

# STUDY THE EFFECT OF TiO<sub>2</sub> ADDITIVE ON THE PROPERTIES OF GLASS-CERAMICS PRODUCTS FROM SODA LIME GLASS

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## ABSTRACT:

In this research, a range of TiO<sub>2</sub> concentration (0 - 10) wt.% was used as a nucleating agent to produced glass-ceramics from soda-lime glass with titanium dioxide TiO<sub>2</sub> by the crystallization process from glass. The samples were prepared by using powder technology. After the powders mixing and pressing, the formed samples were heated to the nucleation temperature (370 C) with heating rate (5°C/min) and held for (2 hours) of time. After that the nucleated samples were heated above to the crystallization temperature ( 550°C) and held for (2 hours) of time in order to grow the formed titanai nucleus to crystals and to convert the glass into glass – ceramic. The physical properties (density, porosity, XRD and visual properties), mechanical properties (compressive strength and hardness) and thermal properties (DSC) were tested for all the produced samples. The results showed that increasing of compressive strength, hardness, density, glass transition temperature and crystallization temperature for glass-ceramic samples with increase of TiO<sub>2</sub> additive percentage. Also it was showed that decreasing of porosity with increase of TiO<sub>2</sub> additive percentage. While the X-ray diffraction analysis showed a present of crystalline phases in the glass matrix, this means production of glass-ceramic from the prepared compositions.

## دراسة تأثير التيتانيا المضافة على خواص الزجاج السيراميكي المنتج من زجاج الصودا لايم

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### الخلاصة:

في هذا البحث استعمل مدى من تركيز ثنائي اوكسيد التيتانيوم (0-10) % نسبة وزنية كعامل تنوية لانتاج الزجاج السيراميكي من زجاج الصودا- لايم مع ثنائي اوكسيد التيتانيوم بعملية التبلور من الزجاج. حضرت النماذج باستعمال تكنولوجيا المساحيق. بعد خلط المساحيق وكبسها تم تسخين النماذج المشكلة الى درجة حرارة التنوية (370°C) بمعدل تسخين (5) م/دقيقة وبقيت لمدة ساعتين في درجة الحرارة تلك ثم رفعت درجة الحرارة الى درجة التبلور (550°C) وبقيت ايضا لساعتين في درجة حرارة التبلور لتنمو البلورات من النويات المشكلة من التيتانيا ويتحول الزجاج الى زجاج سيراميكي. ثم فحصت الخواص الفيزيائية (الكثافة، المسامية، حيود الاشعة السينية والخواص المرئية)، والخواص الميكانيكية (مقاومة الانضغاط والصلادة)، والخواص الحرارية (DSC) لجميع النماذج المنتجة. وظهرت النتائج زيادة كل من مقاومة الانضغاط والصلادة والكثافة ودرجة حرارة الانتقال الزجاجي ودرجة حرارة التبلور لنماذج الزجاج السيراميكي مع زيادة النسبة الوزنية للتيتانيا المضافة ونقصان المسامية بزيادة نسبة التيتانيا. بينما اظهر تحليل حيود الاشعة السينية وجود اطوار بلورية في ارضية الزجاج مما يعني انتاج زجاج سيراميكي من التراكيب المحضرة.

## KEY WORDS:

glass- ceramic, titanium dioxide  $\text{TiO}_2$ , soda-lime glass, XRD, DSC.

## NOMENCLATURE

$\bar{\sigma}_c$  = Compressive strength in (MPa).

$m_d$  = the dry mass (g).

F = Applied load until fracture (N).

$m_s$  = mass of the sample suspended in water (g).

$A_t$  = Cross section area ( $\text{mm}^2$ ).

$m_w$  = the water saturated mass (g).

P = the indentation load (kg).

$\rho_{water}$  = the density of water ( $\text{g}/\text{cm}^3$ ).

a = half the indentation diagonal (mm).

$P_o$  = percentage of the open porosity.

$\rho$  = the bulk density ( $\text{g}/\text{cm}^3$ )

## INTRODUCTION:

Glass is a homogeneous material with a random, non-crystalline (liquid-like) molecular structure. Glass is a fourth state of matter that combines the rigidity of crystals with the random molecular structure of liquids. It is often described as a vitreous or glassy state. Glass should be about five times as strong as steel because of the nature of its atomic bonds. Soda-lime Silica glass is the most common (90% of glass made) and least expensive form glass. It usually contains (60-75%) silica, (12-18%) soda and (5-12%) lime. Resistance to high temperatures and sudden changes of temperature are not good and resistance to corrosive chemicals is only fair. The glass transition temperature for soda-lime glass is (500-600°C), while melting temperature is about (1000°C) (Frank, 1998). The glasses of the ( $\text{Na}_2\text{O}-\text{CaO}-\text{SiO}_2$ ) system are used in diverse applications such as components of furniture, houses, automobiles, packages, etc. nevertheless, its fragility is an aspect of technological and industrial interest. It can be considered as a development of diverse techniques among are the addition of some metal either one or more oxides of the alkaline type. The  $\text{TiO}_2$  conferred improvement in the mechanical properties of vitreous systems, which have solved the problem of formation of cracks and the growth of surface crystalline layer is slowed down in its initial stage as happens in the ( $\text{CaO}-\text{P}_2\text{O}_5$ ) and ( $\text{MgO}-\text{CaO}-\text{SiO}_2-\text{P}_2\text{O}_5$ ) systems, materials very important in the biological and industrial field to elaborate artificial bones and teeth (Parra, 2009).

Glass ceramics can be described as polycrystalline materials formed, through the controlled nucleation and crystallization of glass as shown in **figure (1)**. 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 (Wolfram, 2002). 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 (Charles, 2001). 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. These are the nucleation, formation of crystallization centers and the growth of crystals on these formed centers. 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 which named nucleating agent. 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 or heat treatment. Nucleating agents are widely used in most of

glass-ceramic production processes. The most commonly used nucleating agents are ( $\text{TiO}_2$ ), ( $\text{ZrO}_2$ ) and ( $\text{P}_2\text{O}_5$ ). The Pt group and noble metals, and fluorides are also used (Weyl, 1960). Many researchers have studied the effect of adding some materials onto properties of glass ceramics such as (Sascha et al., 1999) studied the effect of adding ( $\text{P}_2\text{O}_5$ ) on the crystallization and microstructure of glass-ceramics using high temperature, (Toshihiro et al., 2001) prepared the machineable glass-ceramics via ( $\text{P}_2\text{O}_5$ ) as glass former with ( $\text{TiO}_2$ ) as a doping material, (Sutatip, 2010) studied the effect of adding ( $\text{CaO}$ ) on the thermal parameters, physical properties, phase formation and microstructures properties of ( $\text{P}_2\text{O}_5$ - $\text{CaO}$ - $\text{Na}_2\text{O}$ ) glass ceramics.

In this study,  $\text{TiO}_2$  used as nucleating agent (heterogeneous nucleation). Titanium dioxide ( $\text{TiO}_2$ ) is a white solid inorganic substance that is thermally stable, non-flammable, poorly soluble and not classified as hazardous according to the United Nations' (UN) Globally Harmonized System of Classification and Labeling of Chemicals (GHS).  $\text{TiO}_2$ , oxide of the metal titanium, occurs naturally in several kinds of rock and mineral sands. Titanium is the ninth most common element in the earth's crust. ( $\text{TiO}_2$ ) is typically thought of as being chemically inert. Titanium dioxide has been used for many years in a vast range of industrial and consumer goods including paints, coatings, adhesives, paper and paperboard, plastics and rubber, printing inks, coated fabrics and textiles, catalyst systems, ceramics, floor coverings, roofing materials, cosmetics and pharmaceuticals, water treatment agents, food colorants and in automotive products, etc. (Gamer, 2006).

When the ( $\text{TiO}_2$ ) crystallites exist in the glass matrix, the ( $\text{TiO}_2$ ) crystallites dispersed in the glass matrix will exhibit a stable characteristic property even with surface polishing. However, literature on crystallization of glass containing ( $\text{TiO}_2$ ) crystallites by a heat treatment is scarce. Although studies of phase-separated ( $\text{TiO}_2$ ) glass have been reported, the obtained bulk glass is usually heterogeneous with a mixture of  $\text{TiO}_2$  crystallites and other crystallites (Hosono et al., 1990). Indeed, it is extremely difficult to obtain selective crystallization of ( $\text{TiO}_2$ ), because a ( $\text{TiO}_2$ ) crystal acts as a nucleus of other crystalline phases and also because it forms another crystal structure with other glass forming oxides, such as  $\text{Al}_2\text{O}_3$  or  $\text{SiO}_2$ . It can propose ( $\text{TiO}_2$ ) glass-ceramic as a promising material for several applications. First application is as a photocatalytic transparent material in which precipitated ( $\text{TiO}_2$ ) crystallites will play permanent photocatalytic property because of the fully dispersion. Second application is use in an optical element as a lasing optical device. The ( $\text{TiO}_2$ ) nano-crystallites in the glass matrix can confine light, which is suitable and interesting for random lasing, because the refractive index of ( $\text{TiO}_2$ ) is (2.52 (anatase) ~ 2.728 (rutile)) (Hirokazu et al., 2010). Glass-ceramics are also used as biomaterials in two different areas (as in glass-ceramic containing calcium phosphate and  $\text{TiO}_2$ ): First, they are used as exceptionally durable materials in restorative dentistry and second, they are applied as bioactive materials for the replacement of hard tissue. Dental restorative materials are materials which restore the natural tooth structure (both in shape and function), exhibit durability in the oral environment, exhibit high strength and are wear resistance (Sukaina I., 2010).

## EXPERIMENTAL WORK

In this study, the samples from soda lime glass (as powder with particle size approximately 60  $\mu\text{m}$ ) and different percentages of titanium dioxide ( $\text{TiO}_2$  with particle size approximately 15  $\mu\text{m}$ ) were made by using powder method and then made tests on the produced samples which include physical, mechanical and thermal tests.

### Materials Preparation.

Materials preparation includes weighing and mixing four types from soda lime glass with different percentages of titanium dioxide (nucleating agent). These types are explained in **Table 1**. The weighing process was carried out by using a sensitive balance which has accuracy (0.0001 g) type : mettler AE200 while the mix process was made by using electrical mixer.

## **Samples Formation.**

Single direction Semi-dry pressing method was used in samples formation by using hydraulic uniaxial pressing machine at a pressure of (80 MPa). Press force for all samples was (25 KN) by using Stainless-Steel die with (d= 20mm). Liquid paraffin wax was used as the lubrication to reduce the friction between the two parts of the die and to prevent adhesion between the particles with die wall during getting out the sample from the die after the pressing. Polyvinal alcohol (PVA) binder was used to prepare the samples, the percentage required of (PVA) to each sample ( 10% ) from sample weight as the pressing is semi-dry. After that the samples were dried at temperatures (110°C) for four hours to remove the moisture from the samples.

## **Heat Treatment.**

Controlled heat treatment was made on all samples in order to promote the process of crystallization and the conversion of the glass into a glass-ceramic. The thermal cycle, which carried out on the sample, included two stages of heat treatment which it nucleation stage and crystallization stage as shown in **Figure (2)**. An electrical furnace was used for heat treatment in this study. In nucleation stage, the samples were heated to the nucleation temperature (370°C) with heating rate (5°C/min) and held for (2 hours) of time in order to form the nucleus from nucleating agent (TiO<sub>2</sub>) . After that the nucleated samples were heated above to the crystallization temperature ( 550°C) and held for (2 hours) of time in order to grow the formed nucleus to crystals and to convert the glass into glass – ceramic.

## **TESTS.**

The glass-ceramic samples were tested by several tests which include mechanical, physical and thermal tests as follows:

### **1-Mechanical Properties:-**

#### **A-Compressive Strength**

The general testing machine was used to measure the compressive strength for samples. Each test result is the average of three test samples. This test is done according to the ASTM (C 773-88) standard (ASTM Annual book of standards, 1988). Compressive strength is calculated from the equation (1).

$$\bar{\sigma}_c = F / A_r \quad (1)$$

#### **B-Hardness**

The hardness of glass-ceramic samples were tested by Vickers hardness. Vickers hardness values were measured on polished surfaces by Vickers indentation technique at a 9.8 kg load applied for (10) seconds. The hardness values were obtained from an average of (3) indents on each of the three samples. Equation (2) used to calculate Vickers hardness (ASTM Annual book of standards, 1988).

$$H_v = 1.854 \times P/a^2 \quad (2)$$

### **2-Physical Properties:-**

#### **A- Visual Properties**

Visual properties for samples (the color and the outer shape) were tested. The visual test carried out to ensure that the sample is suitable and there are not any cracks or deformations which may effect on the physical and mechanical tests.

## B-Density and Porosity:

The glass-ceramic samples density were determined by Archimedes technique. The glass-ceramic samples were boiled in water for (4) hr in order to fill the pores with steam. The samples were cold to ambient temperature. The suspended sample mass in water was determined ( $m_s$ ) and the water-saturated mass ( $m_w$ ). The water-saturated mass was done by drying the surface of the sample with a paper towel then determining its mass. An average of three readings was taken for each mass (both  $m_s$  and  $m_w$ ). The samples were then dried in the furnace at (105°C) for (25) minutes and the dry samples mass was measured ( $m_d$ ). Density values were obtained from an average of three samples. The density and open porosity were calculated by using equation (3) and equation (4) respectively. This test is done according to the (ASTM C373-88) standard (ASTM Annual book of standards, 1988) (Kaya 2013).

$$\rho = \frac{m_d \rho_{water}}{m_s - m_w} \quad (3)$$

$$P_o = \frac{m_w - m_d}{m_w - m_s} \times 100 \quad (4)$$

## C- X-ray Diffraction

The heat treated glass-ceramics samples were tested by X-ray diffraction analysis of the powder crystalline samples to identify the crystalline phases developed by crystallization of the glass. The glass – ceramic samples were grounded by a mortar and pestle into a fine powder that was tested by XRD. The X-ray patterns were obtained using a (SHIMADZU XRD – 6000). A Cu anode voltage of (40 kv) and currents of (30 mA) were applied. The X-ray diffraction was performed at continuous scan mode with range ( $2\theta$ ) between (20°) and (60°) and a step size of ( $2\theta = 0.0200^\circ$ ). A scanning speed of (5 degrees ( $\theta$ )/min) was used for the analyses.

## 3-Thermal Tests (Differential Scanning Calorimetry (DSC)):

Differential scanning calorimetry (DSC) was used to examine the thermal transitions of the glass-ceramic compositions including glass transition temperature ( $T_g$ ) and crystallization temperature ( $T_c$ ). The (DSC) analysis was performed within a temperature range from (0°C to 550°C) at a heating rate of (10°C/min). The (DSC) device is connected to a control and program unit that show the data. Specimen (10 mg) from the glass-ceramic powder was put in an aluminum pan of (DSC) device, with an empty aluminum pan as a reference, ( $T_g$  and  $T_c$ ) values were determined on (DSC) curves. This test was made for all the prepared compositions.

## RESULTS AND DISCUSSION:

The present study was conducted to evaluate effect of the ( $TiO_2$ ) addition to soda lime glass on the physical, mechanical and thermal properties of the glass-ceramic which produced from it.

**Figure (3)** shows the compressive strength of the produced glass-ceramic samples from soda lime glass with different percentages of titanium dioxide (0,3,6 and 10 % wt. of  $TiO_2$ ). It has been shown that the increasing of compressive strength happen with increasing of additive percentage of  $TiO_2$ . Also the hardness for samples increase with increasing of additive percentage of ( $TiO_2$ ) as shown in **Figure (4)**. An improving on the mechanical properties of the produced samples had happen compared with the original glass, because of the crystalline phases formation in the glass matrix, which represented by the phase ( $Na_2Ca_2Si_3O_9$  at 6% wt.  $TiO_2$ ) and anatase phase at (10% wt.  $TiO_2$ ) as shown in the X-ray diffraction analysis which means the increase in the chemical bonds between the material particles and the decrease the pores between them which makes the

glass network more rigid, also because increasing the glass transition temperature of samples with increasing of (TiO<sub>2</sub>) contain as shown in the (DSC) curves, which lead to increase in mechanical strength of the samples.

In the visual properties test, the samples without (TiO<sub>2</sub>) were transparent while the samples with (10% wt.) of (TiO<sub>2</sub>) were translucent and tend to the white color gradually with increase the (TiO<sub>2</sub>) percentage because there was a difference in refractive index between the precipitated crystallites and the surrounding glass matrix, which lead to lose of transparency of the glass because of light scattering by (TiO<sub>2</sub>) crystallites with a large refractive index. Also the edges curvature was observed on the outer shape of the glass-ceramic samples as a result to the heat treatment.

**Figure (5)** shows effect of the (TiO<sub>2</sub>) percentage on the bulk density of glass- ceramic samples, where density of the samples increases with increasing of (TiO<sub>2</sub>) percentage. While **Figure (6)** shows effect of the (TiO<sub>2</sub>) percentage on the porosity of glass- ceramic samples, where porosity of the samples decreases with increasing of (TiO<sub>2</sub>) percentage. This may be attributed to the closer packing of atoms to the formation of strong structure, where the titanium forms some new interconnections within the glass network because it has a large electrical charge (+4). Also it is shown that the density of the glass- ceramic was higher than that of the corresponding glass (soda lime glass). It may be attributed to the fact that, in most cases, the densities of crystals are higher than those of the glass with the same composition because the higher atomic structural compaction (Cumpston et al., 1992).

**Figures (7, 8, 9 and 10)** show the X-ray diffraction patterns for the produced glass ceramic samples from soda lime glass with different percentages of titanium dioxide (0,3,6 and 10 % wt. of TiO<sub>2</sub>). The X-ray diffraction analysis shows present of crystalline phases in the glass matrix, this means production of glass ceramic from the prepared compositions. The important feature of all these figures is the increase of the addition weight percent of (TiO<sub>2</sub>) lead to produce a peak related to this additive. **Figure (7)** shows the X-ray analysis for the prepared glass sample without (TiO<sub>2</sub>). In **Figure (8)** X-ray analysis for composition (3% wt. of TiO<sub>2</sub>), the reflection at (28°) identified the internal standard of (Si), the reference data for the interpretation of X-ray diffraction patterns were obtained from the ASTM X-ray diffraction file index and from other publications. **Figure (9)** X-ray analysis for composition (6% wt. of TiO<sub>2</sub>) shows reflection at (33.7°) which identified the phase (Na<sub>2</sub>Ca<sub>2</sub>Si<sub>3</sub>O<sub>9</sub>). In **Figure (10)** X-ray analysis for composition (10% wt. of TiO<sub>2</sub>), a peak in (27.5°) (2θ) identified the present of (TiO<sub>2</sub>) (anatase) phase. The addition of more powder content leads to slightly decrease of the intensity, as shown this difference in intensity between **Figures (7 and 10)**.

Glass transition temperature (T<sub>g</sub>) and crystallization temperature (T<sub>c</sub>) were measured from temperature of the maximum peak of (DSC) curves for the glass- ceramic samples as shows in **Figures (11, 12, 13 and 14)**. The value of glass transition temperature and crystallization temperature increased for the glass- ceramic samples with increase of (TiO<sub>2</sub>) additive percentage as shown in **Figure (15)**. The (DSC) peak shifted toward higher temperature when compared with the original glass **Figure (11)**, the increase was expected due to the fact that (TiO<sub>2</sub>) is known to increase the glass viscosity and strengthen the glass network because the melting temperature of (TiO<sub>2</sub>) is higher than that of all components of the original glass.

## CONCLUSIONS

It can be concluded as follows:-

1. Production of the glass-ceramic from the soda lime glass with different (TiO<sub>2</sub>) percent (0, 3, 6, 10 %wt.) was done successfully and the (XRD) patterns of the prepared samples proved that.

2. The compressive strength and hardness increase with increasing of additive percentage of ( $\text{TiO}_2$ ) and that is an improving in the mechanical properties of the produced glass-ceramic samples.
3. The porosity values of the prepared samples decrease with increasing additive percentage of ( $\text{TiO}_2$ ), while density of the samples increases with increase additive percentage of ( $\text{TiO}_2$ ).
4. The glass transition temperature ( $T_g$ ) and crystallization temperature ( $T_c$ ) increase when the ( $\text{TiO}_2$ ) additive percentage increase.
5. The prepared samples without ( $\text{TiO}_2$ ) were transparent while the samples with (10% wt.) of ( $\text{TiO}_2$ ) were translucent and tend to the white color gradually with increase the ( $\text{TiO}_2$ ) percentage, also the edges of glass-ceramic samples were curved as shown in the outer shape.

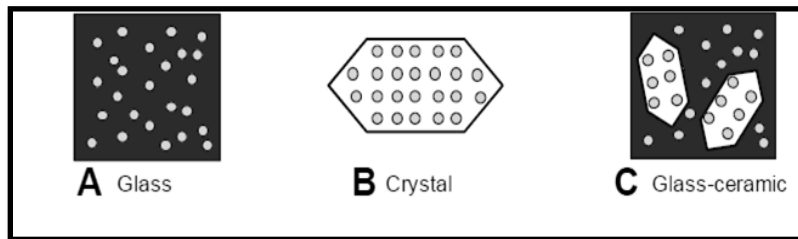


Figure (1) Schematic representations of (A) glass, (B) crystal and (C) glass-ceramic (Wolfram, 2002).

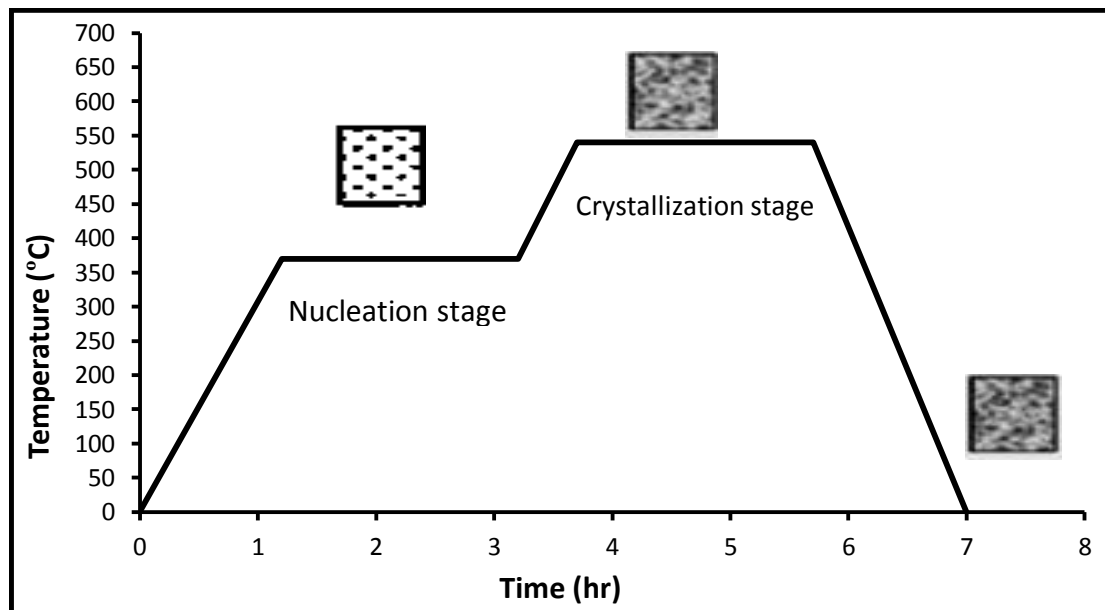


Figure (2): Shows the thermal cycle which made to the formed samples.

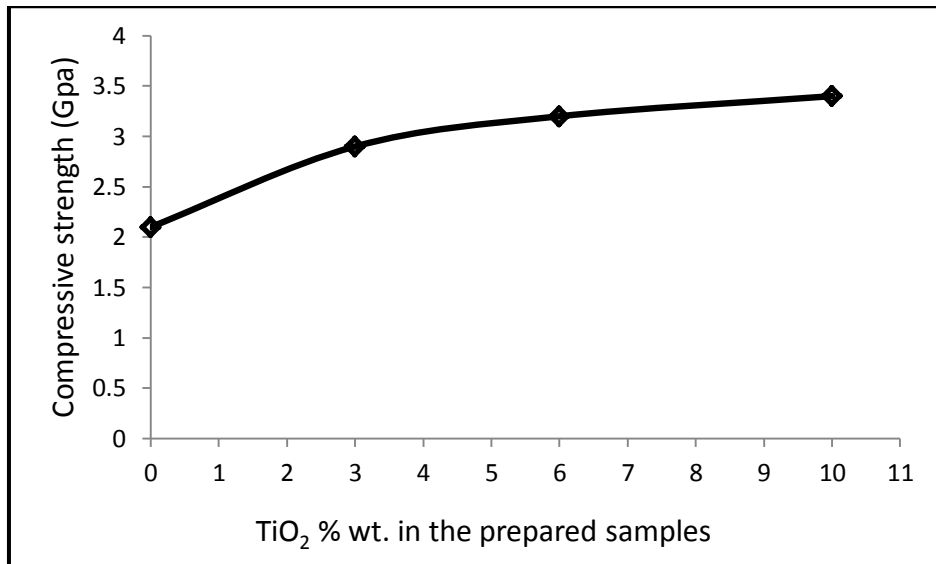


Figure (3): Shows effect of the (TiO<sub>2</sub>) additive %wt. on compressive strength of the glass-ceramic samples.

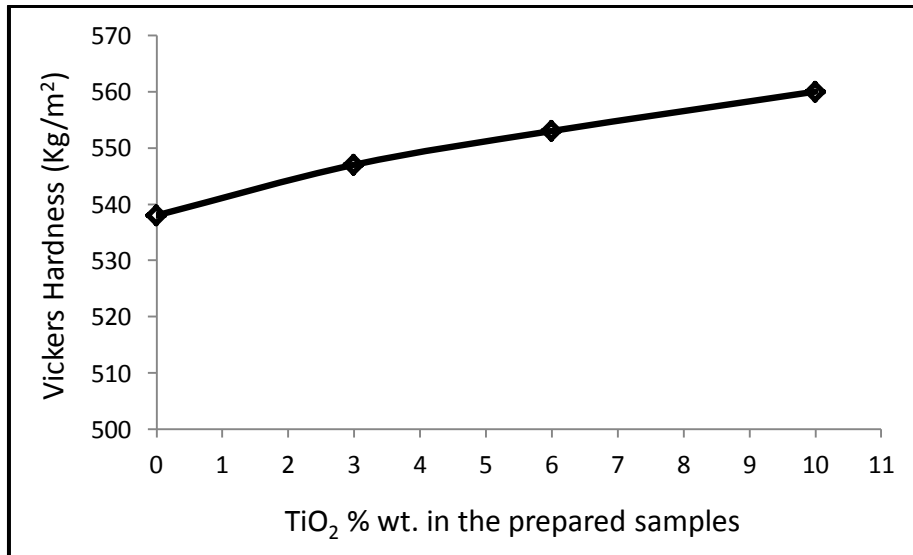


Figure (4): Shows effect of the TiO<sub>2</sub> additive %wt. on Vickers Hardness of the glass-ceramic samples.



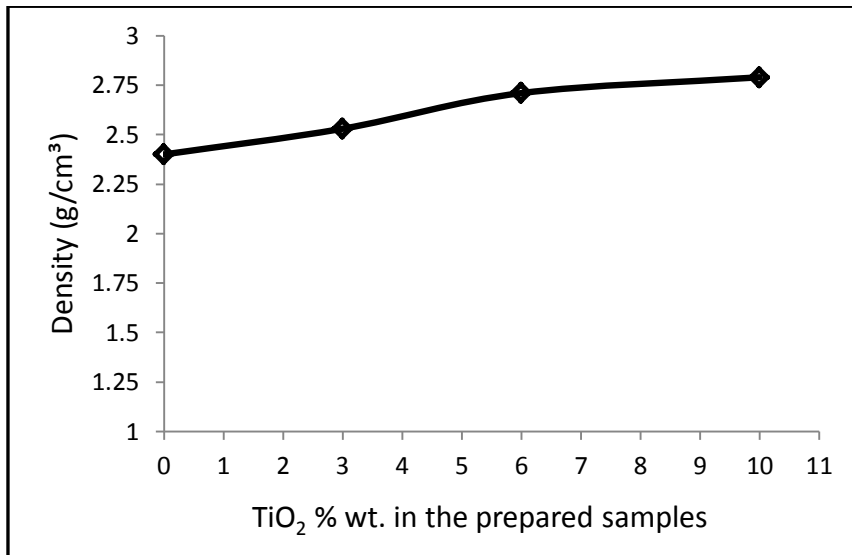


Figure (5): Shows effect of the TiO<sub>2</sub> additive %wt. on bulk density of the glass-ceramic samples.

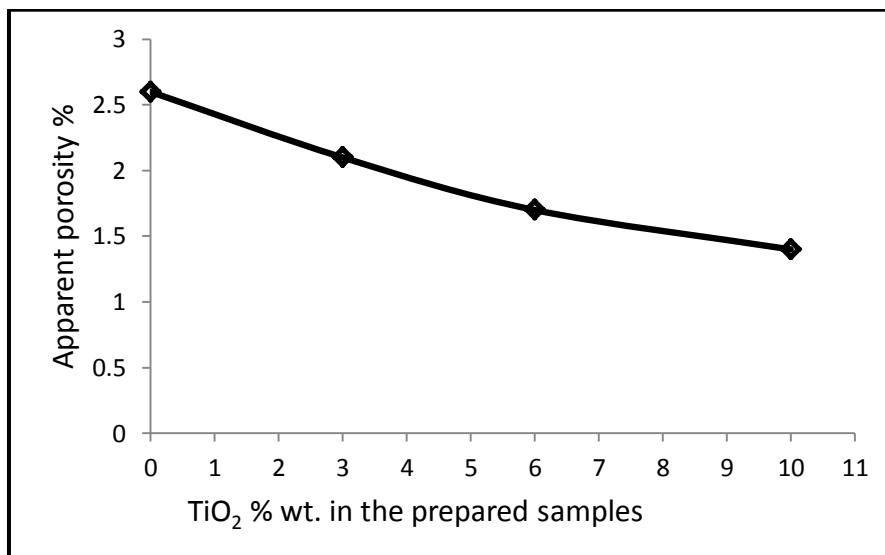


Figure (6): Shows effect of the TiO<sub>2</sub> additive %wt. on apparent porosity of the glass-ceramic samples.

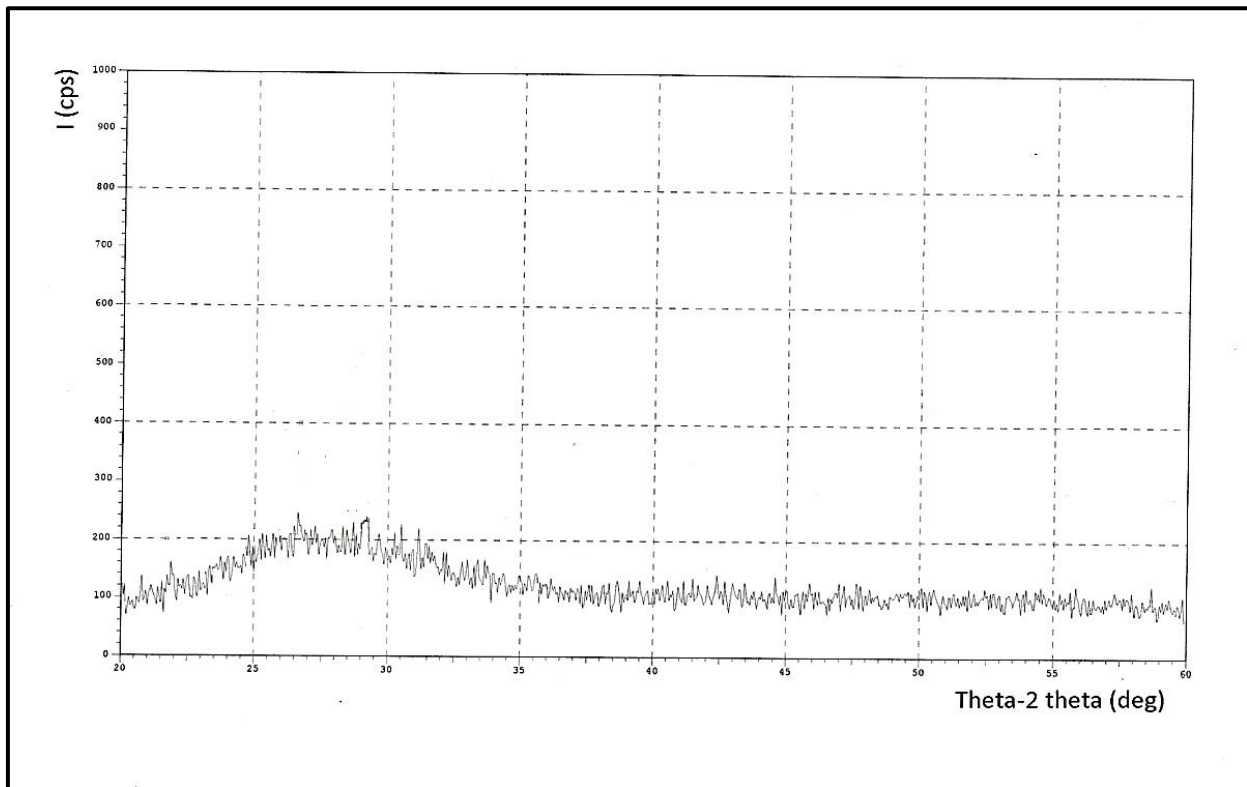


Figure (7): Shows the X-ray diffraction pattern for the glass sample without ( $\text{TiO}_2$ ).

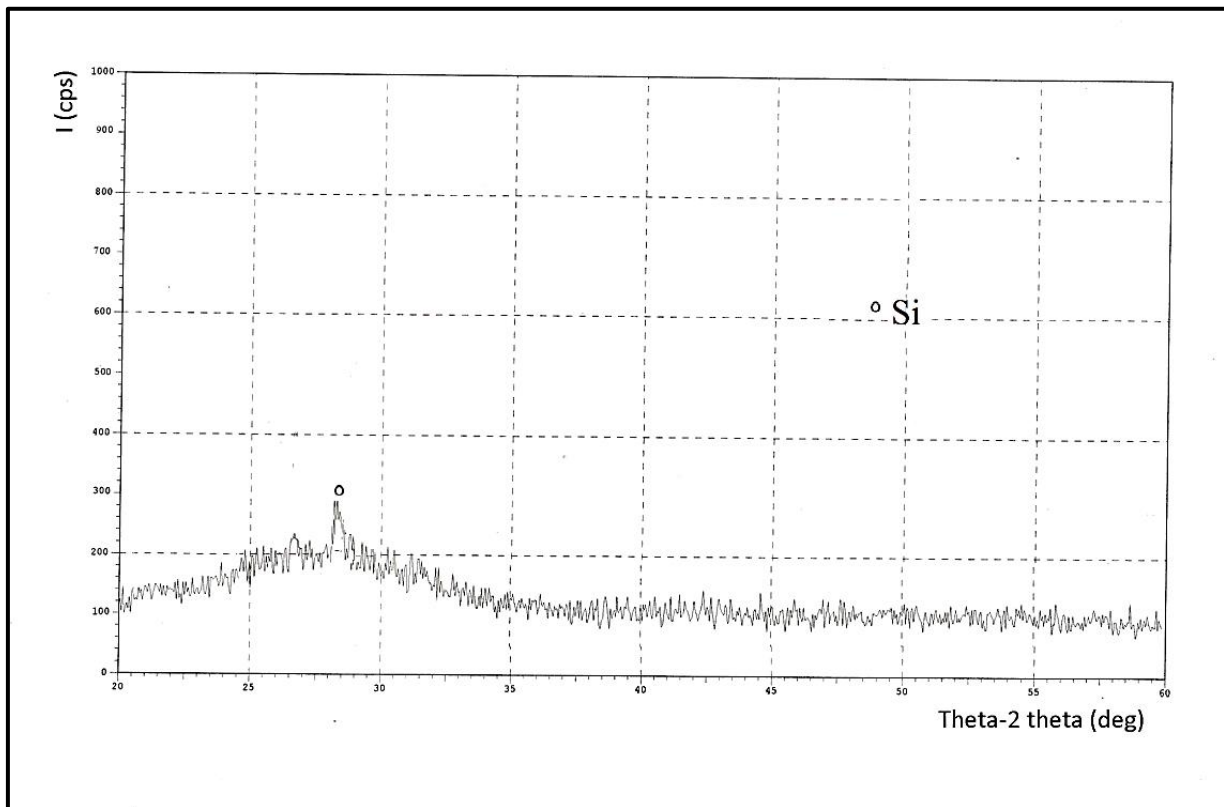


Figure (8): Shows the X-ray diffraction pattern for the glass-ceramic sample with (3% wt. of  $\text{TiO}_2$ )

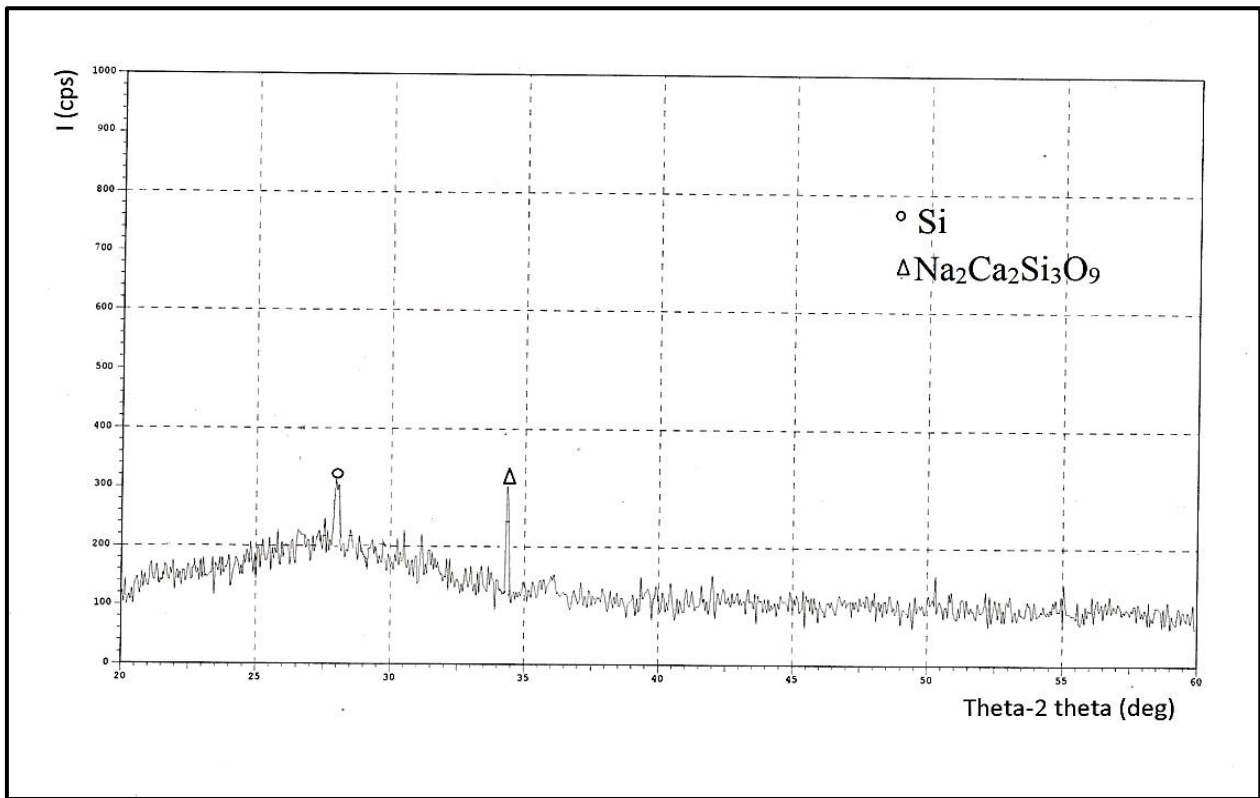


Figure (9): Shows the X-ray diffraction pattern for the glass-ceramic sample with (6% wt. of  $\text{TiO}_2$ )

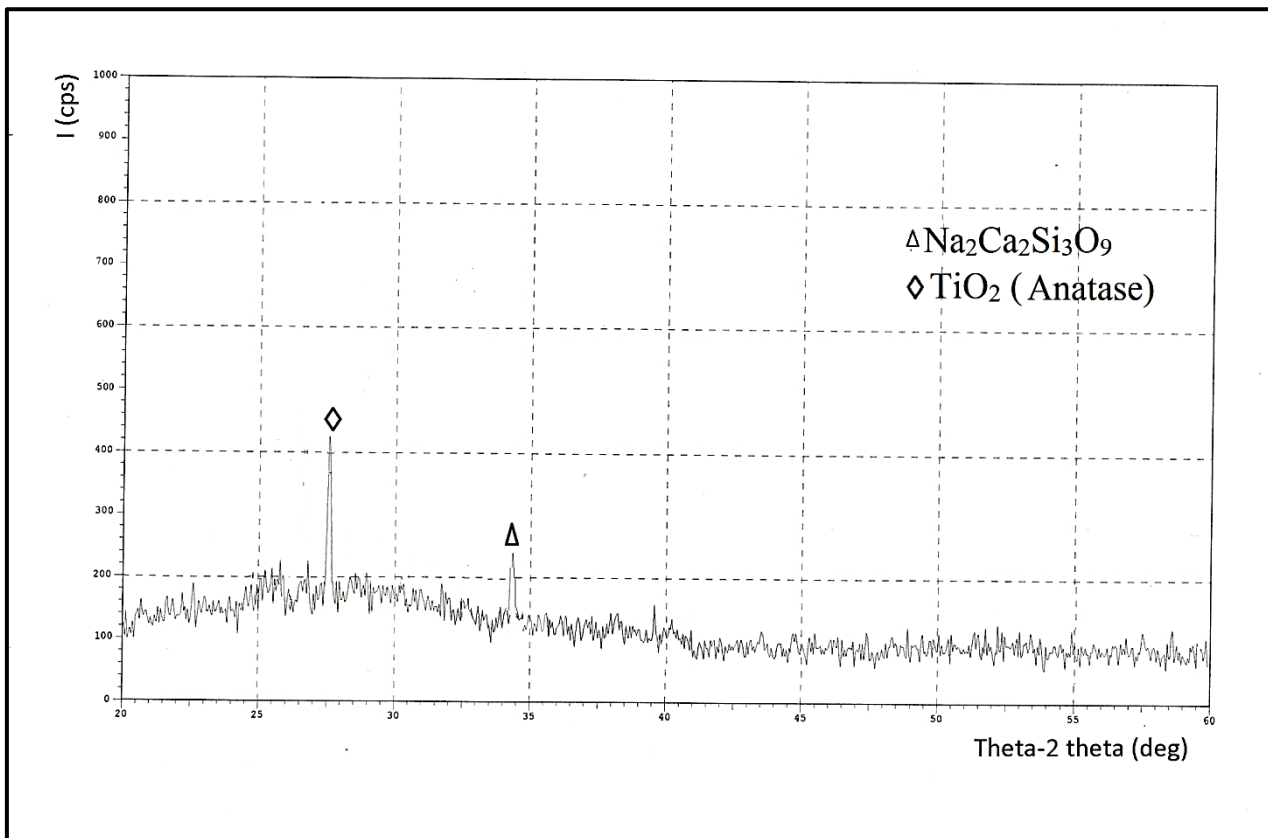


Figure (10): Shows the X-ray diffraction pattern for the glass-ceramic sample with (10% wt. of  $\text{TiO}_2$ ).

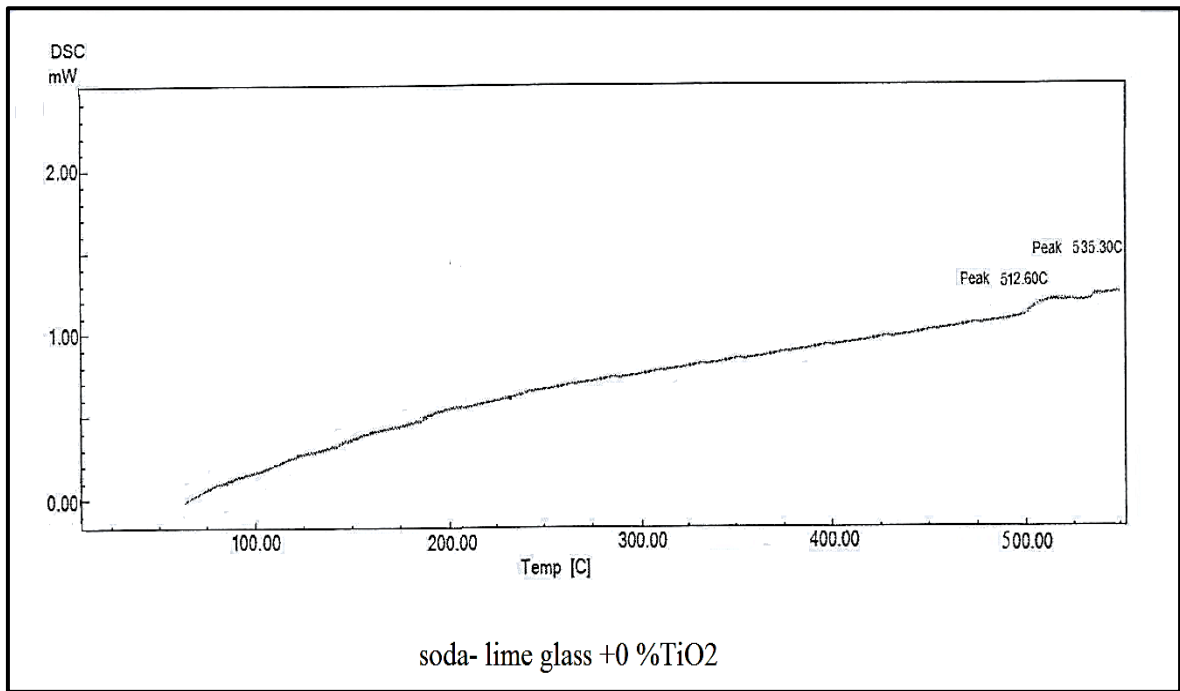


Figure (11): Shows (DSC) curve for the glass sample without (TiO<sub>2</sub>).

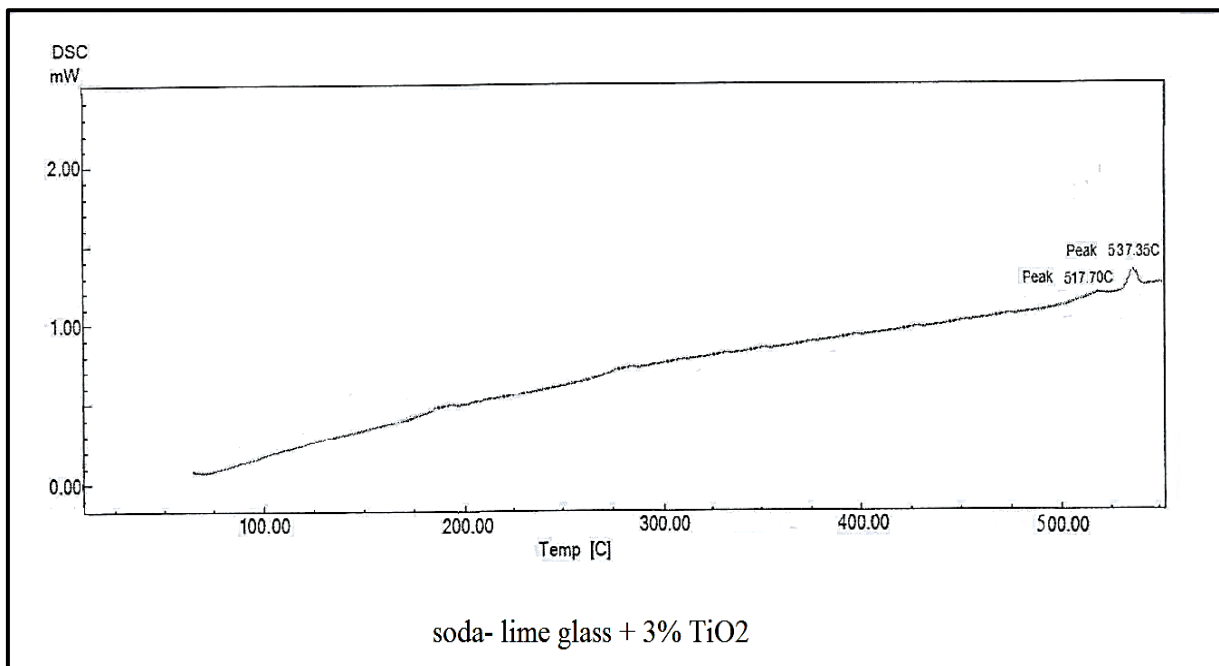


Figure (12): Shows (DSC) curve for the glass-ceramic sample with (3% wt. of TiO<sub>2</sub>).

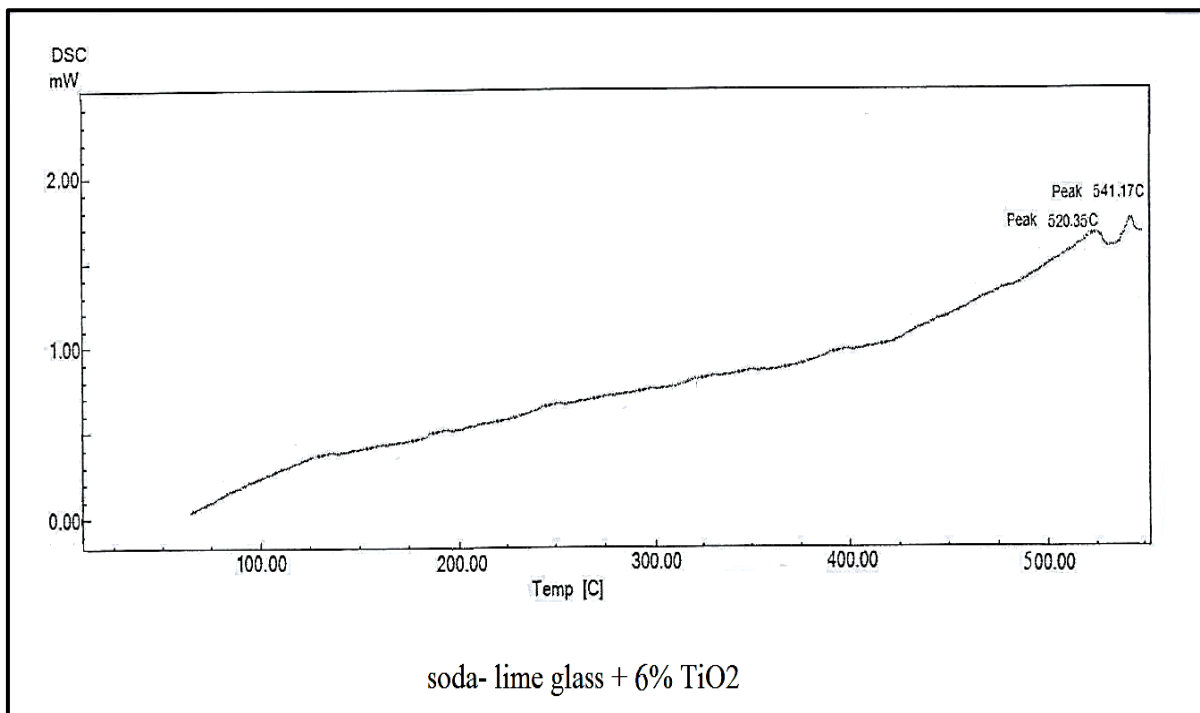


Figure (13): Shows (DSC) curve for the glass-ceramic sample with (6% wt. of TiO<sub>2</sub>)

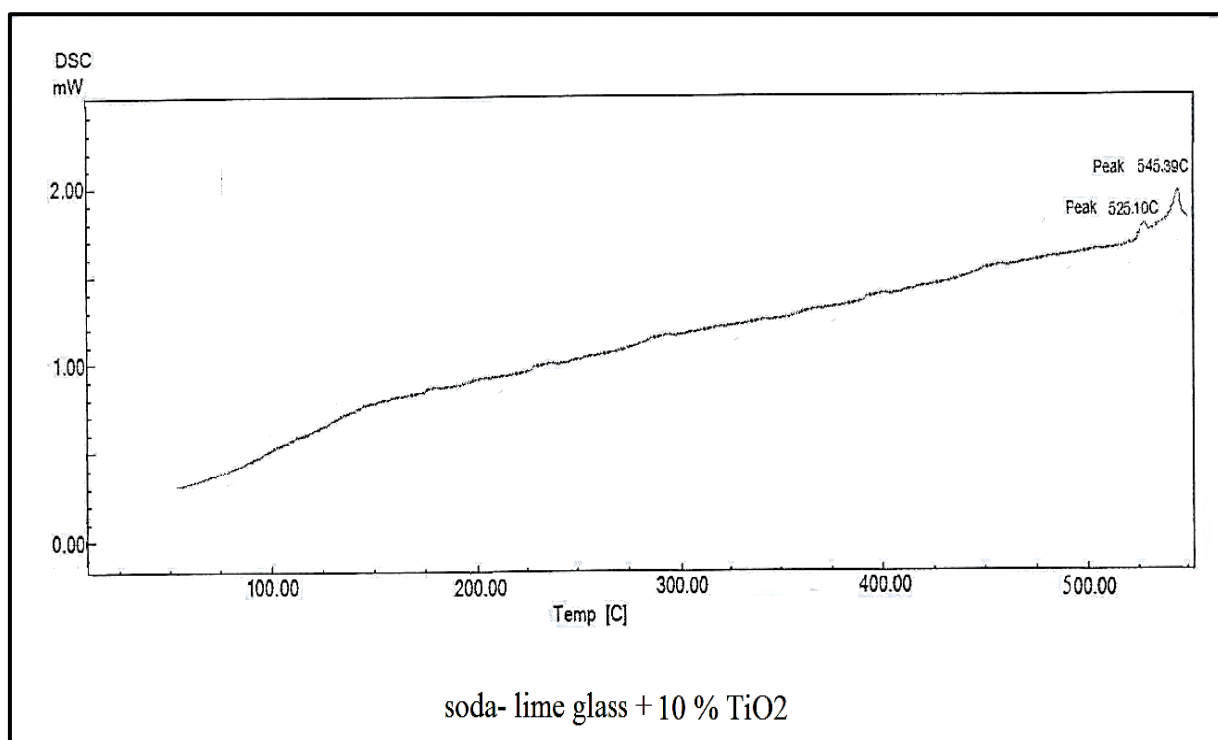


Figure (14): Shows (DSC) curve for the glass-ceramic sample with (10% wt. of TiO<sub>2</sub>).

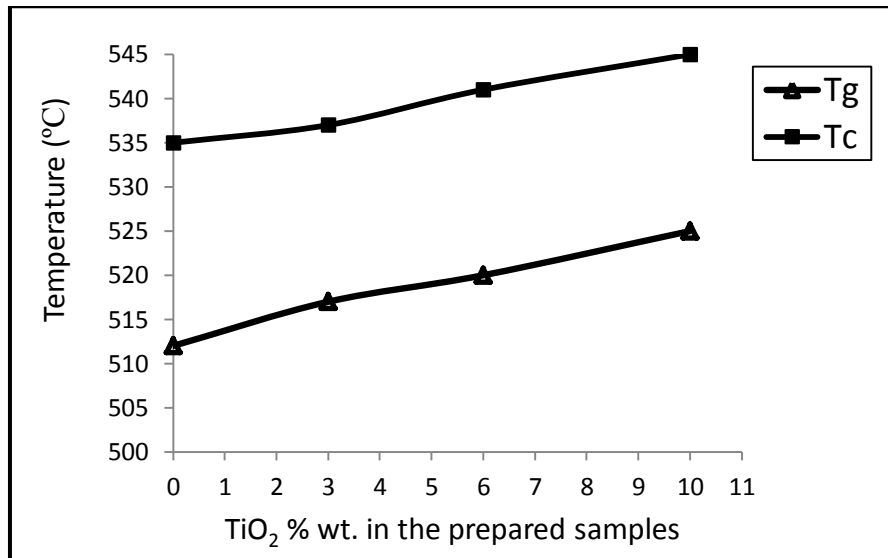


Figure (15): Shows effect of the (TiO<sub>2</sub> % wt.) on glass transition temperature (Tg) and crystallization temperature (Tc) of the glass-ceramic samples.

Table (1): Shows the percentage and the weight of soda lime glass and titanium dioxide in samples

Sample no.	Sample weight (gm)	Soda lime glass %	Titanium dioxide %	Soda lime glass weight (gm)	Titanium dioxide weight(gm)
1	9	100	0	9	0
2	9	97	3	8.73	0.27
3	9	94	6	8.46	0.54
4	9	90	10	8.1	0.9

## REFERENCES

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