar to a current in an ideal capacitor.
2- A component of current in phase or parallel to the applied voltage. This component is denoted by (I sin δ) and is called real component of current. This component results in a power loss within the dielectric.

If δ is small then,

$$\sin\delta \approx \delta \approx \tan\delta$$

The quantity tan δ is a measure of power loss. It is commonly known as loss tangent, dissipation factor or power factor. It may be defined as the ratio of imaginary component of dielectric constant (ε_r'') to the real component (ε_r') [52, 29,75]. Thus power factor,

$$\tan\delta = \frac{\varepsilon_o''}{\varepsilon_r'} \quad \text{----------(2-11)}$$

It is evident from the above relation that if there are no losses, then $\varepsilon_r'' = 0$. this means that $\delta = 0$ and current in a capacitor leads the applied voltage by 90°.

The dielectric loss is the energy absorbed by the dielectric from the applied voltage and is proportional to the imaginary compound of the dielectric constant (ε_r''). It occurs due to the fact that during charging of a capacitor, permanent dipoles require some energy to align themselves in the direction of the applied electric field. This energy is dissipated within the dielectric in the form of heat.

The dielectric loss is a function of the frequency of the applied field. Its value is very high at certain frequencies lying in the audio and radio range as shown as in figure (2-11). The increased dielectric loss at such frequencies is because of a resonance. The resonance occurs at these frequencies, when the period of the voltage is in the same range as the relaxation time of the polarization process.

2.4.2.3 Dielectric Capacitance

The electrical engineer is most concerned with dielectric materials in relation to a capacitor in an electrical circuit. The principal characteristic of a capacitor is that an electrical charge Q can be stored. The charge on a capacitor is

$$Q = C\,V \quad \text{---------- (2.12)}$$

where V is the applied voltage and C is the capacitance. The voltage is directly proportional to the amount of charge stored, and the current passing through the capacitor is given by

$$V = \frac{Q}{C} = \frac{\int I dt}{C} \qquad I = C\,\frac{dV}{dt} \qquad \text{---------- (2.13)}$$

With a sinusoidal voltage

$$V = V_o \exp iwt \qquad \text{---------- (2.14)}$$

as used in ac circuits, a charging current results

$$I_c = iwCV \qquad \text{--------- (2.15)}$$

which is exactly 90° advanced in phase in relation to the applied voltage. In Eqs. 2.14 and 2.15, i equals $\sqrt{-1}$, and w equals $2\pi f$, where f is the frequency in cycles per second.

The capacitance C contains both a geometrical and a material factor. For a large plate capacitor of area A and thickness d the geometrical capacitance in *vacuo* is given by

$$C_o = \frac{A}{d}\ \varepsilon_o \qquad \text{----------(2.16)}$$

where ε_o is the permittivity of a vacuum. If a ceramic material of permittivity ε is inserted between the capacitor plates,

$$C = C_o\,\frac{\varepsilon}{\varepsilon_o} = C_o.\,\varepsilon_r \qquad \text{---------- (2.17)}$$

where ε_r is the *relative permittivity* or *relative dielectric constant*. This is the material property determining the capacitance of a circuit element and is of principal concern to the ceramist [41].

from eq. (2.16 , 2.17) we obtained

$$C_p = \frac{A.\varepsilon}{d.\varepsilon_o} \qquad \text{---------- (2.18)}$$

Therefore

$$\varepsilon = \frac{C_p.d}{A.\varepsilon_o} \quad \text{---------- (2.19)}$$

2.4.2.4 Dielectric Constant (relative permittivity)

It can best be defined as the ratio of the amount or electrical charge that can be stored in a slab of material between two parallel metal plates to the a mount of electrical charge that can be stored by plates of the same area and separation when the space is evacuated [7]. It is an important property of dielectric, because it determines the capacity of a dielectric to develop charges on its surface due to polarization. Thus a good dielectric should have a high value of dielectric constant [75].

2.4.2.5 Dielectric Breakdown (dielectric strength)

When a dielectric is subjected to an ever-increasing electric field, at some points a short circuit develops across it. **Dielectric breakdown** is defined as the voltage gradient or electric field sufficient to cause the short circuit. This phenomenon depends on many factors, such as sample thickness, temperature, electrode composition and shape, and porosity.

In ceramics, there are two basic types of breakdown: intrinsic and thermal [29,52].

• *Intrinsic breakdown:* In this mechanism, electrons in the conduction band are accelerated to such a point that they start to ionize lattice ions. As more ions are ionized and the number of free electrons increases, an avalanche effect is created. Clearly, the higher the electric field applied, the faster the electrons will be accelerated and the more likely this breakdown mechanism will be.

• *Thermal breakdown:* The criterion for thermal breakdown is that the rate of heat generation in the dielectric, as a result of losses, must be greater than the rate of heat removal from the sample. Whenever this condition occurs the dielectric will heat up, which in turn will increase its conductivity, which causes further heating, etc. This is termed *thermal breakdown* or *thermal runaway* [29].

$$\text{Dielectric Strength} = \frac{V_{av}}{h} \text{ ----------(2-20)}$$

As:

V_{av}: Rate of breakdown voltage (kV)

h : Thickness (mm)

Chapter Three
EXPERIMENTAL PART

3.1 Introduction

In this chapter, identification of raw materials (oxides, carbonate), nature each of them, reasons for their using, ways of their preparing, and then identify the steps used to form the test samples of glass, glass ceramics, will be discussed. Also, investigation of physical and electrical properties will be included. Figures (3-1 a) and (3-1 b) show the followed route by which the glass and glass ceramics prepared, and figure (3-1 c) show the flow diagram of testing.

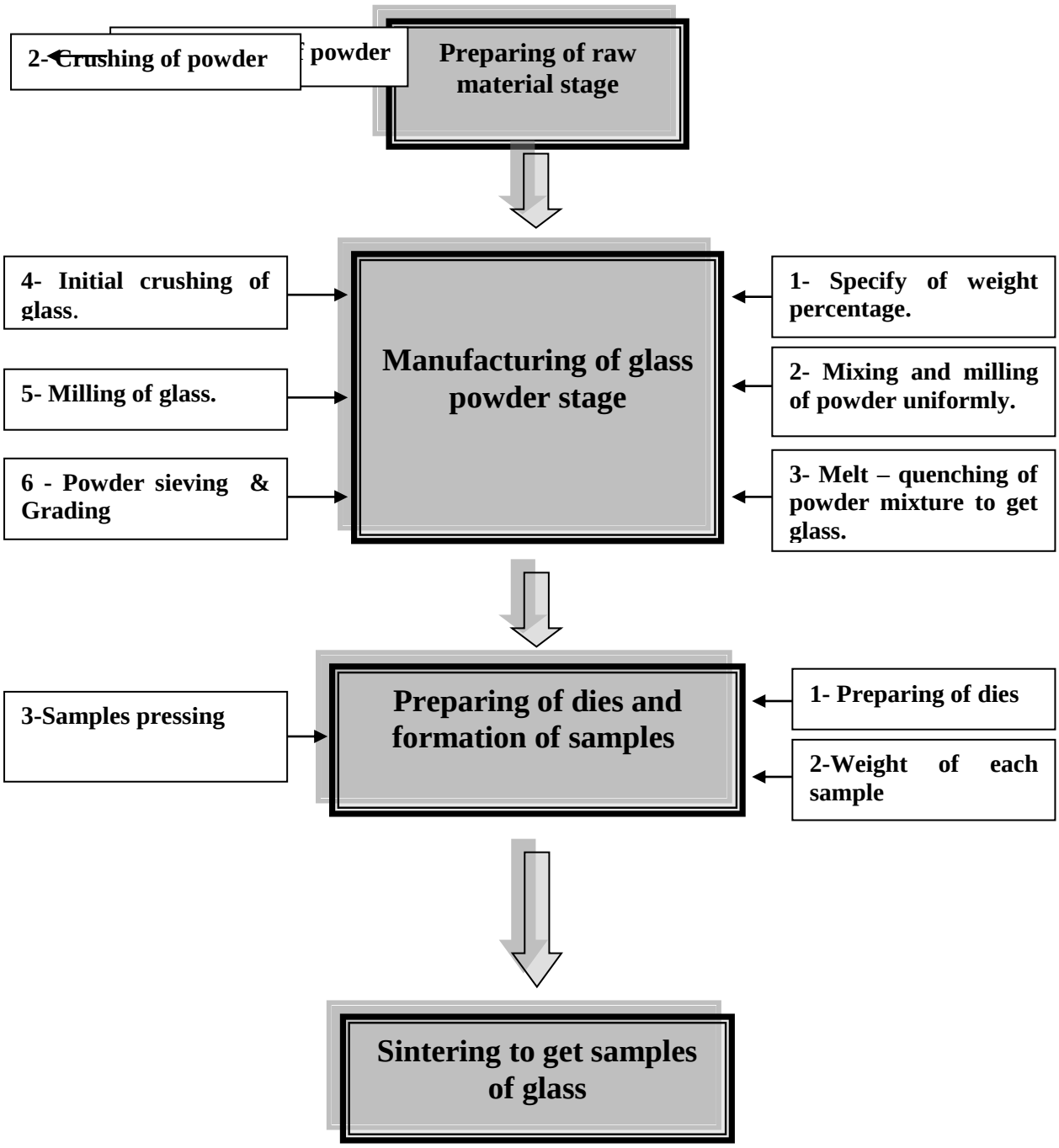


Fig. (3-1 a) Flow Diagram of Experimental steps to get glass samples (B1,B2,B3)

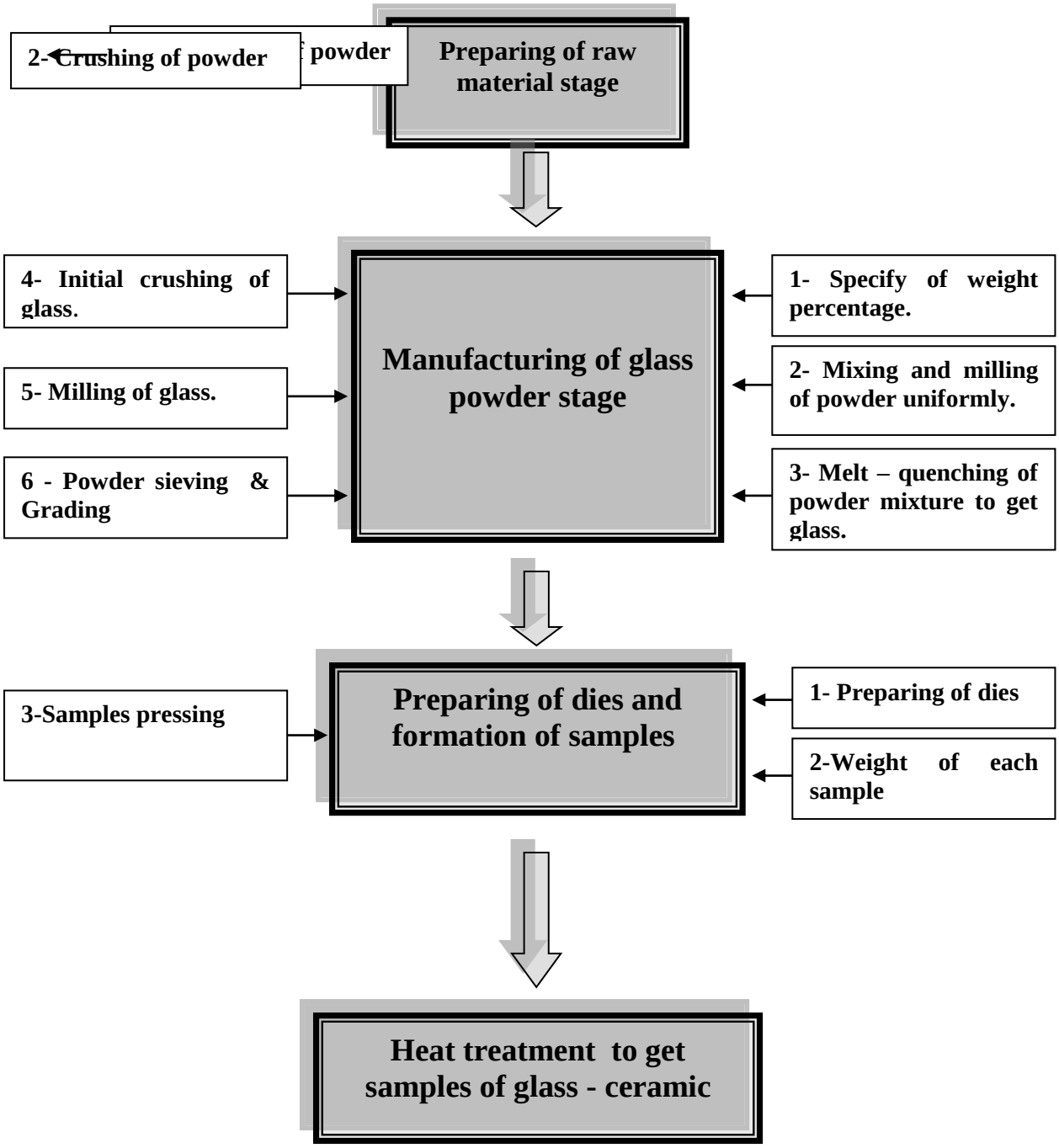


Fig. (3-1 b) Flow Diagram of Experimental steps to get glass-ceramic samples (C1,C2,C3)

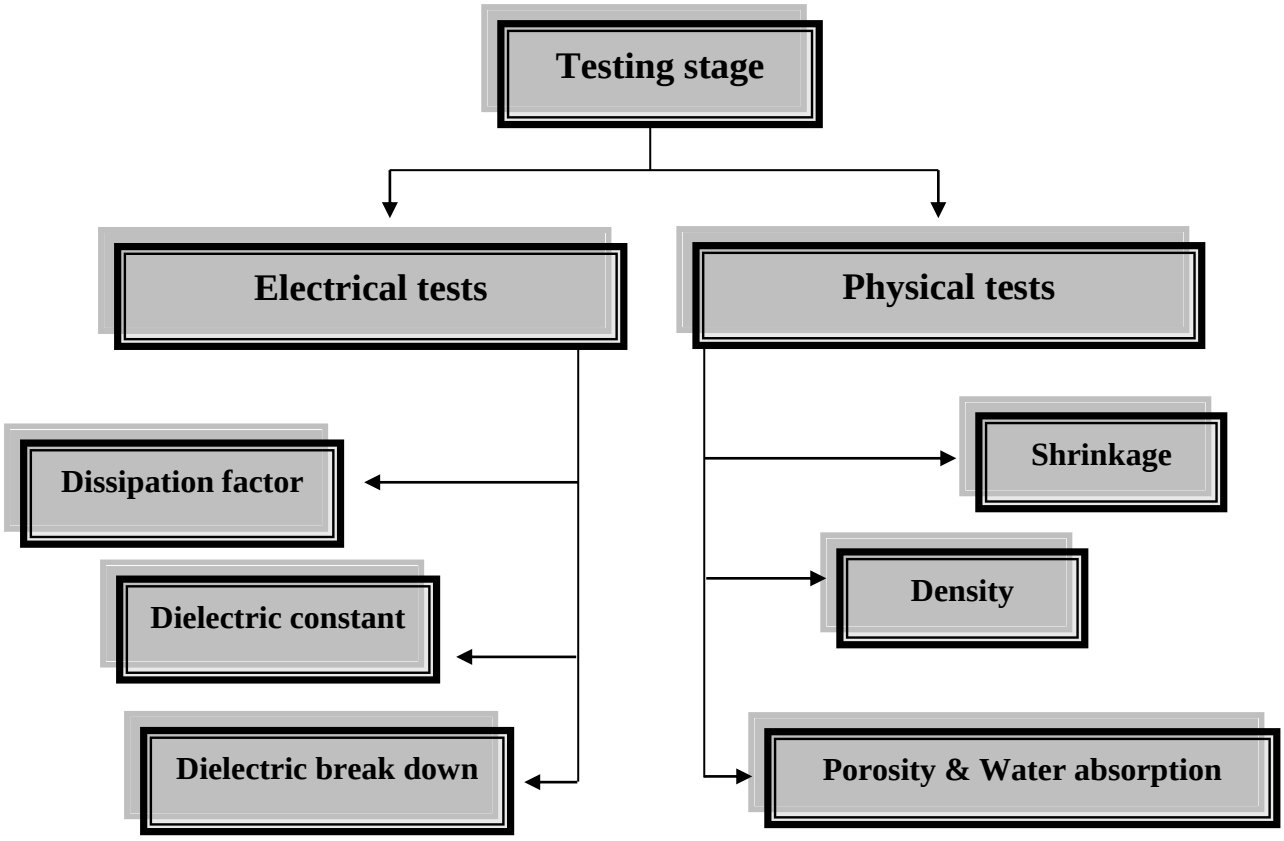


Fig. (3-1 c) Flow Diagram of Testing

3.2 Raw materials

Lead glass was selected in this research for several reasons, notably the low temperature degree of melting, where the manufacturing of glass and glass ceramics basically depend on the temperature due to the use of (melt-quenching technique). As well as the lead glass has a good electrical properties.

The other types of glass such as, fused silica, borosilicate glass which needs higher temperature (> 1750°C), weren't adopted because the higher temperature furnaces wasn't available.

Lead glass consists of the following oxides :

3.2.1 PbO

Its color is yellow. At low molar compositions it acts as a network modifier. It is a good flux like alkaline earth oxides. It has less adverse effect on thermal expansion or chemical durability than alkalis. It significantly increases the reflective index, elastic modulus and working range of the material. At high lead oxide concentration (greater than 50 percent PbO by weight), Lead oxide acts as a network former. This is especially true in binary lead silicates[7]. The presence of lead oxide in the sample increases the x-ray absorption capability of the glass [34].

3.2.2 Al_2O_3

Alumina acts as intermediate compound, can be considered it as network modifier, it improves chemical durability [7].

3.2.3 SiO_2 (network former)

Silica laboratory was used, but due to bad storage has been a process of cleaning the powder from the dust and particulates using a flotation and then drying the powder at temperatures of 110ºC for 24 hours and then milling the Silica by using an electric ball mill and used Silica from

the Western Sahara specifically a quarry or Ardmp Um urdhama. and make it a way that chemical analysis of volumetric method to determine the percentage of Silica and impurities existing in this examination was conducted in the laboratories of the company's public geological survey and mining in order to determine the number of main components and impurities Remaining as shown in table (3-1)

Table (3-1) Chemical analysis of silica [53].

Total	L.O.I	K_2O	Al_2O_3	SiO_2
100 %	Rem.	0.17	0.31	98.34

3.2.4 K_2O

Alkali earth oxide(from potash) has a larger ionic size , so is less mobile and therefore better for electrical insulation properties , it acts as flux oxide, but has been used (potassium carbonate) (K_2CO_3) instead for because it works as flux better than oxide, was calculated from the ratios of the equivalent oxide by combustion equations on the assumption that liberalization (CO_2) during combustion as shown as below. but not quite as good a flux as soda [7].

$$K_2CO_3 \longrightarrow K_2O + CO_2 \uparrow \text{----------(3-1)}$$

3.2.5 Na_2O

Alkali earth oxide (from soda ash) (Na_2CO_3). It is considered the most important alkali for glass making. It is better flux oxide than that of K_2O, it make the glass easier to melt. The melt viscosity is greatly decreased relative to that of silica at all temperatures. This makes melting

and forming easier. hence, alkali – containing glass is more economic as a product . further , since the alkali ions are somewhat mobile within the glass network, the glass becomes more electrically (ionically) conductive , especially as temperature increases , thus decreasing its effectiveness as an insulator. The calculation of the ratio of the equivalent oxide by combustion equations on the assumption that liberalization (CO_2) during combustion as shown as below [7,54].

$$Na_2CO_3 \longrightarrow Na_2O + CO_2 \uparrow \text{----------(3-2)}$$

3.3 Selection of glass compositions

After selection of lead glass in this research and its raw materials, three batches of lead glass composition have been prepared. Table (3-2) show the compositions of these batches.

Table (3-2) composition of lead-glasses

Oxide	B1 %wt	B2 %wt	B3 %wt
SiO_2	63	59	55
Al_2O_3	1	1	1
Na_2O	8	8	8
K_2O	6	10	14
PbO	22	22	22

The amount of mass has been selected (300 g) of the compositions (B1, B2, B3) and was calculated on the basis of its percentage components. Table (3-2) show 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 each of Na_2CO_3 and K_2CO_3, as the CO_2 is liberated during the melting process.

3.4 Equipments

1) Drying oven
2) Electrical furnace (for melting) (1200 ºC)
3) Sensitive balance which has accuracy (0.0001 g)
4) Porcelain ball mill
5) Jugs , mixing containers , clamps, graphite sticks
6) Electrical turning
7) Crucibles made from SiC in different sizes.
8) Open furnace (1200°C) for melting
9) Electrical sieve
10) The pressing dies (double action die)
11) Electronic digital caliper which has accuracy (0.01 mm)
12) Laboratory mixer (magnetic stirrer thermostat hotplate)
13) Electrical Crushers
14) Hydraulic press
15) Laser thermometer
16) Initial crushing mill
17) Electrical furnace(for thermal treatment) programmer by current up to the temperature (1200 ºC)
18) Heater
19) X-ray diffraction device
20) L.C.R device
21) (BAUR) PGO device

3.5 Manufacturing Steps of lead glass powder

These steps are generally followed for the batches (B1, B2, B3):

1) One of the most important material in the batch, which is needed to preparing is (SiO_2) as needed to clean up and removal of salts and particulates resulting from bad storage, this operation is carried out using a float (floating) when the tub is taken as an appropriate quantity of water and then spray the powder of silica on water surface and in this way remains particulates while floating on the surface down SiO_2 particles to the bottom of the tub and then continues with the water formed on the surface of the foam (containing particulates) and the process repeated several times, I used distilled water in the last time, then dried in the oven drying Fig (3-2) in 110 ºC for a period of (24) hours and then mill and fragmentation using an electric mill figure (3-3).

Fig. (3-2) Drying Oven

Fig. (3-3) Electrical mill

2) Weighing, the batches of the lead glass was taken according to Table (3-2). The percentage weight of each oxide within the composition multiplied by 3 times to obtain 300 g , for each batch (B, B1, B2). This step was carried out by using a sensitive balance which has accuracy(0.0001 g) type : mettler AE200 as shown in figure (3-4).

Fig. (3-4) Sensitive Balance

3) Mixing and milling of raw materials which involved in the batch by using a ball mill figure (3-5). 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 [12]. This step carried out in the technical college-Baghdad.

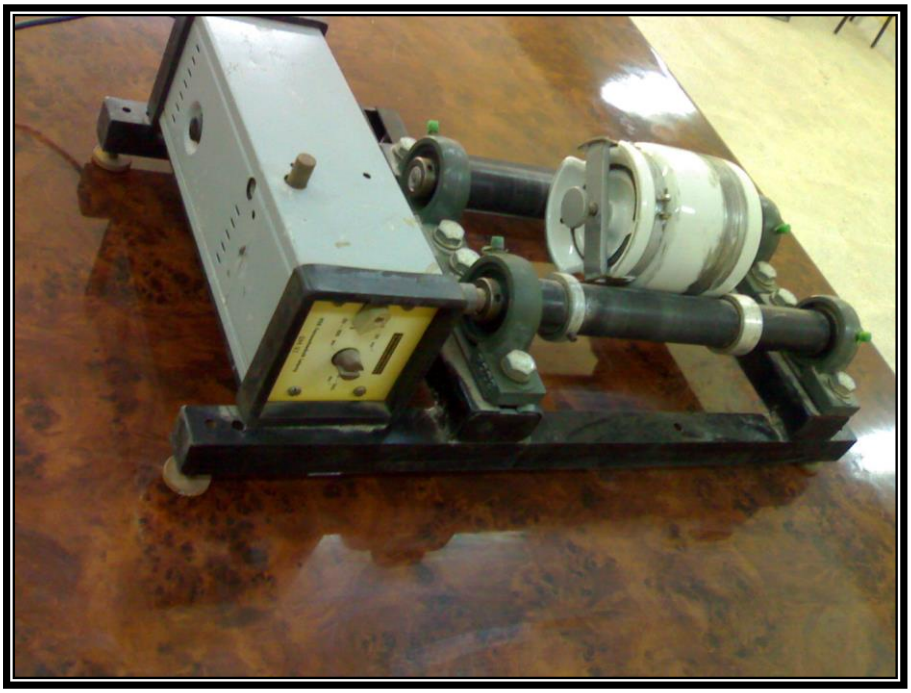


Fig. (3-5) Porcelain ball mill rotated on steel rollers.

4) Glass formation stage was carried out in the technical college-Baghdad by using a (melt - quench technique). Each batch put into a crucible made of silicon carbide (SiC) figure (3-6) to be heated within electrical furnace (Vecstar Ltd Furnace division) figure (3-7) to a temperature about 1200ºC for 2 hours. It may be noted that the powder begin to conglomerate and then softening at 650ºC. Viscous mass of glass was obtained at 1000°C. then 2 hours soaking time at 1200°C was achieved to reduce viscosity of the batch.

Occasionally, stirring of molten glass was done to complete homogeneity by using stick from graphite and then quench the molten glass in distilled water to get the cullet of glass figure (3- 8).

Fig. (3-6) Crucibles

Fig. (3-7) Electrical Furnace

Fig. (3 – 8) a- Melting furnace b- Quenching of molten glass c- cullet of batch (B1) d- cullet of batch (B2) e- cullet of batch (B3).

5) The cullet was dried at 110 ºC for a period of (24) hours.

6) The cullet was milled by using porcelain ball mill as shown in figure (3-5) to an average particle size of less than 45 µm from the glass powder. where the required time to grinds approximately (25) gm was (12 hr)

7) The glass powder was sieved by using electrical sieve (Retsh W.Germany) as shown in figure (3-9) to get particle size of less than 45 µm . where the required time to sieve (25) gm was (15 min).

Fig. (3-9) Electrical sieve

8) The glass powders were then subjected to phase analysis using x-ray diffraction figure (3 – 10) to confirm their amorphous nature. This step was carried out in the Ministry of Sciences and Technology.

Fig. (3-10) X-ray diffraction device

3.6 Preparing of test samples

The specification of the test samples has been determined according to American Standard for Testing Materials (ASTM), as well as in accordance with the requirements of devices that have been tested.

3.6.1 Pressing dies

The dies which have been used in this study, made of the hardening Stainless-Steel. It have ability to work up to maximum 10 ton compression. The internal surface of the die which touching the glass powder is very smooth for two reasons: first, to reduce the friction to the minimum between the two parts of the die and second, to prevent adhesion between the particles with die wall during getting out the sample from the die after the pressing. Therefore, liquid paraffin wax is

used as the lubrication to increase the efficiency of the die for the same reasons above. figure (3 - 11) shows the pressing die.

Fig. (3-11) Pressing die

3.6.2 Formation of samples

Dimensions of the samples have been selected according to the requirements of lab equipment available, and according to American Standard for Testing Materials (ASTM). The final dimensions for the test samples have been obtained after checking the experiment and adjustment of the many variables (sample weight , applied load , proportion of moisture, etc.).

3.6.2.1 Optimum conditions for the formation

3.6.2.1.1 Formation pressure

The necessity pressure has been determined to form samples based on the visual examination, which was used in an upward pressure to reach the best results. (1.4 ton) equivalent to (100 MPa) pressing gives samples have high porosity and hardly holding. Whereas, increasing the pressure

to almost (2 ton = 150 MPa), as shown below results samples free cracks and distortions, as well as its edges were a sharp and well. Therefore, pressure (150 MPa) was adopted in this study.

Disk Sample :

$A = \frac{\pi}{4} d^2 = \frac{\pi}{4} (13)^2 = 132.73 \text{ mm}^2$ ----------(3-3)

$\text{Pressure} = \frac{F}{A} = \frac{2000kg \times 9.81}{132.73} = 147.8 \text{ MPa} \approx 150 \text{ MPa}$---------(3-4)

Semi-dry pressing method has been used by a hydraulic press working in a way that pressing was in one direction from above as shown in figure (3-12).

(3-12) Hydraulic Press

3.6.2.1.2 Binder

(1%) of polyvinal alcohol (PVA) binder was used to prepare the samples. It is prepared by using laboratory mixer (magnetic stirrer thermostat hotplate) figure (3-13). firstly the water is heating and then add the grains of (PVA) and leave magnetic mixer works for 10 minutes until sure making of the granules to be melt and obtained the full solution of (PVA).

Fig. (3-13) Laboratory mixer (magnetic stirrer thermostat hotplate).

The percentage required of PVA to each sample (10%) from sample weight as the pressing is semi-dry, low ratio of PVA not sufficient to obtain a sample of fully coherent , also at more ratio has been noted getting out some of PVA at pressing. beside that is known that the increase in the binder ratio may cause problems in the porosity of the samples during the thermal process.

3.6.2.1.3 Weight of the samples

(1.15 g) weight of the powder sample was achieved to get a disc specimen of (13 mm) in diameter and (4 mm) in thickness when pressed the sample by 150 Mpa.

3.6.2.2 Powder pressing

The glass powders which prepared previously were mixed with a mount of polyvinyl alcohol (PVA). Uniaxially load is applied under a pressure (150 MPa) to obtain green compacts with diameter of (13 mm) and thickness of (4mm). figure (3-14) shows the four steps to obtain the sample [35,55, 56].

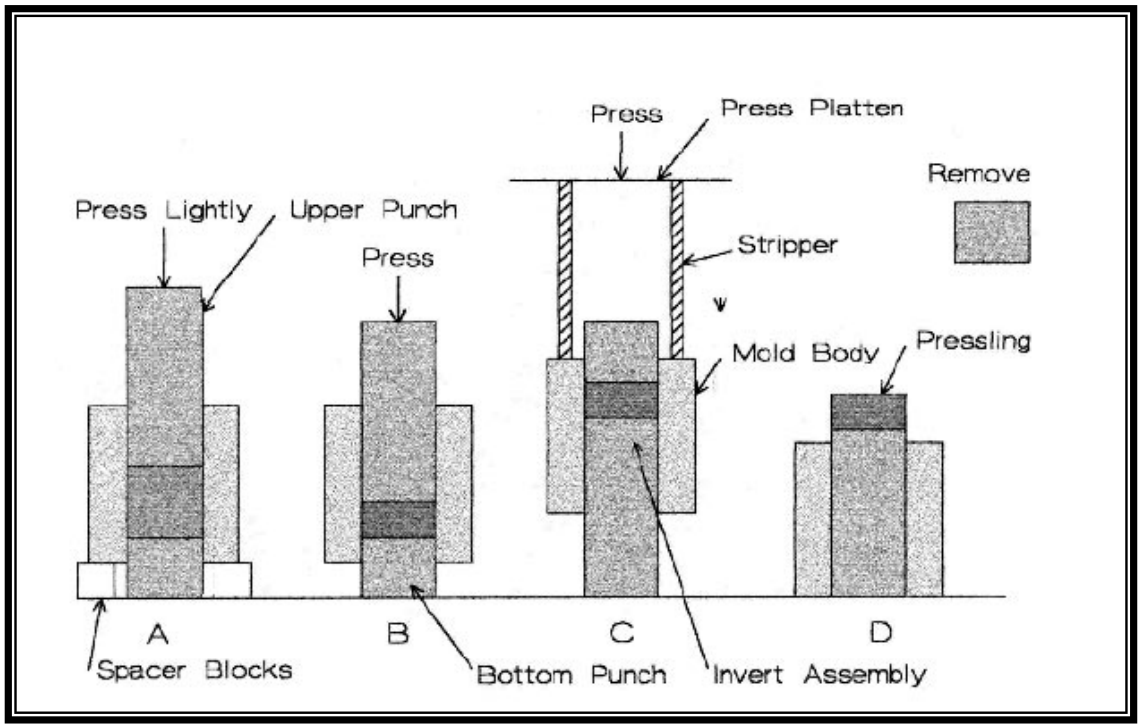


Fig. (3-14 **)** Stripping the Die. There are four steps: A. fill the die and insert the top punch press lightly, B. remove the shims and press the part, C. invert the die and place the stripper on top, and D. press down the strip part out of the die [35,55,56].

3.6.2.2.1 Die Pressing Problems

It has been observed that there are many problems encountered this work (Pressing Problems) Listed as:

1 • Laminations: to reduces it

bump the press, segmented punch face, vacuum evacuation, stripping edge relief, less plastic mixes

2 • End Capping: to reduces it

polish the die, less plastic mixes, die lubricants

3 • Sticking: to reduces it

paper divider, polish the faces, release agents

4 • Hour glassing: to reduces it

double end press, more plastic mix, higher

pressure

5 • Warping: to reduces it

hot hearth, die design, die fill

6 • Cracking: to reduces it

die design, even fill, binder/plasticizer, lower pressing rate, stronger binder, slower binder burn change forming method [55].

End capping was the most Problems occurred with die pressing in this research. It is a crack running from the top edge of the pressing at an angle to the center, as shown in figure (3-15) [55].

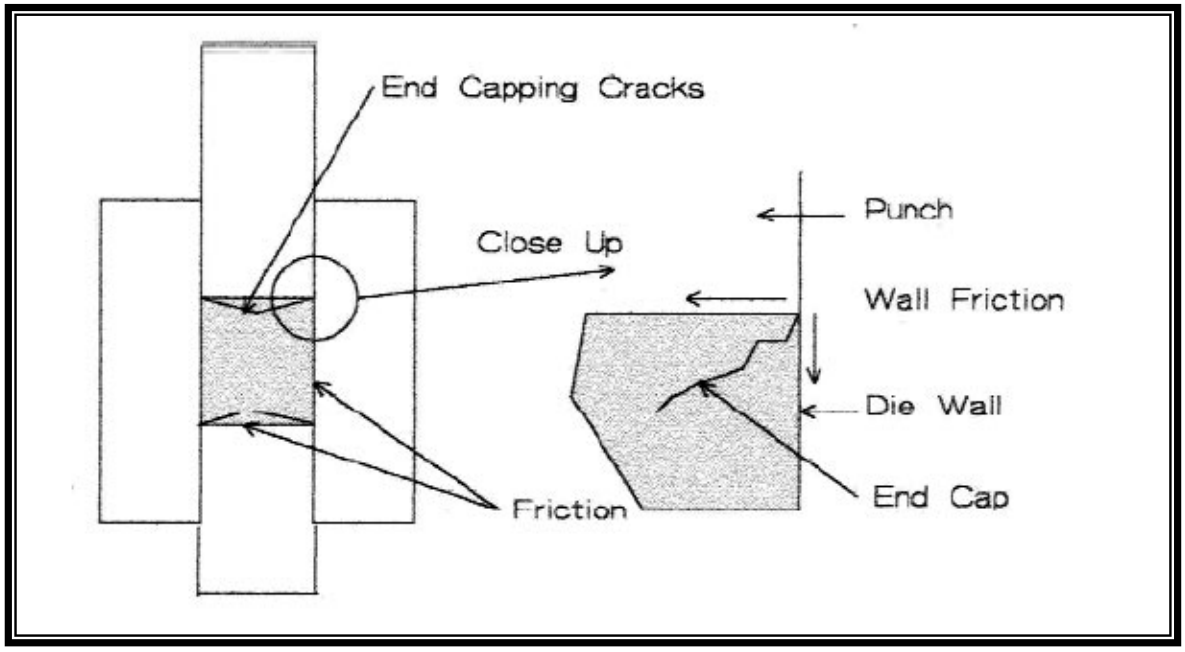


Fig. (3-15) End Capping. Cracks on the end of the piece are produced during pressing **[55]**.

There is an analysis by Thompson on end capping. It is caused by frictional forces across the punch face and along the die walls. It is also affected by the press mix consistency, with fewer plastic mixes tending to end cap. Decreasing friction between the sample, die, and punch faces can be accomplished by polishing. In the lab, the punch face can be lubricated for each pressing.

3.6.3. Heat treatment of glass samples

The samples were heat treated at different temperatures (450-500-525-550-575-600-650-750)ºC, for (1hr) with a heating rate of (5ºC/min).

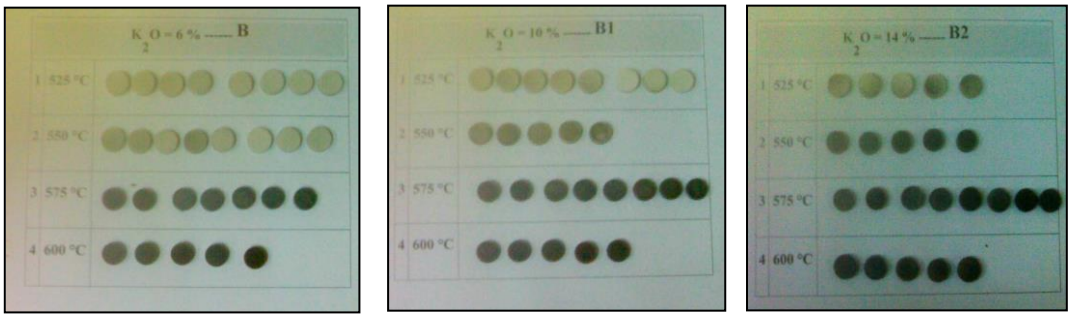
Heat treatment at temperature (450) ºC with a soaking time of (1 hour) is not sufficient to sinter the glass samples, which show the brittleness, and so the sintering temperature is elevated to a degree of 500 ºC.

At a temperature of (650)ºC, distortion features and some softening were observed in the sample and the dimensions of the sample show some deformation.

At a temperature of (750) ºC :

The batch (B1) shows a clear deformation occurred in the shape of sample and for the batches of (B2, B3) result a partial melting in samples, especially in batch (B3) because of the increase in the proportion of (K_2O), and this will be explain in the next chapter.

Therefore, the better thermal extent of sintering temperature for all batches (B1, B2, B3) to obtain glass samples without any distortion, is (525,550,575,600)ºC, figure (3-16) shows the sintering glass samples.



K_2O (6 %) = B1 K_2O (10 %) = B2 K_2O (14 %) = B3

Fig. (3-16) Sintering glass samples

Heat treatment carried out by using electrical furnace (SRJX -5-13 model Box – Resistance furnace control Box) programmer by current up to the temperature (1200 ºC) as shown in figure (3-17).

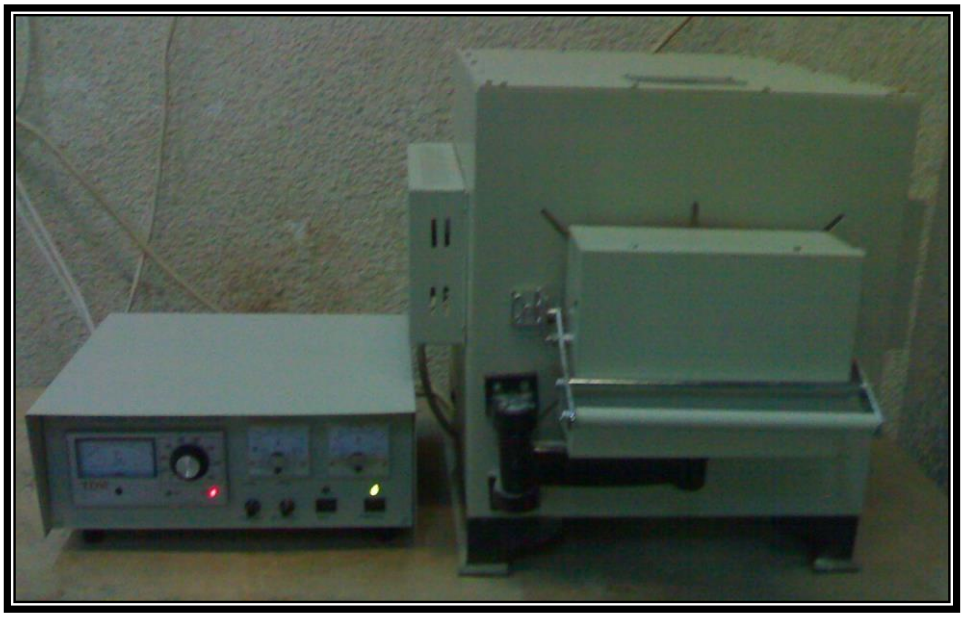


Fig. (3-17) Electrical furnace programmer by current

Table (3-3) shows the sintering temperature and heating rates for the formation of glass samples

Table (3-3) Sintering Schedule.

Temp.ºC	Rate of heating	Time (hr)	soaking time(hr)	Total time(hr)
525	5 º/min	1.39	1	2.39
550	5 º/min	1.47	1	2.47
575	5 º/min	1.58	1	2.58
600	5 º/min	2.05	1	3.05

3.7 Manufacturing Steps of glass-ceramic samples

Glass-ceramic in this research was produce in heterogeneous nucleation. The compositions of the batches as shown in table (3-4), are nucleating by (TiO_2) agent in concentration of 5 wt% .

At first we have manufactured glass samples for compositions (C1, C2, C3) in table (3-4) with the same method which followed in manufactured of glass samples for compositions (B1, B2, B3) (using melt- quenching technique and milling and manufacture by pressing of powder.

Table (3-4) composition of Glass - Ceramic

Material	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

According to the above compositions, the following procedure was adopted in this research:

3.7.1 Heat treatment

The glass samples should be subjected to a controlled heat treatment schedule in order to promote the process of crystallization and the conversion of the glass into a glass-ceramic. For this purpose, (chapter two) two stages of heat - treatment regimes, as shown in figure (2-6) was generally implemented in the present study. This regime first included the nucleation step, which was done for all the glass samples by conventional

heating in an electric furnace, followed by the crystallization step by conventional heating. In such two-stages of heat-treatment, the low-and-high temperatures are designated as the nucleation and the crystallization treatments respectively.

3.7.1.1 Nucleation stage

The glass samples were heated to the nucleation temperature (350°C, 3 hours ramp) in an electric furnace, (SRJX -5-13 model Box – Resistance furnace control Box - programmer by current) shown in figure (3-17)) and held for a certain period of time (3 hours). After such nucleation, the nucleated glass disks were crystallized by other stage.

3.7.1.2 Crystallization stage

The nucleated glass samples were heated above to the crystallization temperature (550 ºC, 3 hr ramp) in order to grow those formed nuclei to crystals and hence to convert the glass into glass – ceramic material.

3.8 Tests

It has been focused several tests on samples of glass and glass-ceramic, which heat treated at different temperatures and for all the batches (B, B1, B2) to determine the physical and electrical properties.

3.8.1 Physical tests

3.8.1.1 Visual tests

The visual tests have occurred on the treated samples for the purpose of identifying the changes that have occurred on the outer shape of the samples, where the cracks and the curves were also observed and change in the color was accompanied heat treatment.

3.8.1.2 X-ray diffraction

Due to the very fine – grains of the obtained glass-ceramic samples, identification of the crystalline phases developed by crystallization of the glass was mainly conducted by x-ray diffraction analysis of the powder crystalline samples . A mortar and pestle were used to grind the glass – ceramic samples into a fine powder that were tested by XRD. The x-ray patterns were obtained using a (XRD – 6000 SHIMADZU- Japan) at the Ministry of Sciences and Technology, fig (3-10) . A Cu tube voltage of 40 kv and currents of 30 mA were applied . A scanning speed of 4 degrees (θ) / min was used for the analyses. The reference data for the interpretation of x-ray diffraction patterns were obtained from the ASTM x-ray diffraction file index and from several other publications .

3.8.1.3 Shrinkage after heat treatment

Shrinkage occurs in the ceramic material after heat treatment, this is a process change in the dimensions and size of the samples after heat treatment, radial shrinkage was measured by calculating diameter of the sample before and after the heat treatment by using electronic digital caliper which has accuracy (0.01 mm) figure (3-18). have been determined the radial shrinkage from the following relationship [57,58,59].

$$\text{Radial shrinkage \%} = \left[\frac{d_1 - d_2}{d_1}\right] * 100 \quad \text{----------(3-5)}$$

Where :

d_1 = Diameter of the sample before heat treatment (mm)

d_2 = Diameter of the sample after heat treatment (mm)

Diameter of a sample has been measured from several angles and take the average diameter of each sample.

Fig. (3-18) Electronic digital caliper

3.8.1.4 Apparent Density , Porosity and water Absorption

1 - **The mass density** is the relationship between the solid part to the gaseous part in the body which represented in pores of ceramic body. The density is the most important physical characteristics that determine the properties and the quality of ceramic products [60]. Density measurement on the samples of glass and glass- ceramic were done using a liquid displacement method (Archimedes method) [61].

2 - **Porosity,** the sintered porous ceramic product, shows changeable porosity dependent on the type and proportions of materials involved in the composition of the product, method of formation, pressure used, speed of drying, firing temperature and remaining time. Since the

porosity is a measure of the presence of both open and closed pores therefore shows two types of porosity of a porous ceramic body, true and apparent porosity. Can be expressed (apparent porosity) as a proportion of the volume fraction of open pores to the total volume [62].

3 - The amount of **water absorbed** in the body are a function of apparent porosity and water absorption is the relationship between the mass of water absorbed in the pores to the mass of the solid part in the body [63].

- Apparent density, porosity and absorption of the water tests have been calculated depending on ASTM standard (C-373-88) and each test result is the average of three samples as shown in the following steps [53,64,65,66].

1- Drying the test specimens to constant mass by heating in an oven at 110°C, followed by cooling in a desiccator . The dry mass (D), was determined to the nearest 0.01 g .

2- Immersing the specimens in a pan of distilled water and boiling them for 5 h, taking care that the specimens are covered with water at all times. Using setter pins or some similar device to separate the specimens from the bottom and sides of the pan and from each other. After 5 h boiling, allowing the specimens to soak for an additional 24 hrs.

3- After impregnation of the test specimen in water, then the suspended mass (S), was determined to the nearest 0.01 g, while suspended in water.

4- After determination of the suspended mass, each specimen was blotted lightly with a moistened cotton cloth to remove all excess water from the

surface. The saturated mass (M), was determine to the nearest 0.01 g after rolling the specimen lightly on the wet cloth.

Excessive blotting of specimen will introduce error by withdrawing water from the pores of the specimen. Make the weighing immediately after blotting, the whole operation being completed as quickly as possible to minimize errors caused by evaporation of water from the specimen.

* After completing the above steps have been calculated density, apparent porosity and water absorption from the following equations[41]:

- Apparent density :

Apparent (Bulk) density = $\left[\frac{D}{M-S}\right]$ ----------(3-6)

- Apparent porosity :

Apparent porosity % = $\left[\frac{M-D}{M-S}\right]*100$ ----------(3-7)

- Water absorption :

Water absorption % = $\left[\frac{M-D}{D}\right]*100$ ----------(3-8)

Where :

M = Weight of sample which is saturated with water (g) .

D = Dry weight of the sample (g)

S = Suspended weight in water (g).

3.8.2 Electrical tests

3.8.2.1 Dielectric constant (ε_r)

The examination included measurement of the amount of dielectric constant (ε_r) of each sample, by changing the frequency and use of a (L. C. R Meter) type (Agilent) at the Ministry of Sciences and Technology. This equipment operates on the frequency range (40 Hz-110 MHz), as shown as in figure (3 -19), with Holder and Kit of test. Before the measurements, the device is calibrating according to the instructions supplied with the device, and the existing standard in the calibration constants of the value of (C) of the air thick (0.1 mm), be read as ($12\ pf \leq C \leq 17\ pf$). Then we can determine the extent of measurement in place in this research is (40 Hz - 5 MHz), and makes the progression of the measurement device automatically identifies the steps of measurement.

The device shows the value of ($\tan \delta - C$) which gave me a shiner in the values of the frequencies within the range, and it is possible to record these values on a CD (compact disc) by the scale of the values of (C) to change the frequency within the range proposed (40 Hz - 5 MHz). Loss angle ($\tan \delta$) is also included in measurements. Then copy that information to the computer, which is calculated the values of (ε) using the program (Microsoft excel) to facilitate the work. Values ($\tan \delta$, C) change with frequency for each sample over (200) value, making it impossible manually calculated and hence the speed and accuracy to be performed by computer, and by applying the following equation:

$$\varepsilon = \frac{C * d}{A * \varepsilon_o} \text{ ----------(3-9)}$$

We have already discussed in chapter two of this research, that all measurements were at room temperature [67].

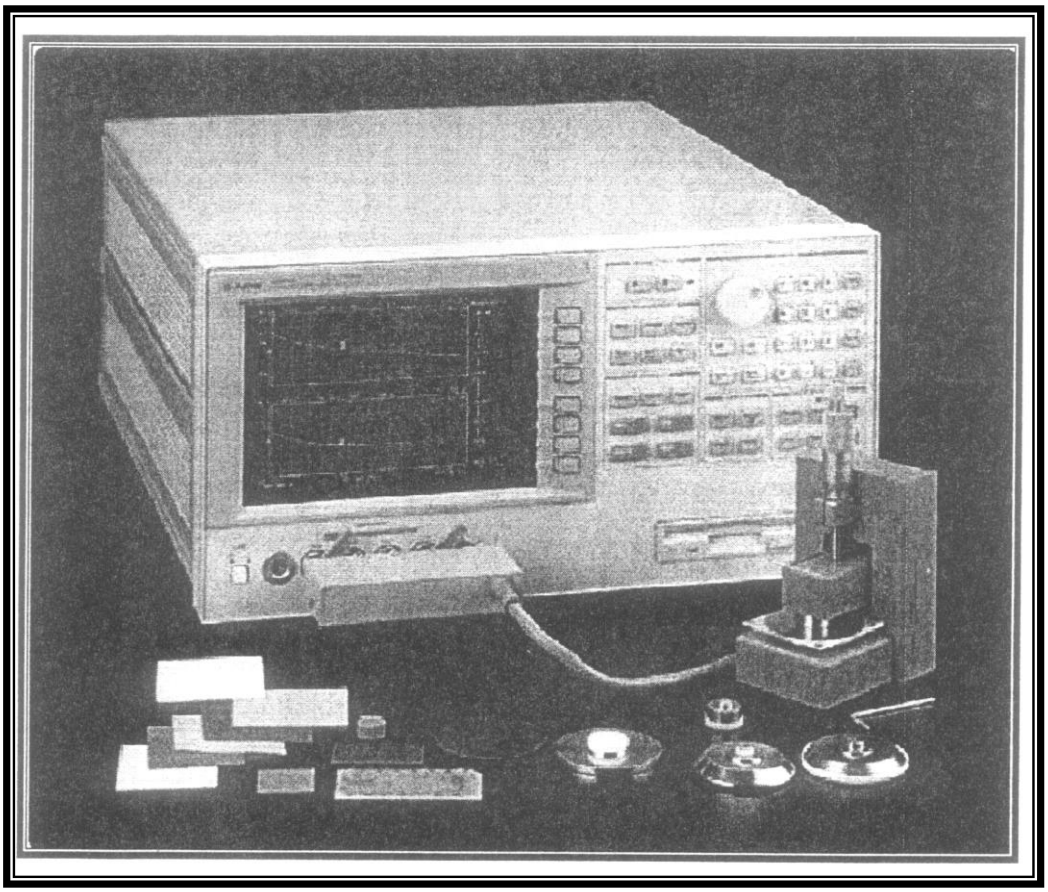


Fig.(3-19) L.C.R device

3.8.2.2 Dielectric Strength

Dielectric strength has been measured of the samples at the University of Technology / Department of Applied Science, using a (BAUR-PGO-S-3) device up to the voltage (300 kV), as shown as in figure (3-20). Applied electrical field was 60 kV (0.5 kV / Sec), and thickness of the samples was (4 mm). The equipment contains the poles of the copper which be contact with the sample, and contains a tub filled with oil, which conducted preliminary testing of the process. It was found that the rate of electricity is the durability (35 kV / mm) for one minute, which is suitable for this purpose, and there is another reason to use the liquid, is high temperature in using (fervency) therefore, make it serve because it acts as inert media, which may get burned by the spark generated

It will be interesting to know that the preferred measure of the breakdown voltage be in many areas for a single sample, and its rate is the best of these measurements due to differences in the homogeneity of the sample, which may occur during the thermal process and the emerging multi-phases [52,68].

$$\text{Dielectric strength} = \frac{V_{av}}{h} \text{ ----------(3-10)}$$

Where :

V_{av}: the rate of breakdown voltage (Kv)

h : thickness (mm)

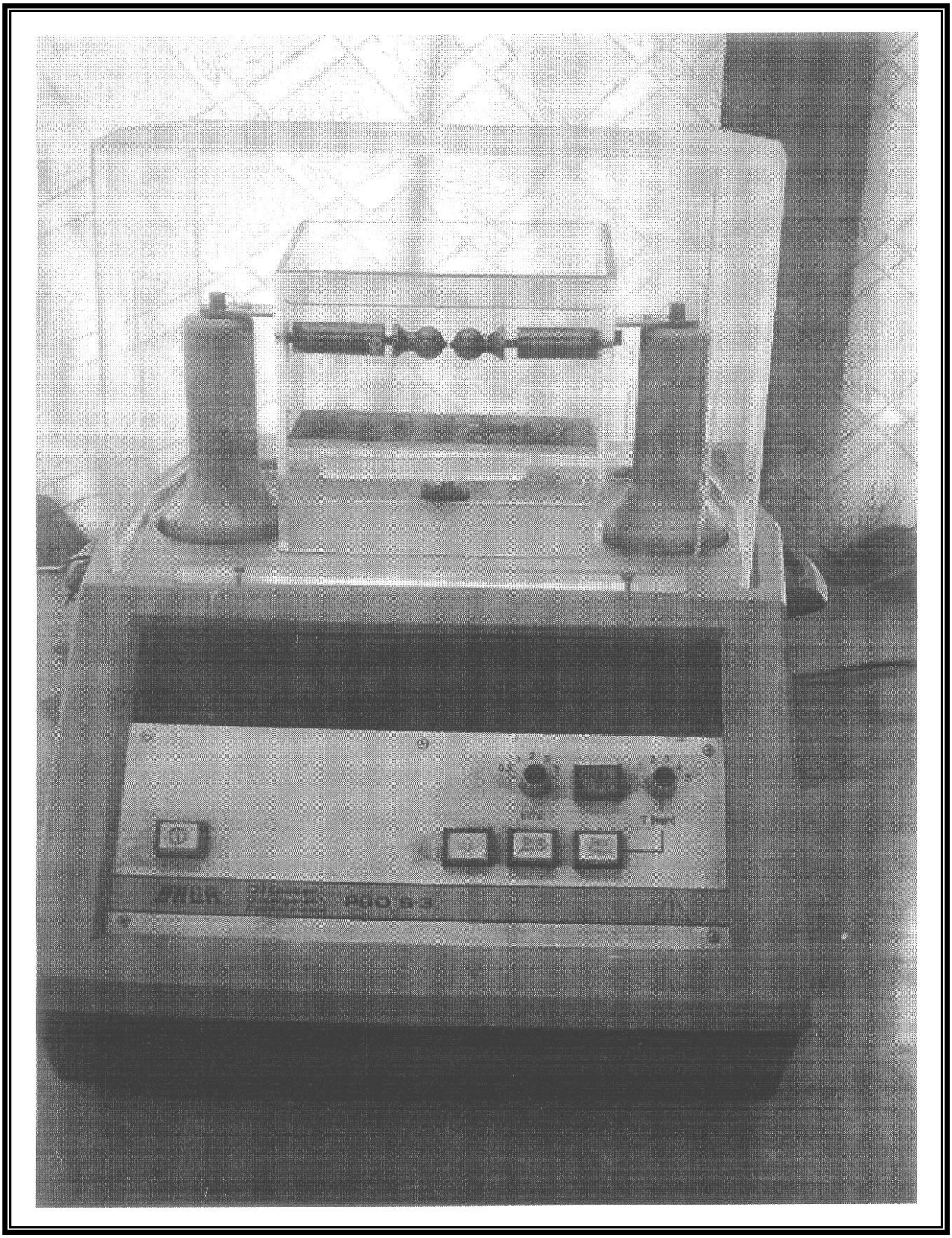


Fig. (3-20) (BAUR) PGO device

Chapter Four
RESULTS AND DISCUSSION

4.1 Introduction

In this chapter the results obtained from experimental tests will be discussed, with process of preparing glass and glass-ceramic samples. Also, we will explain the effect of sintering temperature on the physical and electrical properties of glass samples, and the effect of composition on the physical , electrical and structural properties of glass-ceramic samples.

The tests which will be discuss : dielectric constant , dissipation factor, dielectric strength , density, porosity (which effect on electrical properties directly), water absorption, and x-ray diffraction which used in identification .

4.2 Physical properties

4.2.1 The visual tests

For glass samples which are sintered at different temperatures (525 ,550 ,575 ,600) ºC, it may be noted that the color of the sample vary greatly with the sintered temperature, where white color occurs at 525ºC , and becomes more opaque with increasing temperature and time of exposure .

Also glass-ceramic samples which are heat treated by two stages (nucleation and growth) become more opaque after heat treatment.

The visual test carried out for samples to ensure it suitable and there are not any cracks or deformations which may effect on the physical and electrical tests.

4.2.2 Result of X-Ray Diffraction Analysis

4.2.2.1 Glass

Figures (4-1), (4-2) and (4-3) display the XRD patterns for lead silicate glasses of the batches (B1) (B2) and (B3) respectively.

These figures indicate 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.

This step considered the first step to prepare glass-ceramic where it follows by heat treatment (nucleation and growth).

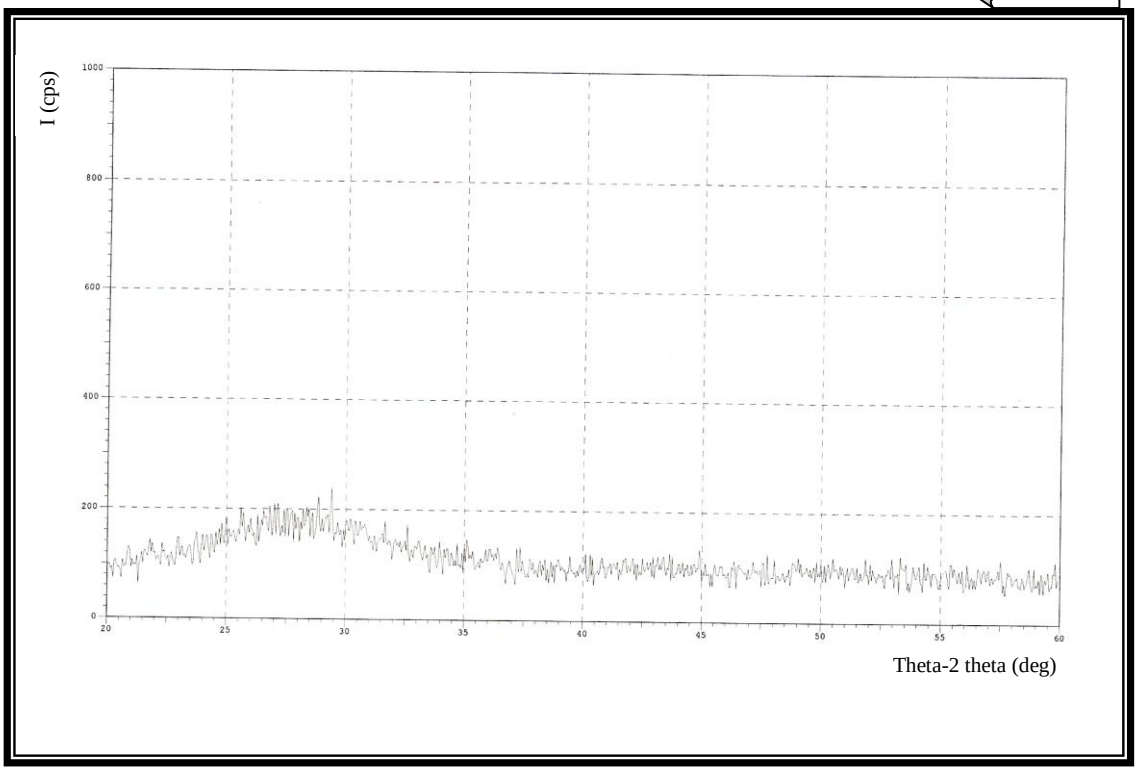


Fig. (4-1) XRD Pattern of glass (B1-composition).

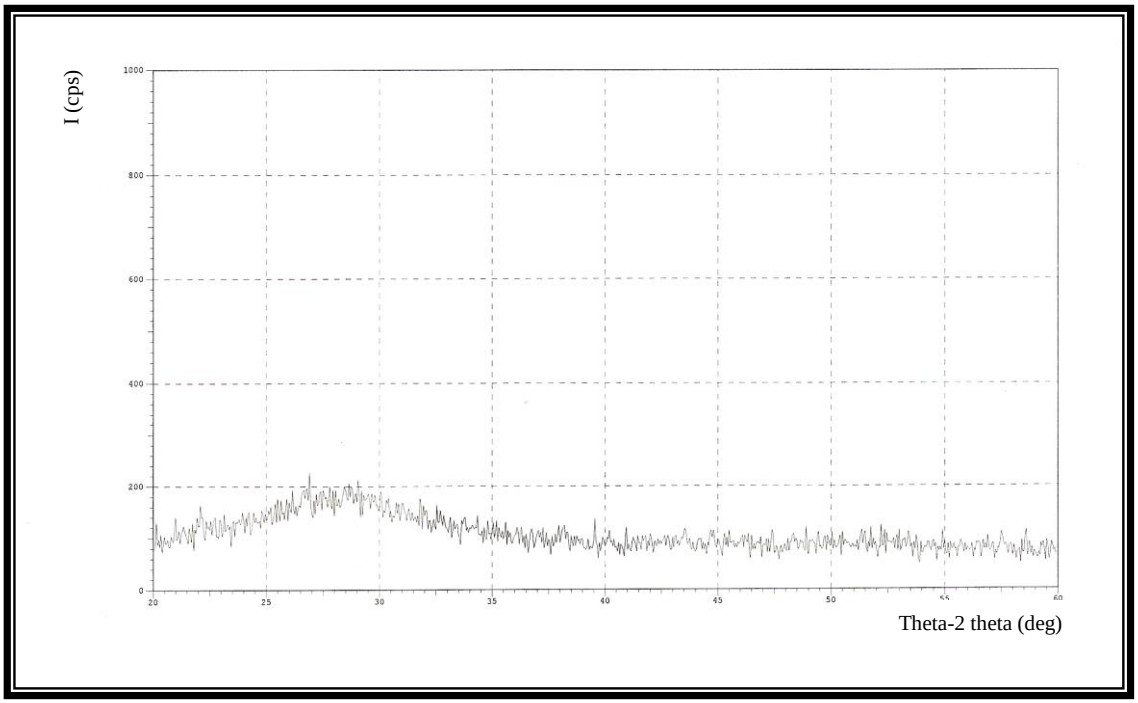


Fig. (4-2) XRD Pattern of glass (B2-composition).

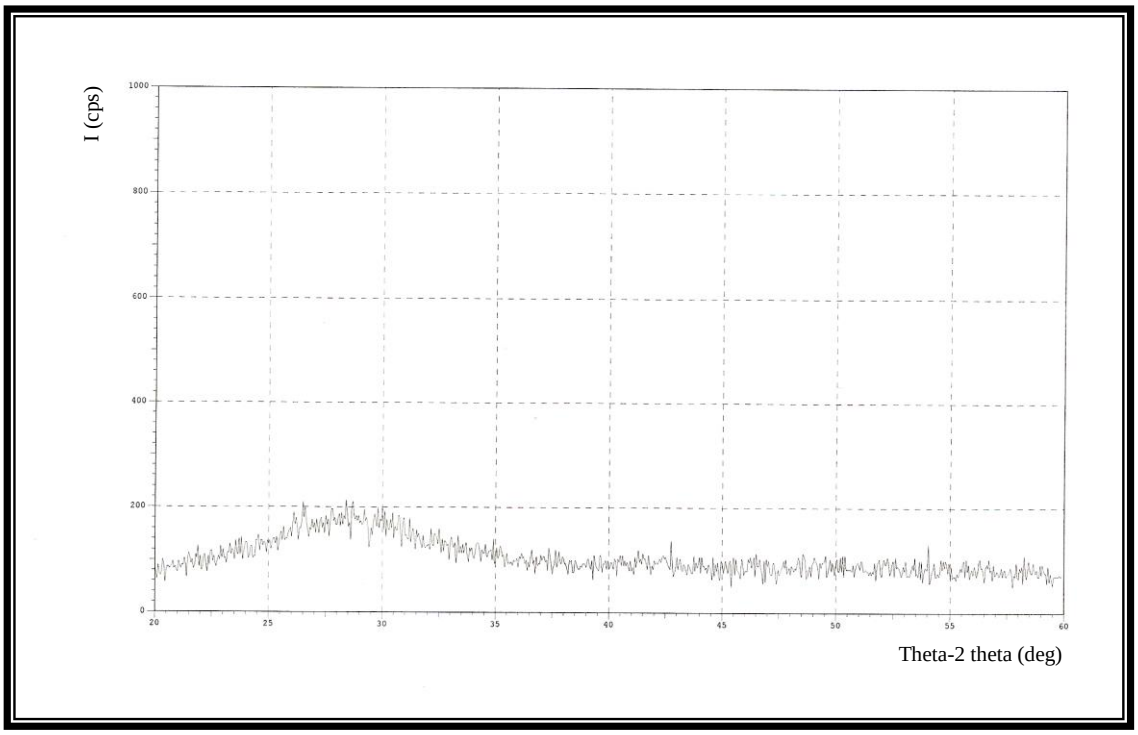


Fig. (4-3) XRD Pattern of glass (B3-composition).

4.2.2.2 Glass – ceramic

Figures (4-4), (4-5) and (4-6) display the 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 + 550°C for 3 hr) and the table (3-4) shows the compositions of these glass- ceramic samples.

These figures show that the heat treatment which used was successfully crystallized into glass-ceramic with its characteristic XRD peaks , crystal phase identification and the crystallographic planes corresponding to the 2θ value for all the peaks was performed using the ASTM x-ray diffraction file index and from several other publications.

Crystallization behavior

Heat treatment protocols for quenched (parent) glass must guide by differential thermal analysis(DTA) to get glass ceramic.

We could not use these techniques in this research because DTA equipment is not available, and hence it must be used many thermal programs on glass samples to obtain suitable heat treatment. XRD chart of batch B 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 become consist of two phases (crystalline and amorphous), which characteristics of glass ceramic structure.

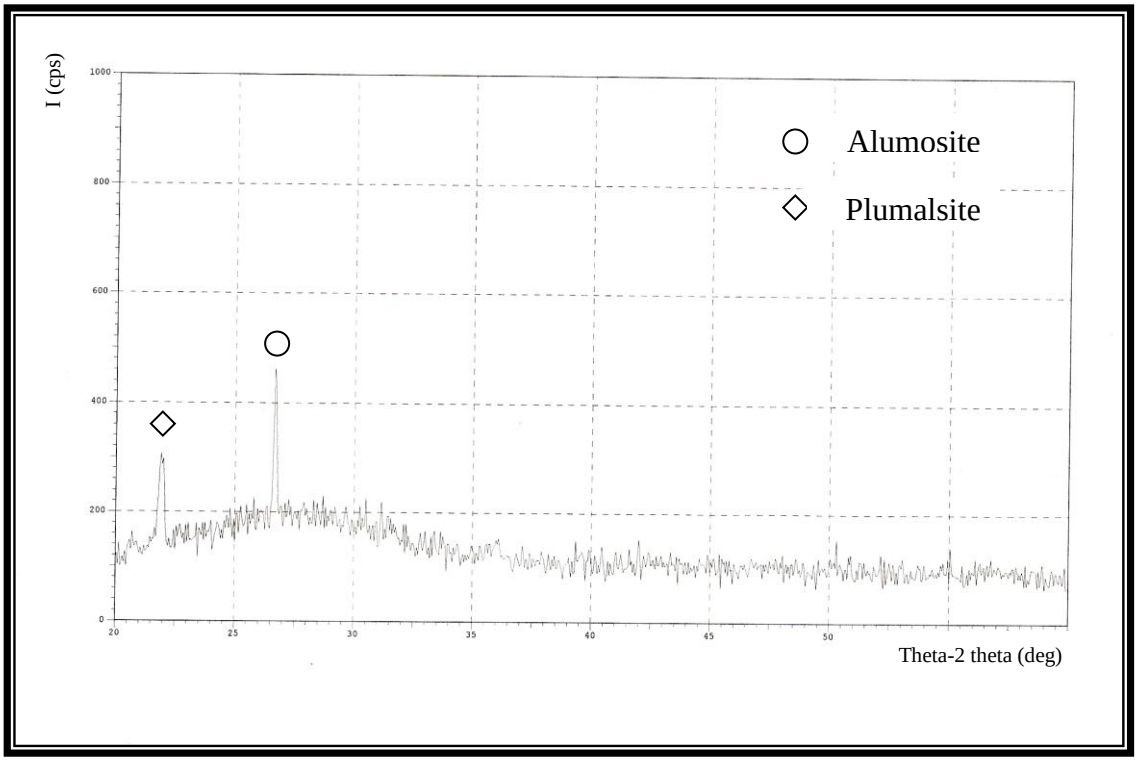


Fig. (4-4) XRD Pattern of glass - ceramic (C1-composition).

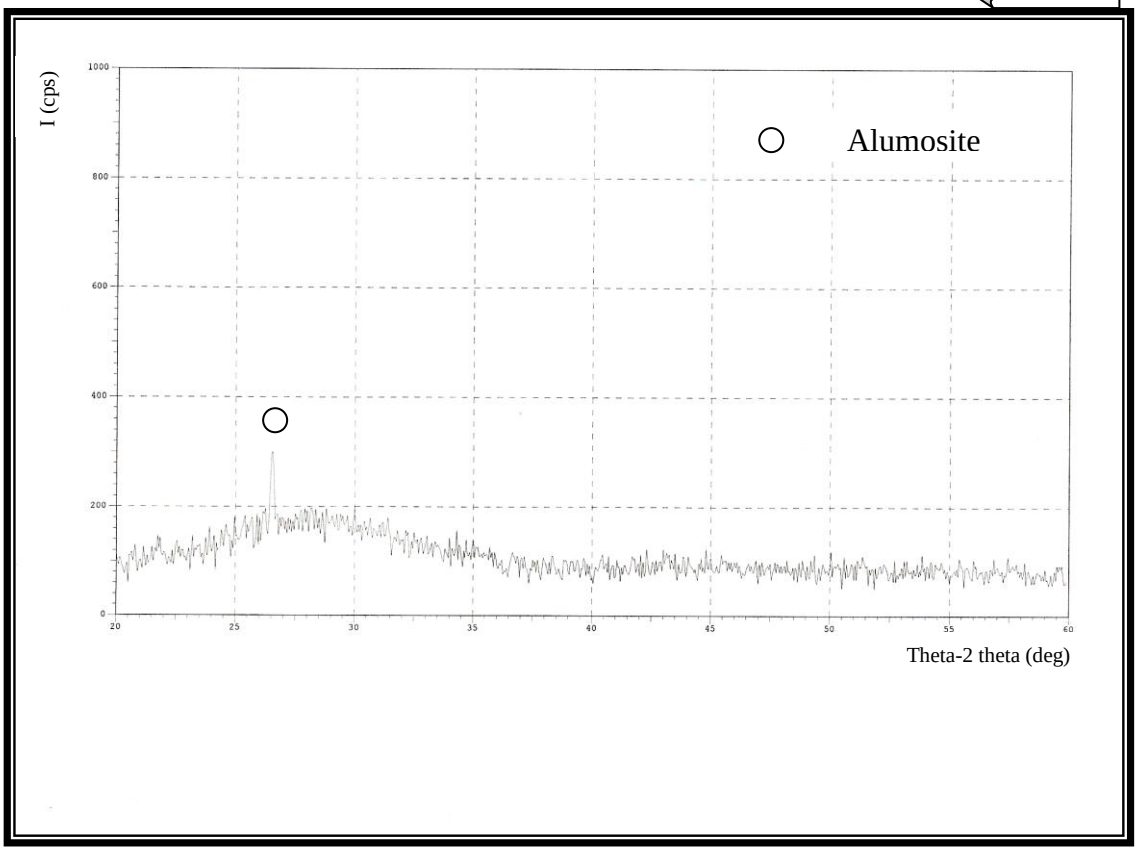


Fig. (4-5) XRD pattern of glass - ceramic (C2-composition).

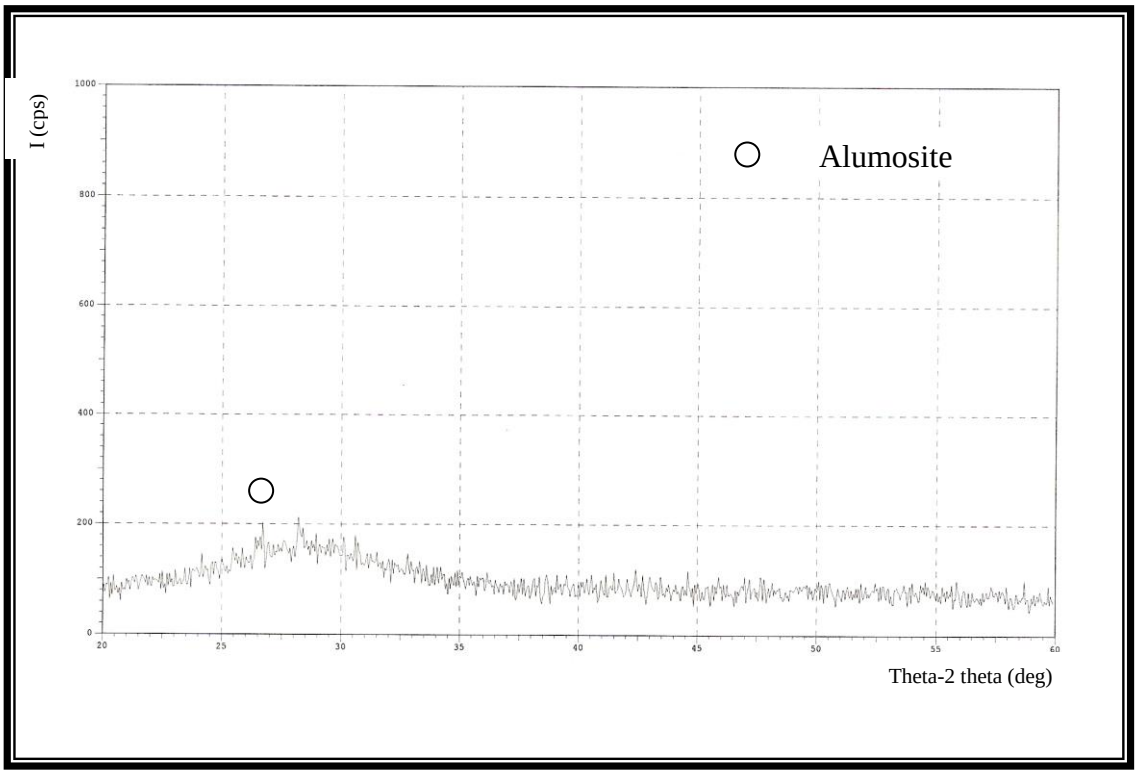


Fig. (4-6) XRD Pattern of Glass - ceramic (C3-composition).

4.2.3. Radial shrinkage after heat treatment

- Glass samples

Figure (4-7) shows the relationship between radial shrinkage and temperature of sintering for three glass compositions (B1, B2 and B3) at different temperatures.

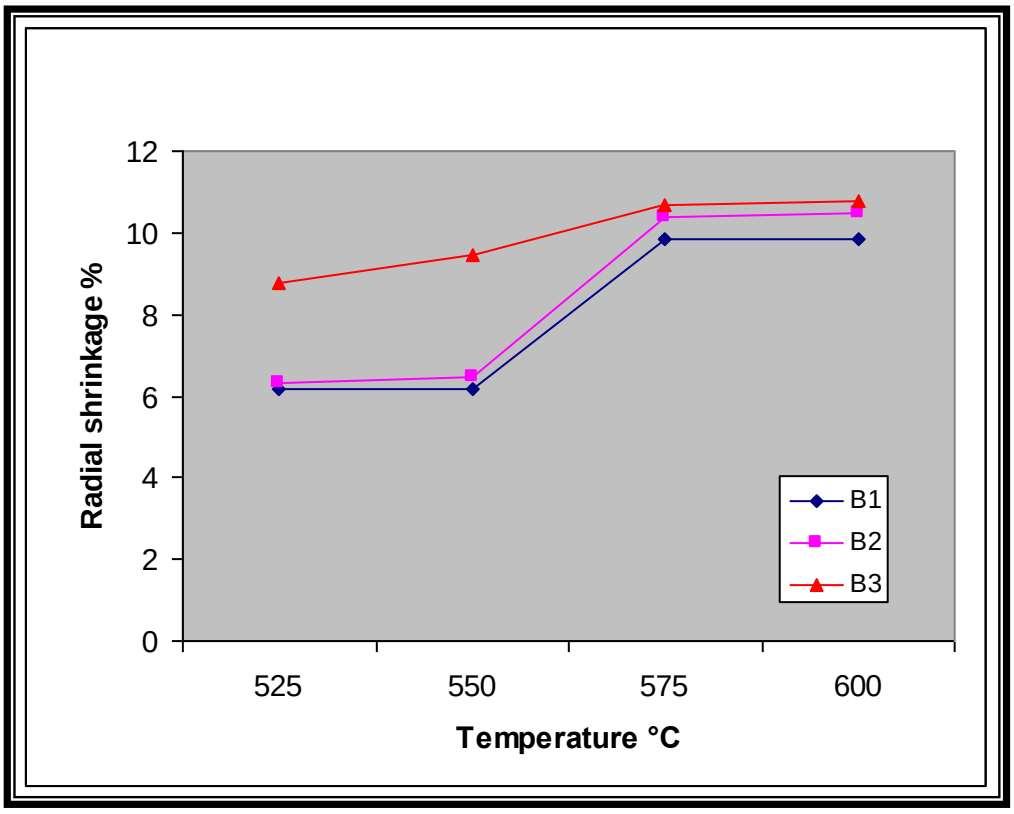


Fig. (4-7) Relationship between radial shrinkage and sintering temperature for glass samples.

The figure above shows that the shrinkage percentage increases with raising the temperature of sintering, where the samples at low temperature (525 ºC) contain high porosity , with raising temperature the rate of densification will increase and make particles close to each other and clog the pores in the body.

Also the figure shows that the value of shrinkage for composition B3 be higher than that of B1 and B2 batches, because the K_2O percentage in

composition B3 higher than other composition , where the role of K_2O is reducing melting and sintering temperatures therefore it increase of sintering rates and subsequently the shrinkage.

- Glass – ceramic samples

Figure (4-8) shows the effect of compositions for three glass-ceramic (C1, C2 , C3) on radial shrinkage at same heat treatment.

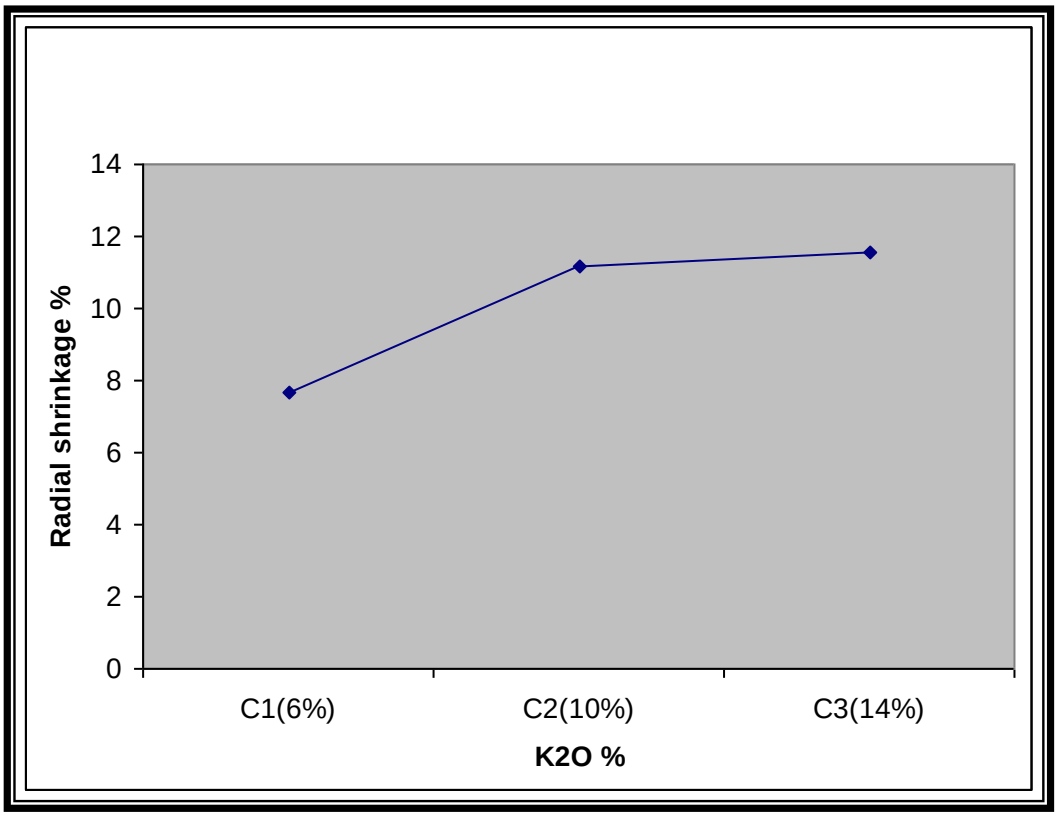


Fig. (4-8) Relationship between radial shrinkage and three glass-ceramic compositions (C1, C2 , C3) at same heat treatment.

Figure (4-8) shows that the shrinkage increases from (C1) to (C3) composition for the same reasons mentioned before (increases of K_2O%).

4.2.4 Density , Apparent porosity and Water absorption

Density

Figure (4-9) shows the effect of sintering temperature on bulk density of glass samples with different compositions, where density of samples are increasing in general with increasing temperatures. This behavior is concluded mainly by increasing of sintering rate at elevated temperature of the samples.

It may be noted that the density of (B3) composition is highest than the other batches, because it containing the excess of (K_2O) percentage.

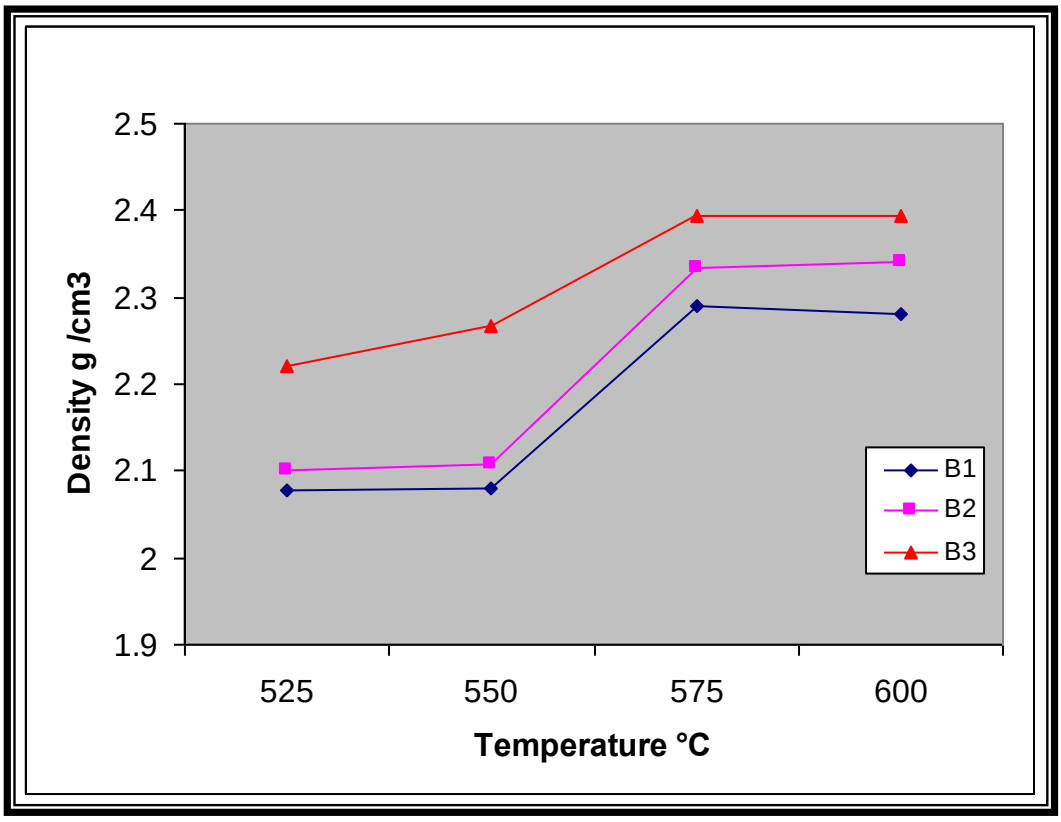


Fig. (4-9) Relationship between sintering temperature and density for glass samples.

Figure (4-10) shows the effect of glass-ceramic compositions on bulk density at same heat treatment (350 ºC 3 hr + 550 ºC 3 hr), where density of samples is increasing in general with increasing of (K_2O) percentage.

Also it was observed that the densities of the glass- ceramic were higher than that of the corresponding glass. It may be attributed to the fact that, in most cases, the crystals densities are higher than those of the glass with the same composition due to higher atomic structural compaction [69].

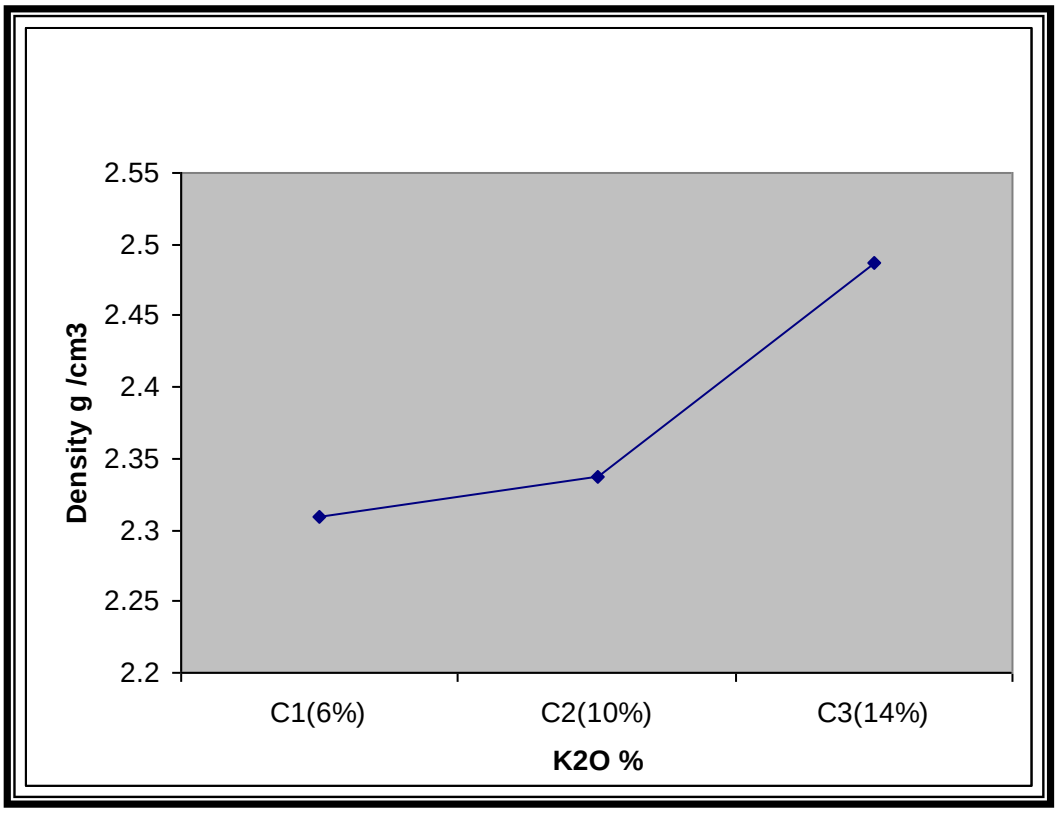


Fig.(4-10) Relationship between compositions and density for glass-ceramic samples.

Apparent porosity and water absorption

Figure (4-11) shows the effect of sintering temperatures on apparent porosity for glass samples , and figure (4-12) shows the effect of sintering temperatures on water absorption for glass samples.

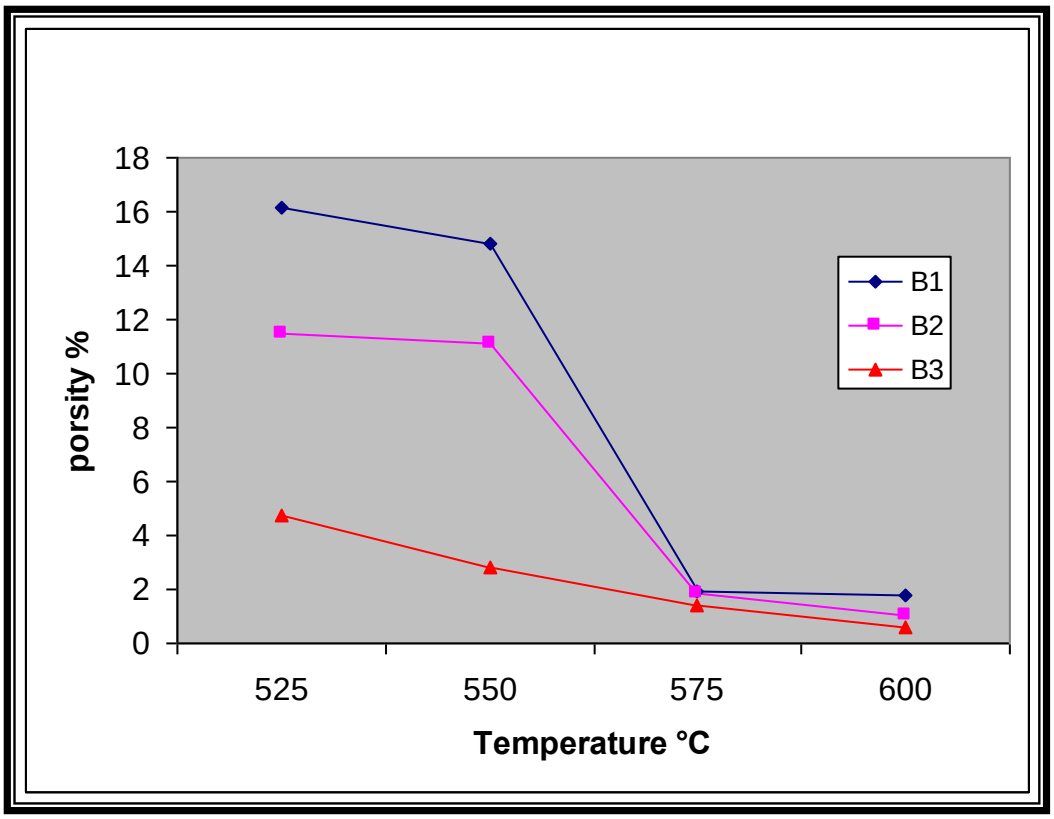


Fig. (4-11) Relationship between the sintering temperatures and apparent porosity for glass samples.

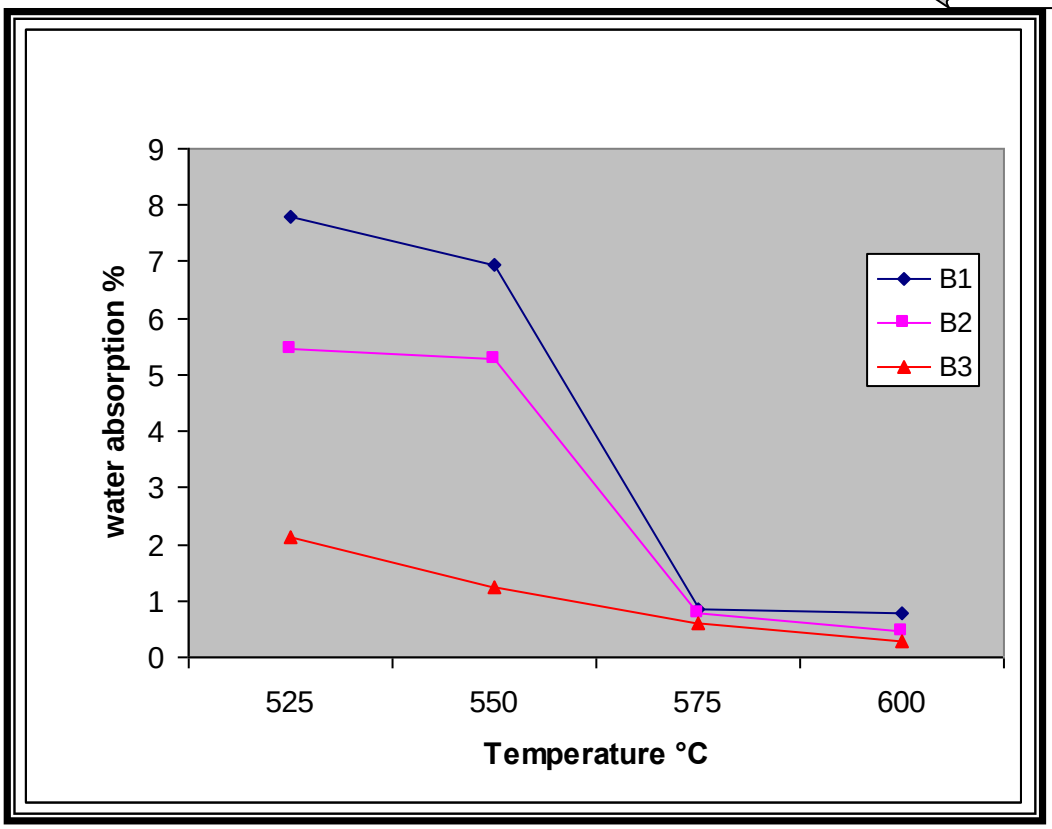


Fig. (4-12) Relationship between the sinter temperatures and water absorption for glass samples.

From figures above (4-11) and (4-12), it may be noted that the maximum values for apparent porosity and water absorption are at low sintering temperature (525ºC), and its decreasing with increasing temperature due to free silica are fluxed by the alkalis (K_2O) which are present. The resulting molten silicates begin to fill the spaces and the whole mass shrinks as a result. Thus there is less space left and the samples are less porous.

Also we have noted that the (B3) composition has lower values of apparent porosity and water absorption relative to (B1 ,B2) compositions. This is because high percentage of (K_2O) which considers the fluxing action and continues work with increasing temperatures until all the spaces are filled and the porosity is nil.

Figure (4-13) shows the effect of composition on apparent porosity for glass – ceramic samples, and figure (4-14) shows the effect of composition on water absorption for glass – ceramic samples.

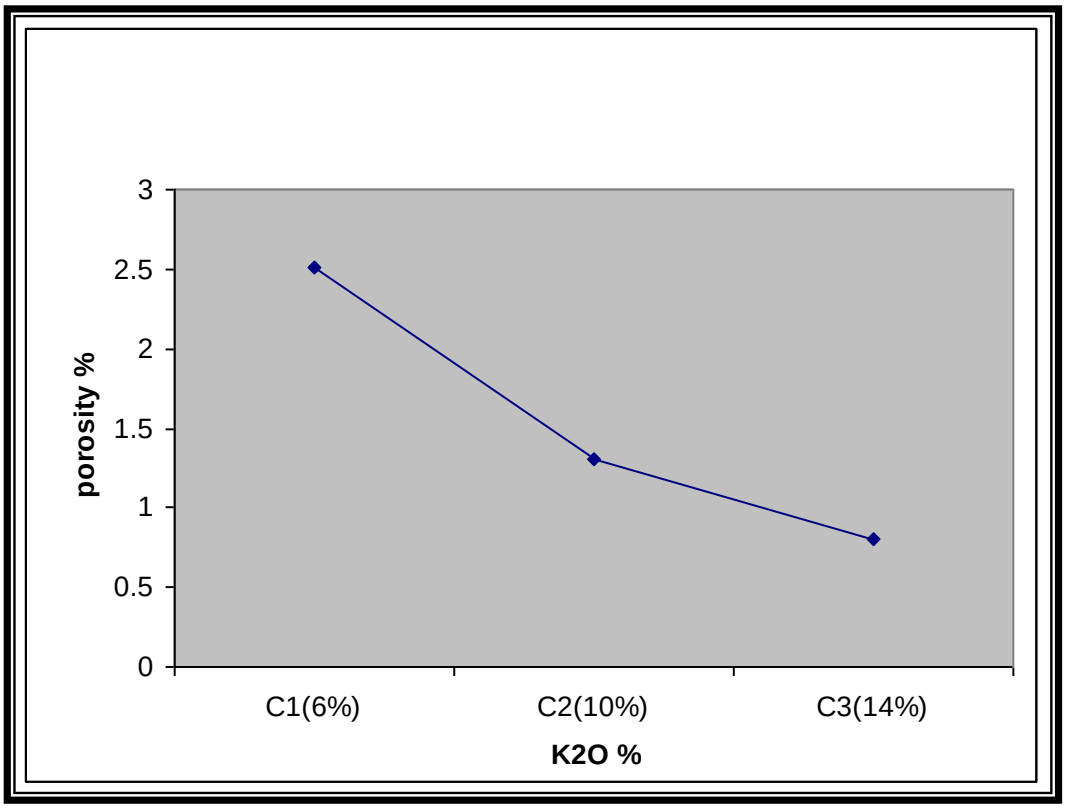


Fig. (4-13) Effect of composition on apparent porosity for glass – ceramic samples.

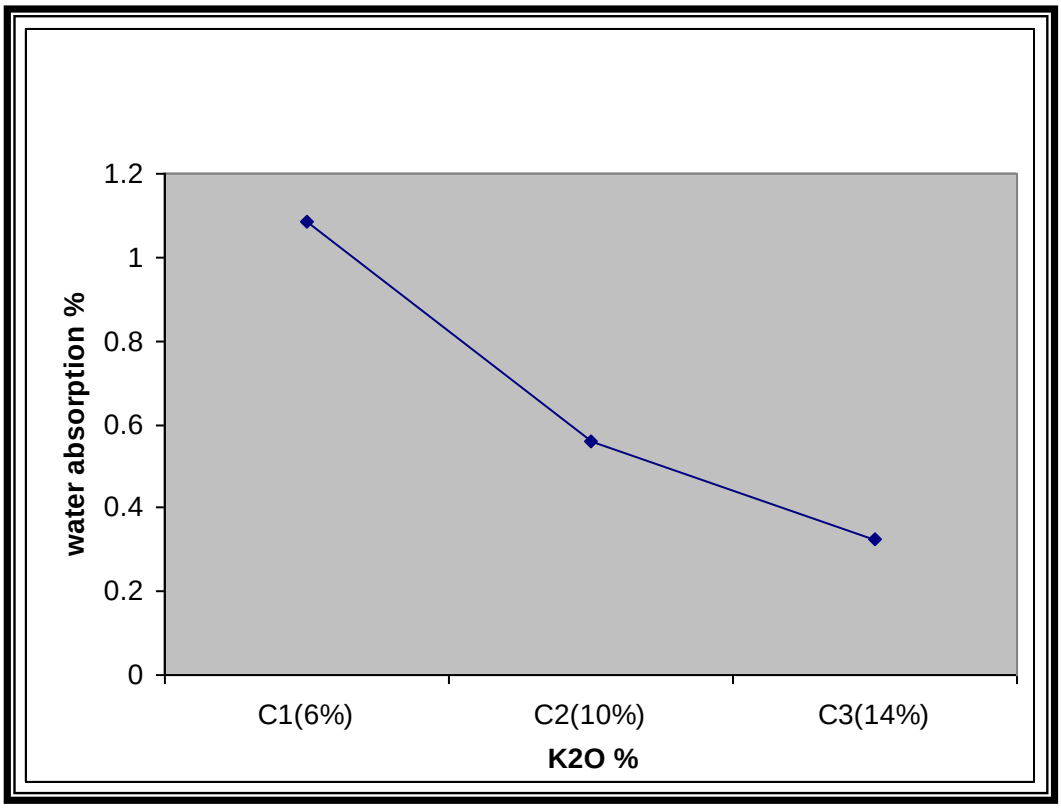


Fig. (4-14) Effect of composition on water absorption for glass – ceramic samples.

Both figures (4-13) and (4-14) have explained that the maximum values of apparent porosity and water absorption at composition (C1) and decreases gradually towards composition (C3), due to increase the percentage of K_2O from composition (C1) to (C3).

4.3 Electrical Properties

4.3.1 Dielectric strength

Figure (4-15) shows the effect of sintering temperatures on dielectric strength for glass samples, where the dielectric strength increases with increasing of sintering temperature, because the increasing in sintering temperature causes decreasing in porosity, where porosity is affected inversely on the dielectric strength (i.e decreasing in the porosity values increase the dielectric strength of glass samples). It will be interesting to know that the increasing in porosity will generated interior electrical fields which causes decreases dielectric strength [70].

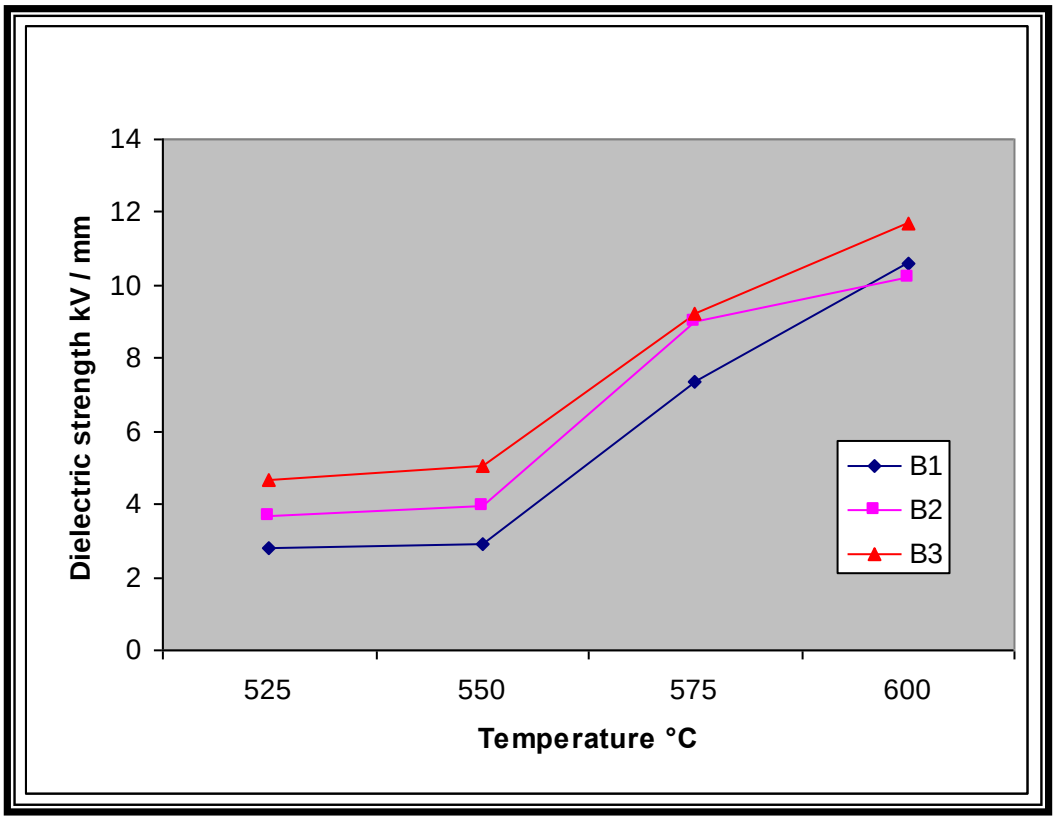


Fig. (4-15) Effect of sintering temperatures on dielectric strength for glass samples.

Figure (4-16) shows the effect of compositions on dielectric strength for glass- ceramic samples. The minimum value for dielectric strength at composition (C1), whereas composition of the batches C2 and C3 have a higher values of dielectric strength. As a matter of fact, K_2O percentage is considered the main reason for increasing in the values of dielectric strength from batch C1 to batches C2 and C3. We have already discussed in article 4.2.4 the effect of K_2O percentage upon the sintering process, in which K_2O 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.

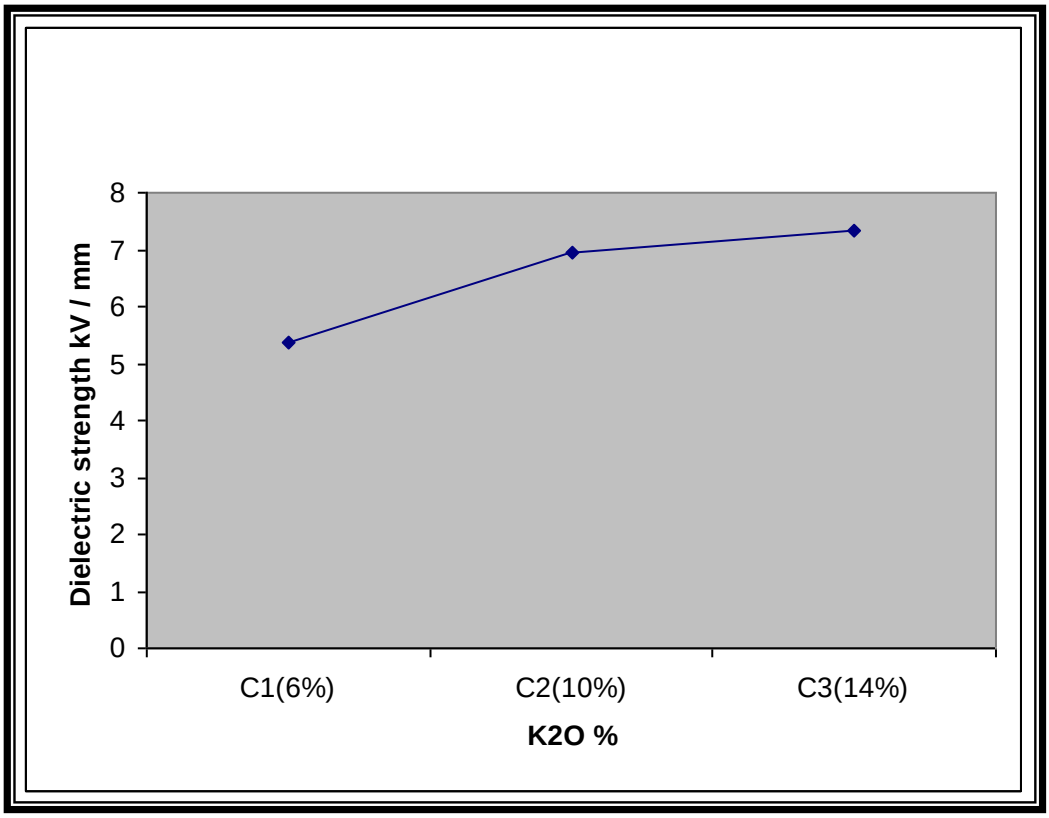


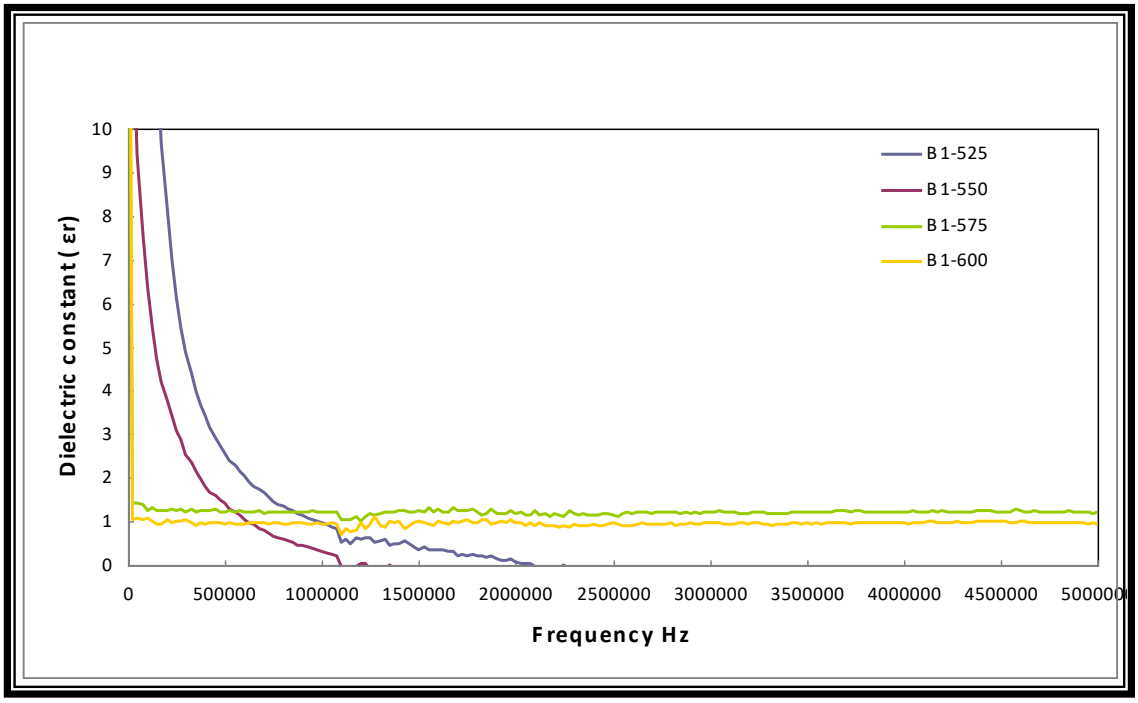
Fig. (4-16) Effect of compositions on dielectric strength for glass - ceramic samples.

4.3.2 Dielectric constant (ε_r)

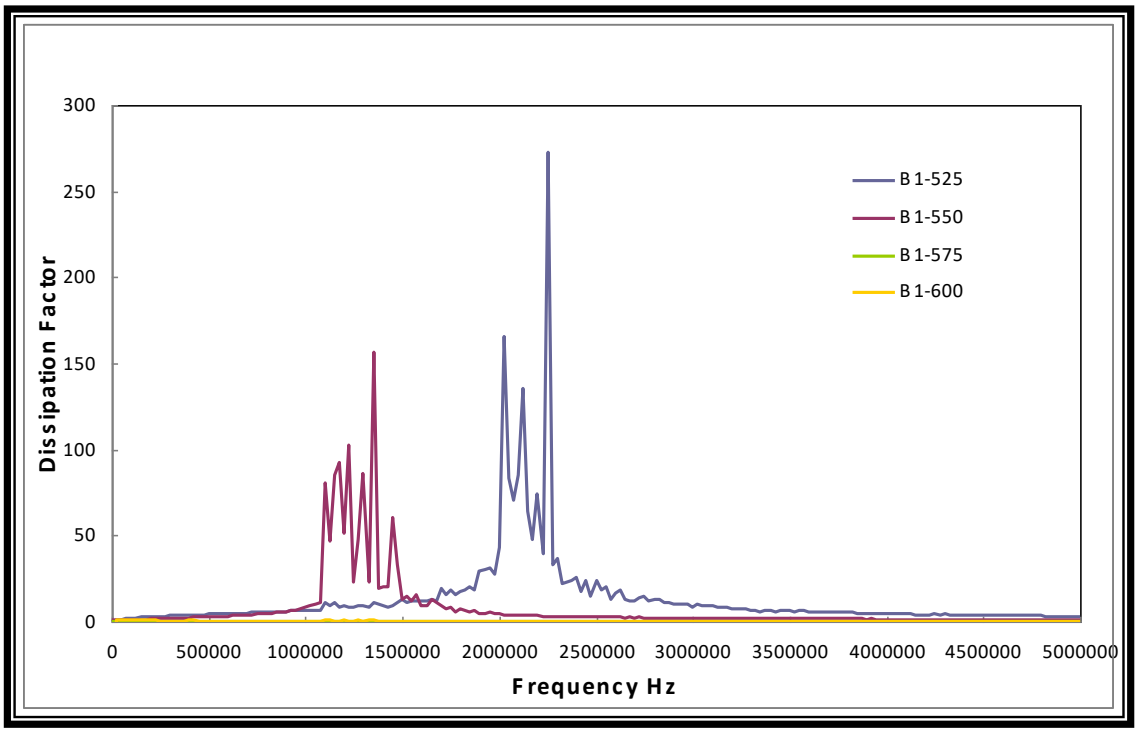
Glass

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 (P_e) and ionic (P_i) 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. Where is K^+ ion has a large atomic radius (1.33 A°), so, the percentage (14 %) of K_2O in the batch B3 should gain high electronic polarization (P_e) [71 , 72]

Figures (4-17A) (4-18A) (4-19A) show the relationship between dielectric constant (ε_r) and frequency (f) for prepared glass samples (B1 , B2 , B3), respectively. These batches are sintered at different temperatures, and the frequency applied was in the range (40 Hz – 5 MHz).

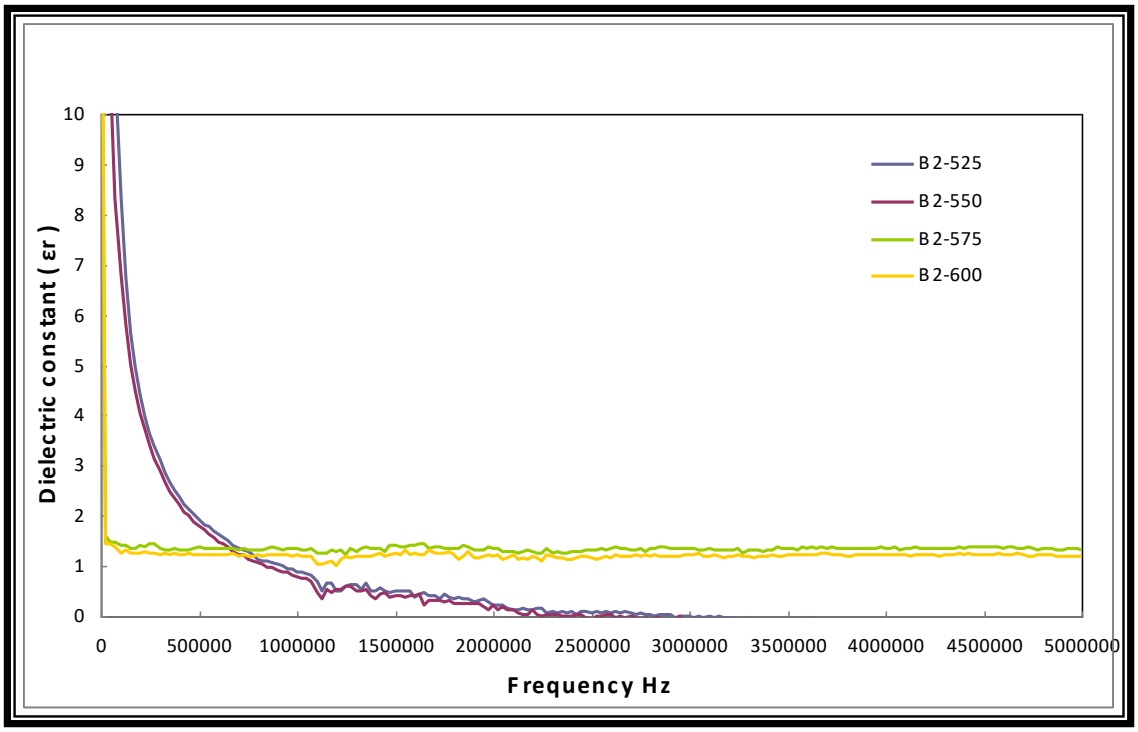


(A)

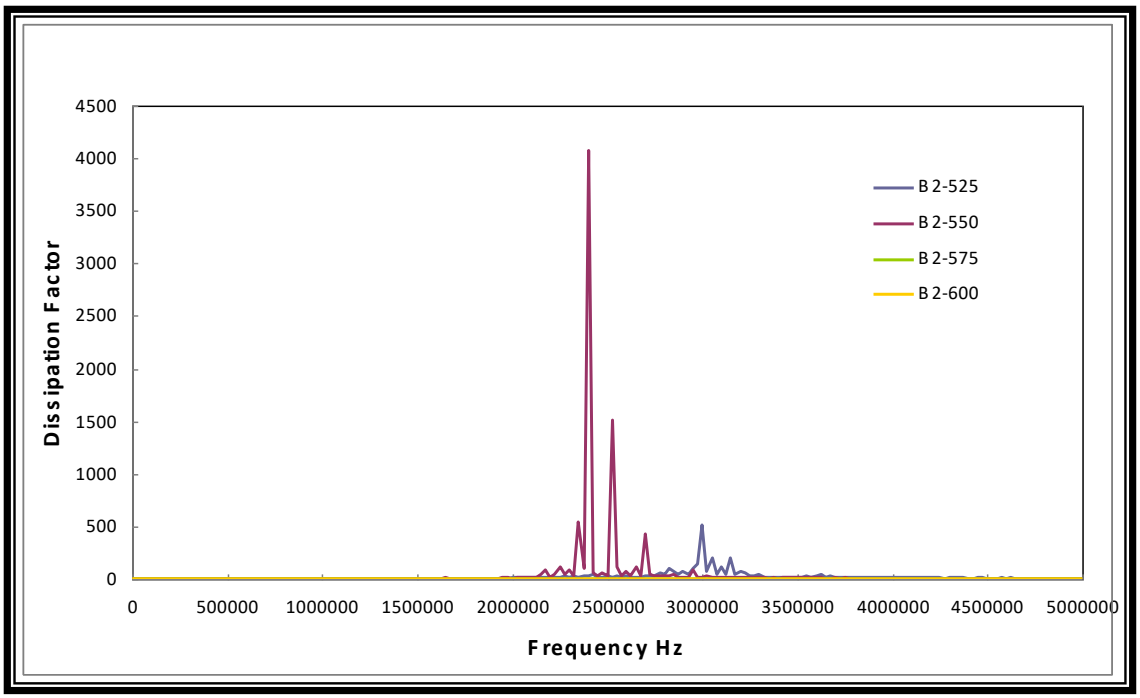


(B)

Fig. (4-17) (A)- Relationship between dielectric constant (ε_r) and frequency (f) for glass sample (B1) at different temperatures ; **(B)-** Relationship between Dissipation Factor and frequency (f) for glass sample (B1) at different temperatures .

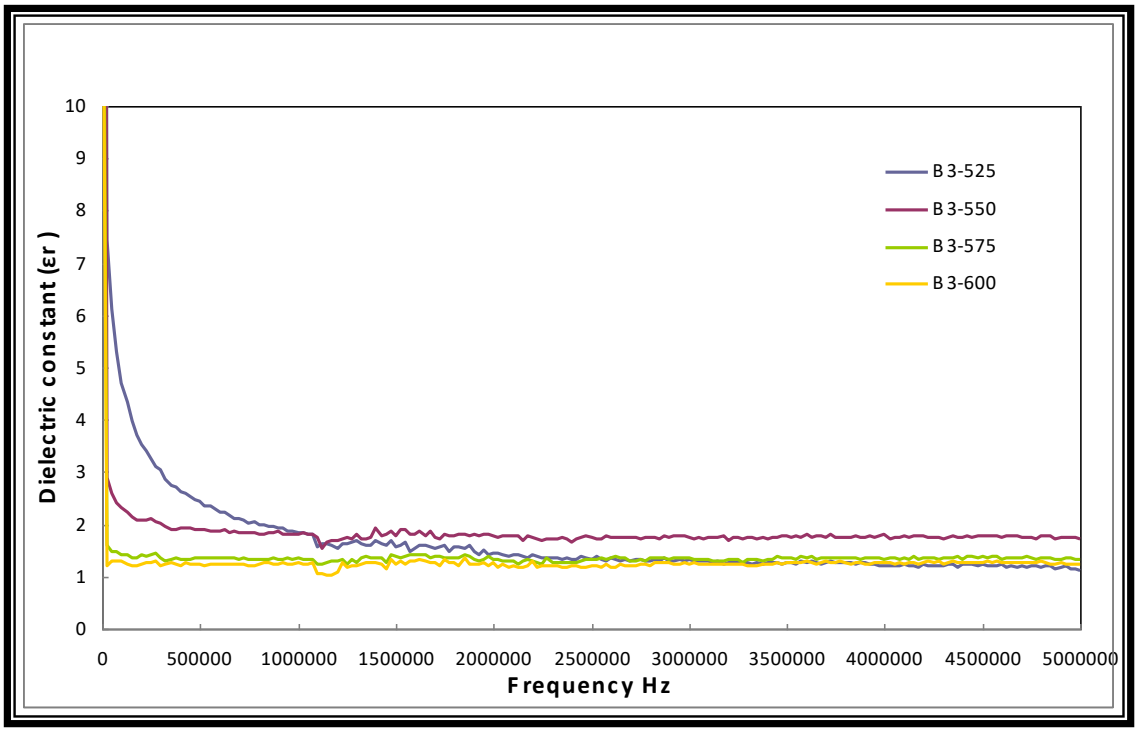


(A)

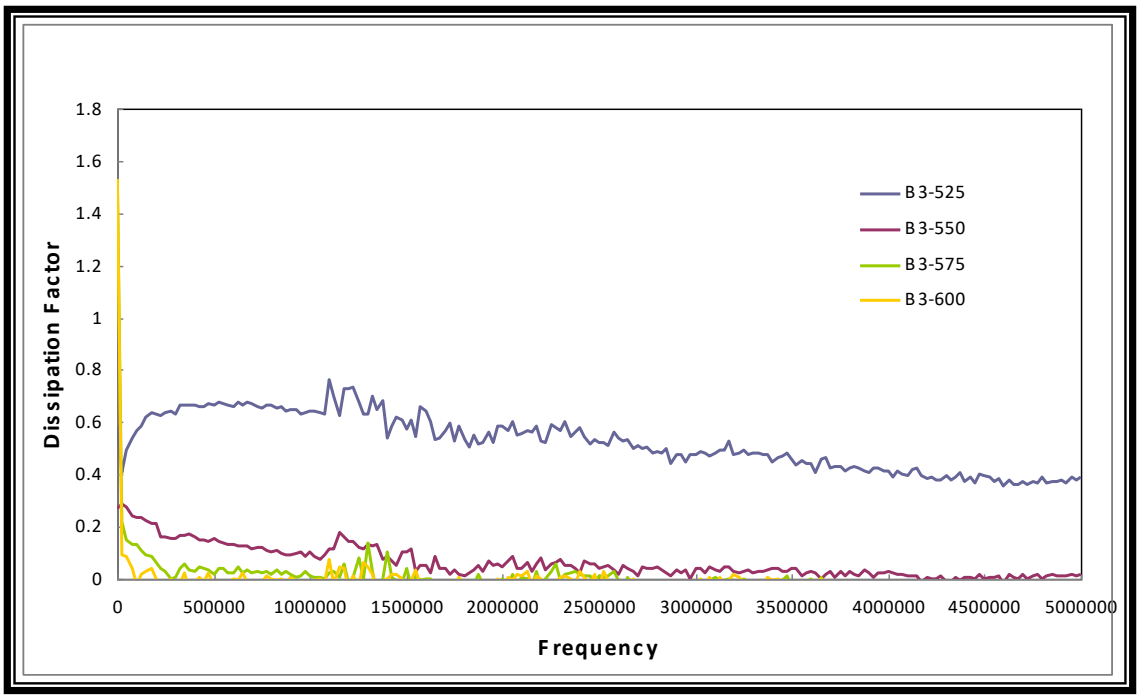


(B)

Fig. (4-18) (A)- Relationship between dielectric constant (ε_r) and frequency (f) for glass sample (B2) at different temperatures ; **(B)-** Relationship between Dissipation Factor and frequency (f) for glass sample (B2) at different temperatures .



(A)



(B)

Fig. (4-19) (A)- Relationship between dielectric constant (ε_r) and frequency (f) for glass samples (B3) at different temperatures ; **(B)-** Relationship between Dissipation Factor and frequency (f) for glass samples (B3) at different temperatures .

It may be noted from previous figures (4-17A), (4-18A), (4-19A), at low frequencies, the maximum values of dielectric constant were at sintering temperature (525ºC), and the minimum values at sintering temperature (600 ºC) for all compositions. 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 frequencies [73].

In the previous at figure (2-11) [chapter two], we have discussed 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 [7,29].

Figures (4-17A), (4-18A) and (4-19A) which have the same sintering temperature, show the same behavior in which the dielectric constant (at low frequencies) be as follow:

$$(\varepsilon_r \text{ B1}) > (\varepsilon_r \text{ B2}) > (\varepsilon_r \text{ B3})$$

It has been observed that the batch composition (B3) has lower value of dielectric constant. This batch as mentioned before has 14% K_2O in its composition, which acts as a flux when the sample is heat treated, and in result becomes lower porosity and hence acquires lower dielectric constant.

Figure (4-17A) which represents batch B1, in which K_2O % equal to 6 %, shows that the dielectric constant (ε_r) for sintered samples (B1-525 , B1-550) has maximum value at low frequencies result of high porosity which increases the effect of space charge polarization contribution.

It may be noted from figure (4-17A) that 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: (1) the absence of

space charge polarization effect at high frequencies, (2) 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 (K_2O) in composition (B1) relative to (B2 and B3) compositions.

Figure (4-18A) which represents batch B2, in which K_2O % equal to 10 % shows that the sintered samples (B2-525 and B2-550) have a dielectric constant (ε_r) less than that of the samples with composition (B) at low frequencies, because low effect of space charge polarization at low frequencies (due to low porosity content) which results from the having large K_2O % on comparison with composition (B1).

It may be noted from figure (4-18A) 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: (1) The absence of space charge polarization effect at high frequencies, (2) The low effect of ionic and electronic polarization on dielectric constant (ε_r) (due to low percentage of K_2O) relative to composition (B3).

The dielectric constant (ε_r) value at high frequency for (B2) samples is higher than (B1) samples due to increasing (K_2O) percentage, which increases 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 .

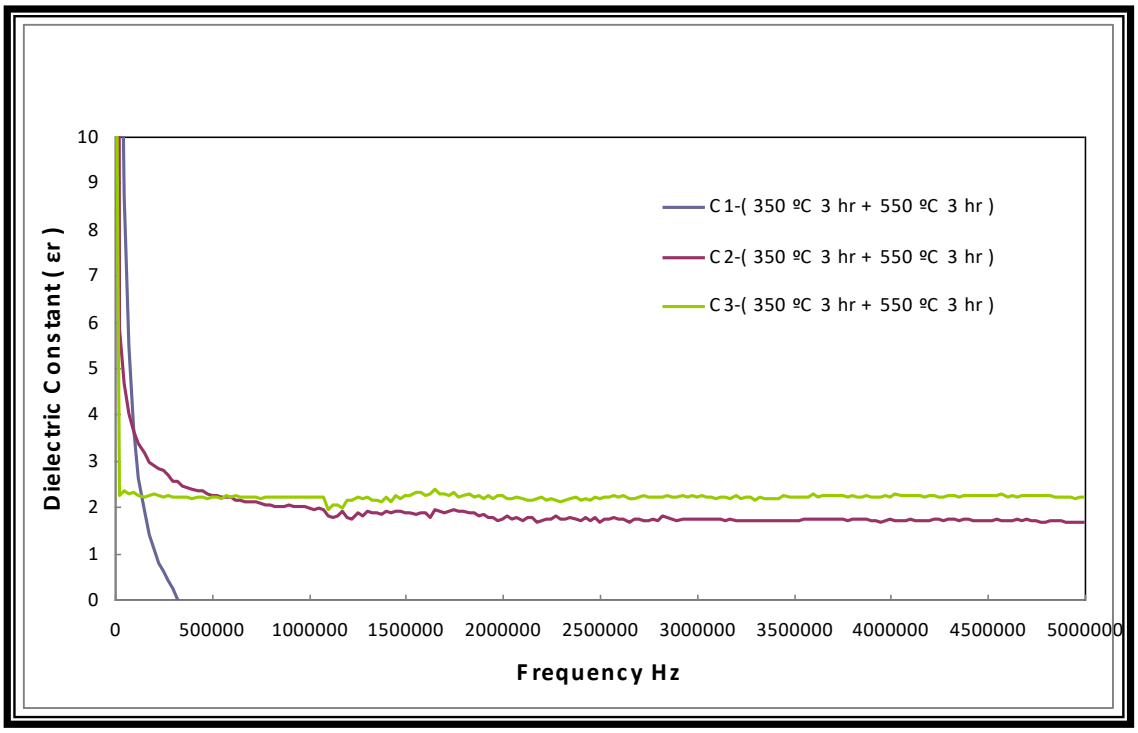
Figure (4-19A) which represents batch B3, in which K_2O % equal to 14 % shows that the sintered samples (B3-525 , B3-550) have the lowest value of dielectric constant (ε_r) at low frequencies relative to samples with compositions (B1 and B2), because low effect of space charge polarization at low frequencies (due to low porosity), which

result of increasing sintering rates relative to compositions (B1 , B2) due to increasing of (K_2O) percentage.

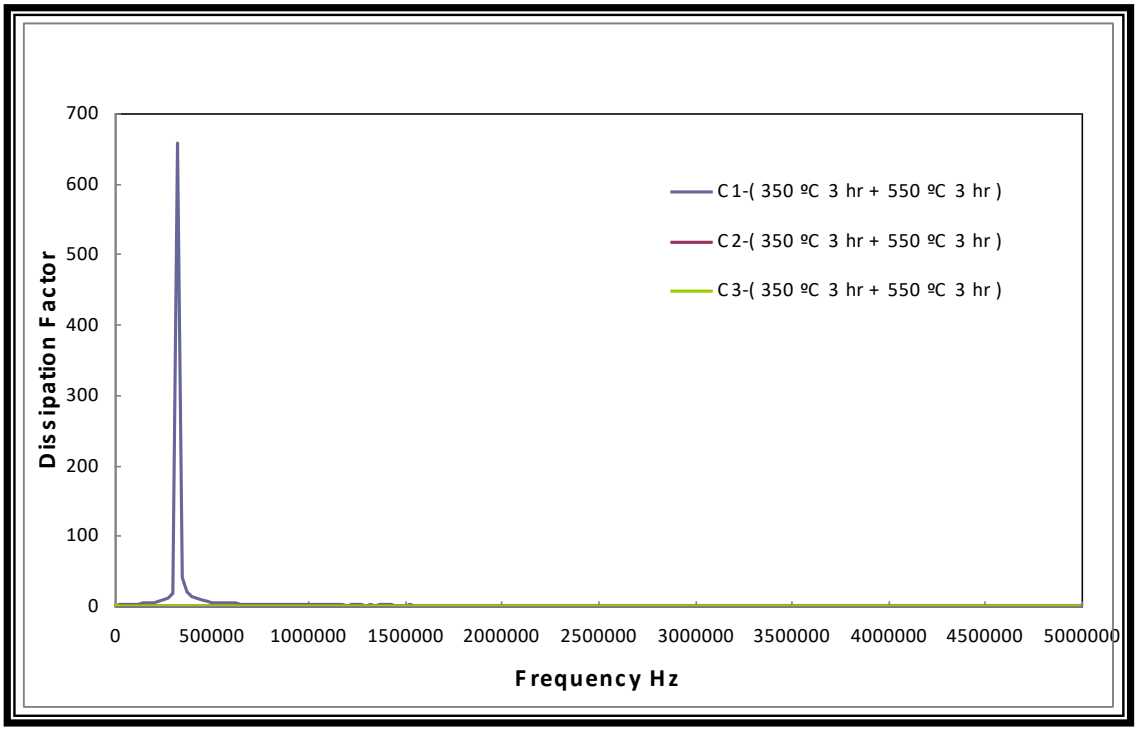
It may be noted from figure (4-19A), a decreasing of dielectric constant (ε_r) with increasing frequency to reach stable value at high frequency, due to the high effect of ionic and electronic polarization at high frequencies, which result from increasing (K_2O) percentage relative to (B1 and B2) compositions.

Glass- Ceramic

Figure (4-20A) shows the effect of frequency on dielectric constant (ε_r) for glass-ceramic samples which prepared from heat treatment (350 ºC 3 hr + 550 ºC 3 hr) on glass samples for three compositions (C1 , C2 and C3).



(A)



(B)

Fig. (4-20) (A)- Relationship between dielectric constant (ε_r) and frequency (f) for glass - ceramic samples at different compositions and treated at same heat treatment ; **(B)-** Relationship between dissipation factor and frequency (f) for glass - ceramic samples at different compositions and treated at same heat treatment.

It may be noted from figure (4-20A) (at low frequency) that

$$\varepsilon_r C1 > \varepsilon_r C2 > \varepsilon_r C3$$

The main reason of that be high contribution of space charge polarization at low frequency where:

$$P_s(C1) > P_s(C2) > P_s(C3)$$

This is a result of high porosity for (C1) composition relative to (C2,C3) where :

$$\text{Porosity \% (C1)} > \text{Porosity \% (C2)} > \text{Porosity \% (C3)}$$

because the densification rates increasing with increase of (K_2O %) which decreases porosity where :

$$K_2O=6\%(\ C1\ ) < K_2O=10\%(\ C2\ ) < K_2O=14\%(\ C3\ )$$

Also we shall explain the behavior of dielectric constant with frequency in figure (4-20A) at high frequency as below :

for samples in composition (C1) in which K_2O =6%

It may be noted that the dielectric constant (ε_r) value is decreasing by increasing frequency to minimum value at (3 MHz). The reasons of that are: (1) the absence of space charge polarization effect at high frequencies, (2) the low effect of ionic and electronic polarization on dielectric constant (ε_r) for composition (C1) relative to compositions (C2 and C3) , because there is low percentage of (K_2O) in composition (C1) in comparison (C2 and C3) compositions.

for samples in composition (C2) in which K_2O =10%

It may be noted that the dielectric constant (ε_r) value is decreasing by increasing frequency to reach stable value at high frequency due to the effect of high ionic and electronic polarization at high frequency, result of increasing in (K_2O) percentage relative to (C1) composition. As we previously explained, K^+ is large in size and contributes high (P_e).

for samples in composition (C3) in which K_2O =14%

It may be noted that the dielectric constant (ε_r) value is decreasing by increasing frequency to reach stable value at high frequency due to the effect of high ionic and electronic polarization at high frequency, result of increasing in (K_2O) percentage relative to (C1 , C2) compositions . As we previously explained, K^+ is large in size and contributes high (P_e).

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).

4.3.3 Dissipation factor (*Dielectric loss*)

As a result of comparison figure (2 – 11) with figures (4-17),(4-18), (4-19), and (4-20) which describe the relationship between dissipation factor, 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 (2-11) 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 figure (2-11) and figures (4-17A),(4-18A), (4-19A), (4-20A) that the dielectric constant at sintering temperatures (525-550)ºC 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 use of ceramic materials is the ion migration losses [41]. 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 contain Li^+ > dielectric losses for same glass but contains Na^+> dielectric losses for same glass but contains K^+ [71,74].

As we are mentioned the dielectric losses of figures (4-17B) (4-18B), (4-19B) which represent (B1- composition K_2O=6%), (B2- composition K_2O=10%), and (B3- composition K_2O=14%), respectively. It is found that the dielectric losses decreases with increasing of K_2O percentage, because of mobility effect of K^+(as we previously explained).

Chapter Five
Conclusions and Recommendations

5.1 conclusions

The following conclusions are corresponding with the objectives discussed earlier in the statements of the work sections :

1- 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.

2- The percentage of K_2O effects on crystallization of this glass, where the maximum percentage may be causes the crystallization was (10 %) and the optimum percentage (6 %).

3- The increasing of (K_2O %) reduce the melting point and facility of glass production, and (1200 °C) is enough to convert the raw materials of three compositions (B1 , B2 , B3) to amorphous structures.

4- We conclude when the add (5 %) of the crystallization agent (TiO_2), in this type of glass may be occurred as a crystallization in the glassy matrix.

5- The optimum range to sinter of glass samples which formation by powder metallurgy process was (525- 600) °C, and the optimum heat

treatment to occur crystallization in glassy phase was (350 for 3 hr + 550 for 3 hr).

6- The decreasing in porosity increase of dielectric strength. In glass sample (B3) sample has a maximum dielectric strength at sintering temperature (600°C). Whereas in glass-ceramic samples (C3) sample has a maximum dielectric strength.

7- 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 (C1 – composition) has a maximum value of dielectric constant at low frequencies, while glass – ceramic sample (C3) has a maximum value of dielectric constant at high frequencies.

5.2. Recommendations

1- Manufacturing glass and glass – ceramic from other compositions for comparison, e.g borosilicate glass.

2- Usage of differential thermal analysis (DTA) technique to determining temperatures, the melting point (T_m), glass transition (T_g) , crystallization temperature (T_c) for production of glass as first stage and formation crystallization phase in glass matrix as second stage

3- Usage of other crystallization agents e.g (ZrO_2).

4- Applied the mechanical testing.