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The Effect of TiO_2 Addition on Glass Ceramic Properties

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ABSTRACT

The* effectofadditiontitaniumoxide *(TiO_2) with different weight (2, 4, 6, 8 and10) wt% to glass ceramic which contain, di-phohsphoruspentoxide(P_2O_5), Calcium oxide (CaO), and Sodium Carbonate (Na_2CO_3)was studied. The effect of TiO_2 content was examined by X-ray diffraction, Raman spectroscopy and scanning electron microscopy (SEM).

Keywords: glass ceramic,P_2O_5 , TiO_2 addition, casting.

1. INTRODUCTION

Glass can be defined as "an amorphous solid completely lacking in long range, periodic atomic structure, and exhibiting a region of glass transformation behavior." Any material inorganic, organic, or metallic formed by any technique which exhibits glass transformation behavior is a glass[1]. Ceramics are compounds between metallic and nonmetallic element; they are most frequently oxides, nitrides, and carbides. The wide range of materials that fall within this classification includes ceramics that are composed of clay minerals, cement, and glass [2]. Most ceramics materials fall into an application-classification scheme [3]. Many researchers have studied the effect of adding some material onto properties of glass ceramics such as Sascha et. al. 1999 [4]studied the effect of P_2O_5 on the crystallization and microstructure of glass-ceramics using high temperature, Toshihiro *et al.* 2001[5].Preparation of machineable glass-ceramics via P_2O_5 as glass former with TiO_2 as a doping material,Sutatip 2010 [6] studied the effect of CaO on the thermal parameters, physical properties, phase formation and microstructures properties of P_2O_5-CaO-Na_2O glass ceramics. In this research we will studied the effect of TiO_2 addition on glass ceramic properties.

2. EXPERIMENTAL PROCEDURE

An electric melting furnace type (Mario demaio) heat up to 1200°C with a heating poles made of carbon. The composition of prepared samples with a melting temperature 1050°C and melting time 2 hr was listed in table (1).

Table 1 the components percentage of prepared glass.

Sample No.	1	2	3
Composition	45 P_2O_5	43 P_2O_5	41 P_2O_5
	25 CaO	25 CaO	25 CaO
	30 Na_2O	30 Na_2O	34 Na_2O
	-	2 TiO_2	4 TiO_2

The weighted materials were dried in oven at 110°C . Introduced to blender for a half hour to produce a homogeneous composition then sit in an oven at 110 °C for 24 hr to eliminate the effect of humidity. Then mixture was put in alumina crucible and then enters to furnace for melting. The temperature of furnace was rises automatically 20°C per minute up to 1050 °C each sample was kept for 2h at this temperature with, the mixing process by using long tongs for every 20 mints to produce a homogeneous melting and to ensure the escaping of bubbles from the mixture. At the end of melting time (2hr) the molten compound poured to graphite mold heated previously at 400 °C to obtained a disk sample with a diameter 2 cm and thickness about 3 mm. The mold is placed in a furnace at 400°C for 2h to avoid the localized stresses inside the glass composition which appear as a result of sudden transfer of molten from melting to heat treatment temperature. For smoothness surface, fine-polishing machine laboratory with a rotating disk diameter 20 cm and equipped with pipe water connected to a pump for the cooling purpose. Samples were polished using different granular silicon carbide polishing paper ranges from 800, 1000, 1100, and 1200 respectively. Diamond paste was used eventually to produce a shiny surface like mirror. Finally polished samples were washed with a distilled water and alcohol to become ready for tests. X-ray diffraction (XRD) pattern of the CdS film deposited on corning glass substrate is recorded by SHIMADZU XRD-6000 X-ray diffractometer (CuKα radiation λ=0.154nm) in 2θ range from 20° to 60°. The interplaner distanced d_{hkl} for different planes is measured using Bragg law[7].

$$2d \sin \theta = m \lambda \qquad 1$$

The SEM was carried out by (Hitachi FE-SEM model S-4160, Japan) in University of Tehran. Scanning electron microscope equipped with Energy Dispersive Analysis X-ray (EDAX) to determine the energy of the X-ray microanalysis. Raman spectroscopy type (SENTERRA) with specifications:Company: BRUKER (Germany), Confocal depth profiling with True-Focus, High spatial & spectral resolution (Spectral Resolution: < 3 cm-1), CCD detector, Spectral Range: 200-3500 cm^{-1}, Laser wavenumber: 785 nm . The analysis system SENTERRA is equipped with high-energy laser diodes. These laser diodes emit both visible and invisible laser radiation in the near infrared region. According to the standard EN 60825-1/10.2003, laser class is 3B products.

3. RESULTS AND DISCUSSION

Figure (1) shows the X-ray diffraction patterns for prepared glass ceramic with different TiO_2ratio (0, 2 and 4) wt%. This figure indicate all films have polycrystalline structure and have a good identically with standard peaks .

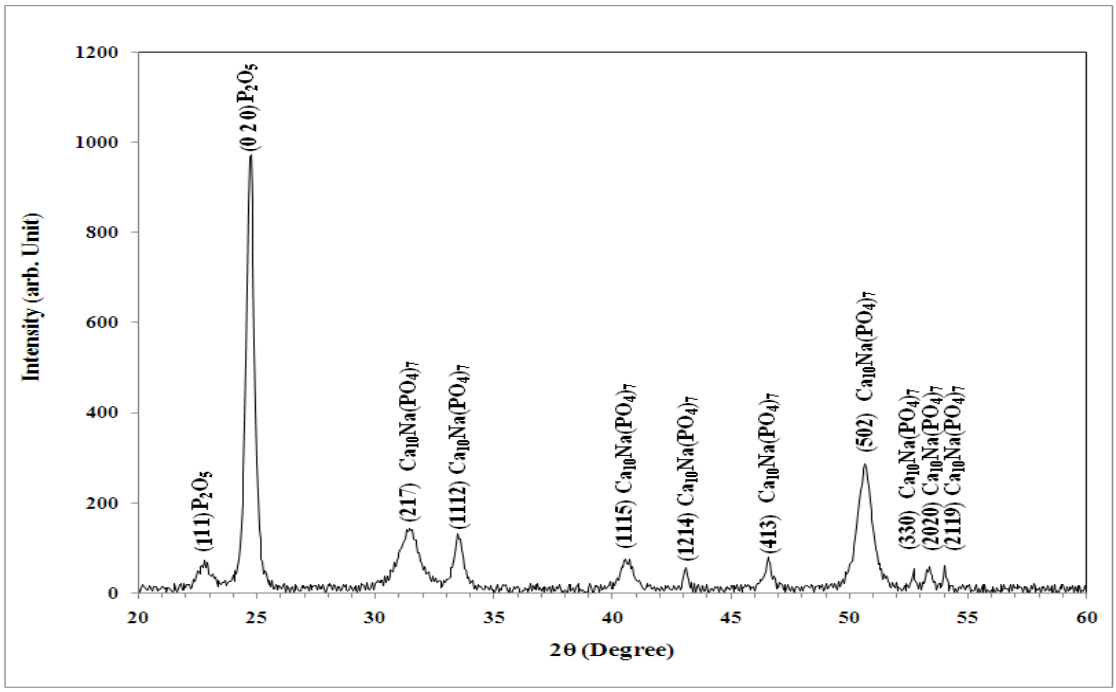

Figure1XRD patterns of glass-ceramic specimen containing 45 wt % P_2O_5, 30 wt%,Na_2O, 25 wt% CaO and without TiO_2 melting at constant temperature 1050 °C .

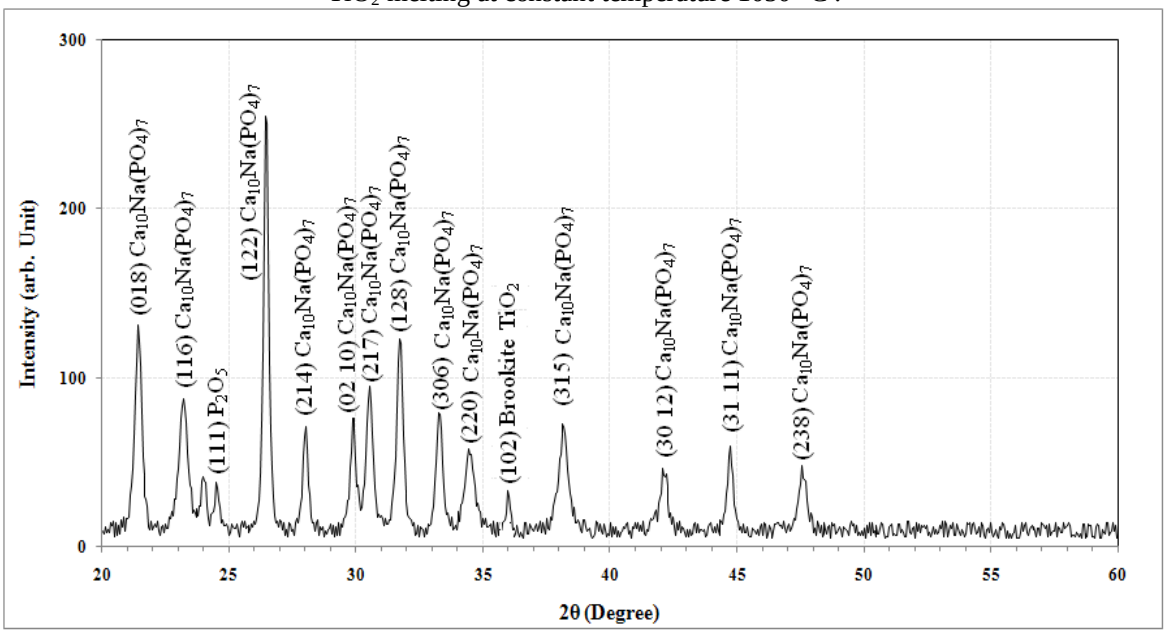

Figure 2XRD patterns of glass-ceramic specimen containing 43 wt % P_2O_5, 30 wt%,Na_2O, 25 wt% CaO and 2wt% TiO_2 melting at constant temperature 1050 °C

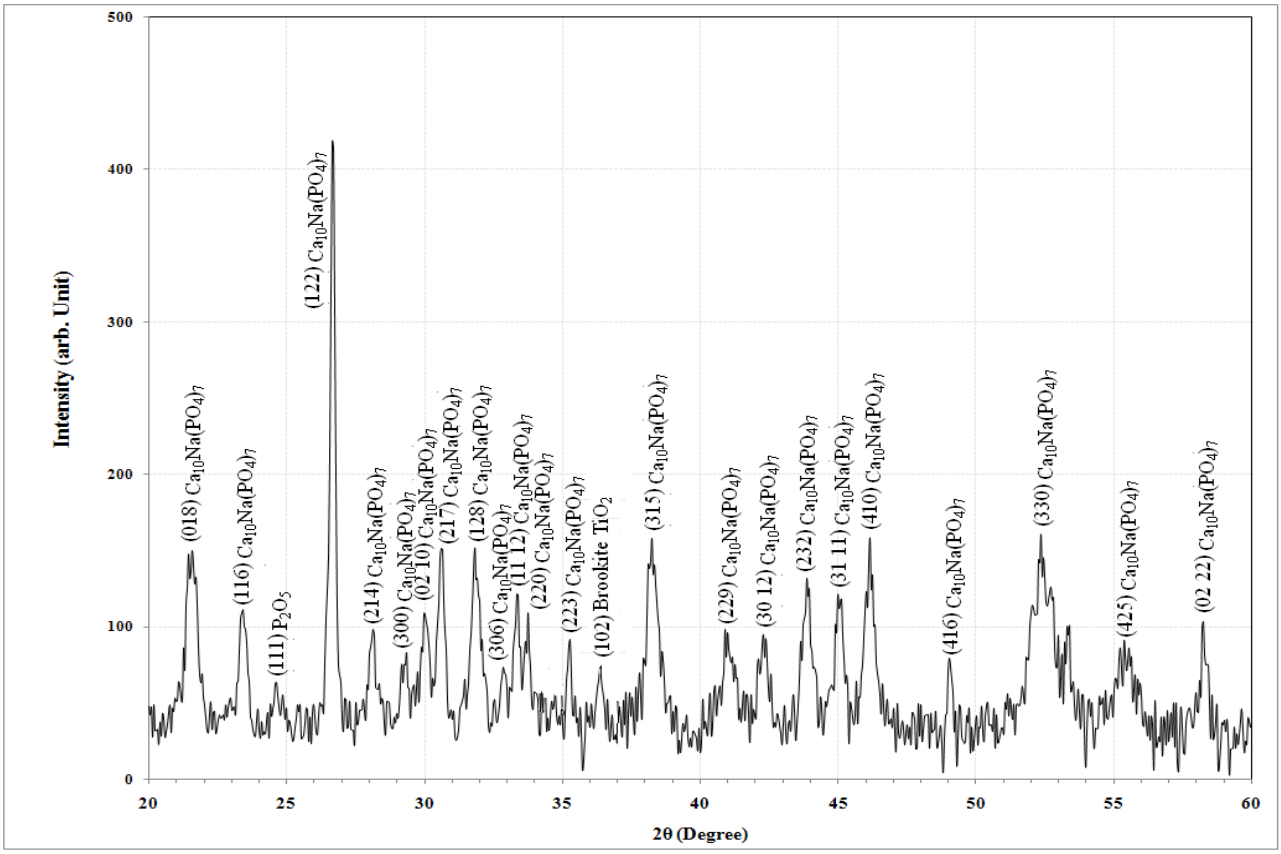

Figure3XRD patterns of glass-ceramic specimen containing 41 wt % P_2O_5, 30 wt%,Na_2O, 25 wt% CaO and 4wt% TiO_2 melting at constant temperature 1050 °C

The XRD patterns of the prepared glass ceramics without and with addition of TiO_2 powder were shown in figures (1,2 and 3). The important features of all these figures that the increase of the addition wieght percent of TiO_2 lead to produce a peak related to this additive increased gradually with the increasing percentage.Figure (1) show the X-ray analysis for the prepared sample without TiO_2. There were specific high intensity peak at ~ 2θ=25°related to the glass formerP_2O_5 and several peaks belonging to the same phase $Ca_{10}Na(PO_4)_7$.A first addition of phase (2wt %) TiO_2 revealed a highly decreasing of the predominant intensity peak (for P_2O_5), as well as, the growing of the same phase in new diffracting angels. This result can understanding in the way, that the reaction of glass composition at this percentage additive and temperature lead to the dominate of the $Ca_{10}Na(PO_4)_7$ phase. Addition of 4wt% of TiO_2 leads to the growing of the dominate phase $Ca_{10}Na(PO_4)_7$ in new positions at 2θ=40-45° and 2θ = 50-60° Figure (3) . This is the same result obtained in the previous addition (2wt%). The destructive of these phases is may be related to the reaction between the constituents leads to the hidden of some peaks and appearance of new peaks due to formation of new crystals phases .The formation of new crystallization phases may be related to the presence of P_2O_5 which was responsible to promote the precipitation and growth of crystals in glass-ceramics as mentioned by Z.Xiao et.al [8]. They deduced that the glasses containing a few mol% of Na_2O, volume crystallization results in the formation of dense glass-ceramics .J.Parkyobtained that, the intensity increases with increasing of TiO_2 content in the glass samples till it reach its maximum value at 4 wt% TiO_2 , the addition of more powder content leads to slightly decreasing intensity [9]. Another search studies the effect of temperature on the same composition used in this search with a specific additive of TiO_2 (2wt %) found that the increases of temperature lead to an increase of crystallization process which leading to increase in the intensity of peaks. Also, the growth of crystals may leads to the shifted position of creation peaks due to the different dimensions of the crystalline material [10]. The SEM was used to measure the grain size of all prepared samples. The results of this measurement provide information about the effect of TiO_2 content on the microstructure of the phosphate glass ceramic that the increasing of oxides glass leads to increasing of grain size, table (2). The first looking on these figures revealed that, in the sample that has no oxide content the grain boundaries were small and there was a groves making there way crose the surface of the prepared sample. Also, there were several heights distributed among the surface which give an indication to the agglomeration process at these places, figure, (4 - 6). The increasing of TiO_2 percentage to 2wt% lead to produce a distribution of a homogeneous grain size at the surface, as well as, the disappearance of groves and highest. The increasing of titanium oxide beyond this percentage (2 wt%) showed the formation of clusters through the glass structure which give an indication to the demonstration of formation of necks as a result of annealing process. All these outcome SEM information reinforce the previous results that obtained from x-ray and AFM analysis.

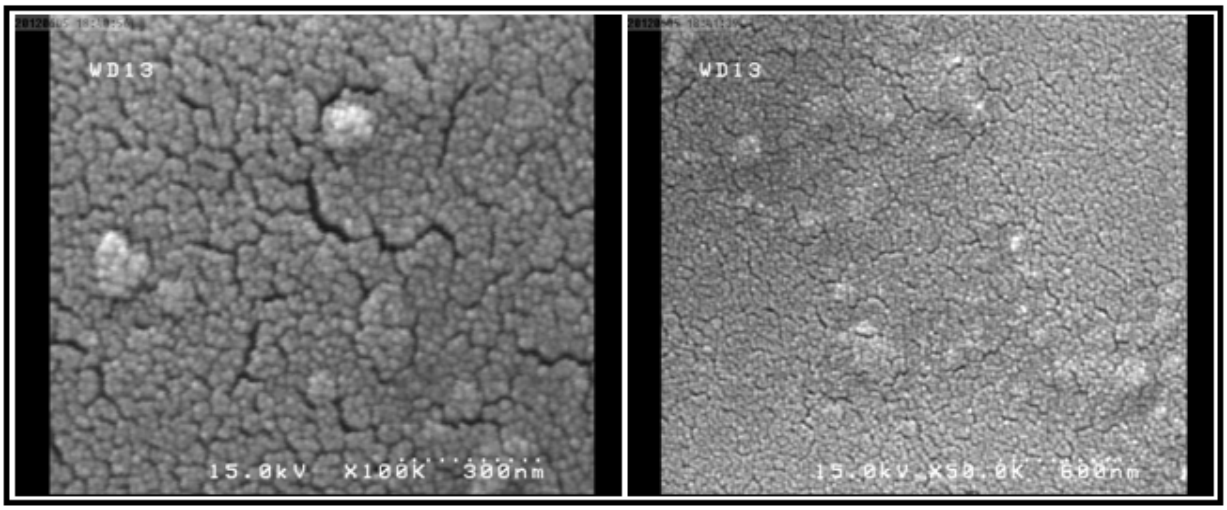

Figure 4 The SEM photo of glass-ceramic specimen containing 45 wt % P_2O_5, 30 wt%,Na_2O, 25 wt% CaO and without TiO_2 melting at constant temperature 1050 °C .

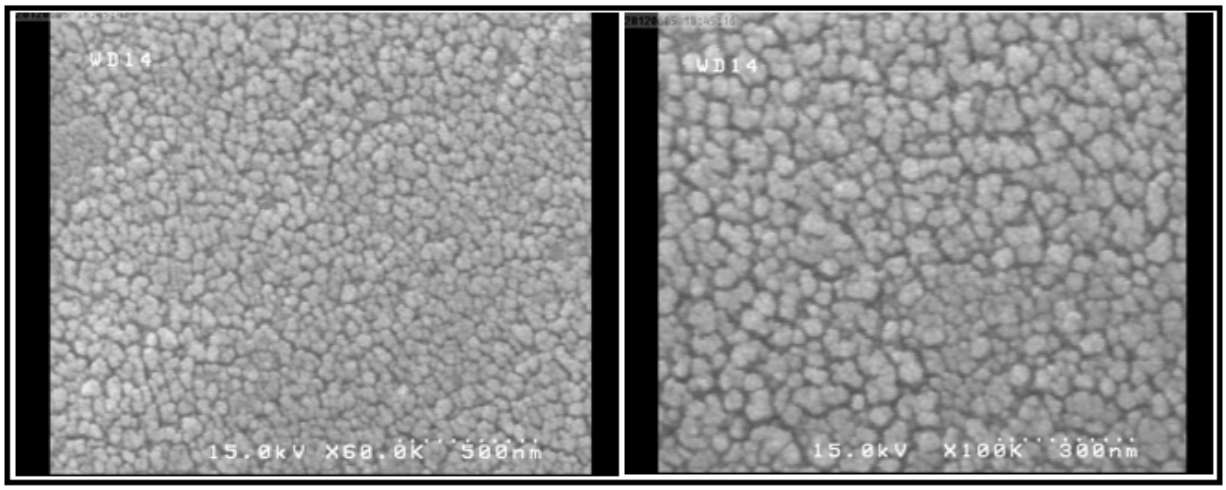

Figure 5 The SEM photo of glass-ceramic specimen containing 43 wt % P_2O_5,30 wt%,Na_2O, 25 wt% CaO and 2wt% TiO_2 melting at constant temperature 1050 °C.

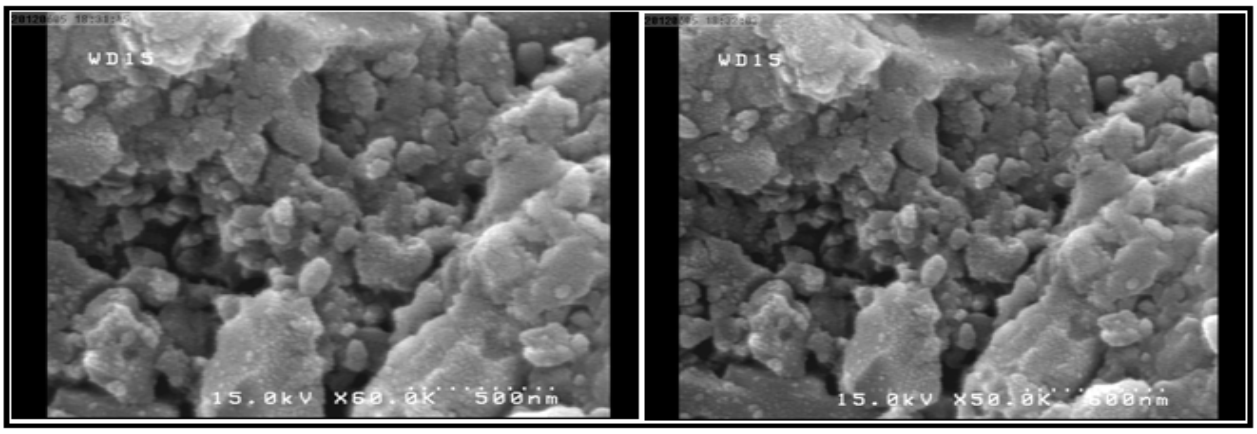

Figure 6 The SEM photo of glass-ceramic specimen containing 41 wt % P_2O_5, 30 wt%,Na_2O, 25 wt% CaO and 4wt% TiO_2 melting at constant temperature 1050 °C.

Table 2 give information about the samples composition and grain size.

Sample No.	Grain Size Av.(nm)
1	26
2	40.5
3	108

In general, a characteristic of phosphate glasses are the molecular groups as P=O, P-O^{-}, PO_4^{3-}, P-O-P bending, P-O-P stretching and P-O. The frequency of absorption of each of these bands depends on composition and combination of bonding toother groups and the vibrations of these bands. The Raman spectrum of prepared glass ceramic showing the fundamental OH –stretching vibration (3275 cm^{-1}) used for quantitative determination of dissolved water concentration in the glass. This can be explained on the depending of this band on the experience process or formation of new structure inside the sample. P-O-P stretching due to bridging oxygen Q^1 species, where Q° and Q^1 indicate Orthophosphate (PO_4^{3-}) and pyrophosphate ($P_2O_7^{4-}$) groups, respectively. Band appear at 1048 cm^{-1} in the samples contain 2wt% and at those which have gradually increasing content. That means, this band was attributed to the introducing of TiO_2 in the glass ceramic structure and the increasing concentration of this contain lead to destructive it .As the atomic number of the metals increases, the field strength of these atoms will decrease which leads to attributed to the increase in the angle of P-O-P bond in PO_4 tetrahedra[11].Raman bands in the range 700±750 cm-1 are attributed to both pyrophosphate and titanyl groups (as Ti±O single bonds) present in the phase $(TiO)_2P_2O_7$. The weak double peak at about 730 cm^{-1}(in sample has 4wt% TiO_2 and subsequently) is assigned to symmetric stretching vibrations P-O-P groups. the highest peak at 1002 cm^{-1} (P-O stretching) in the reference sample in the Raman spectrum became one of the smallest peaks for the samples contain gradual increasing of TiO_2 percentage and was diminished in the highest TiO_2 content. The obvious destructive of the band at 1002 cm^{-1} with the first introducing TiO_2 can explain in the formation of new phosphate titanium structure.

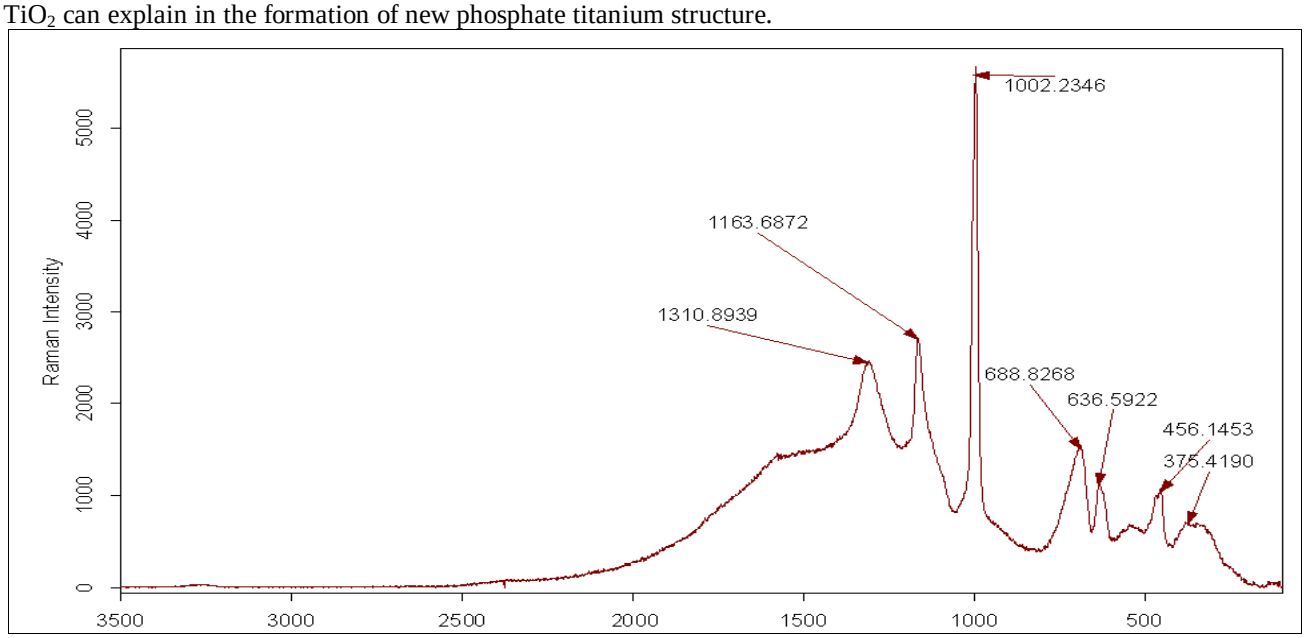

Figure 7 Raman spectrum of glass-ceramic specimen containing 45 wt % P_2O_5, 30 wt%,Na_2O, 25 wt% CaO and without TiO_2 melting at constant temperature 1050 °C .

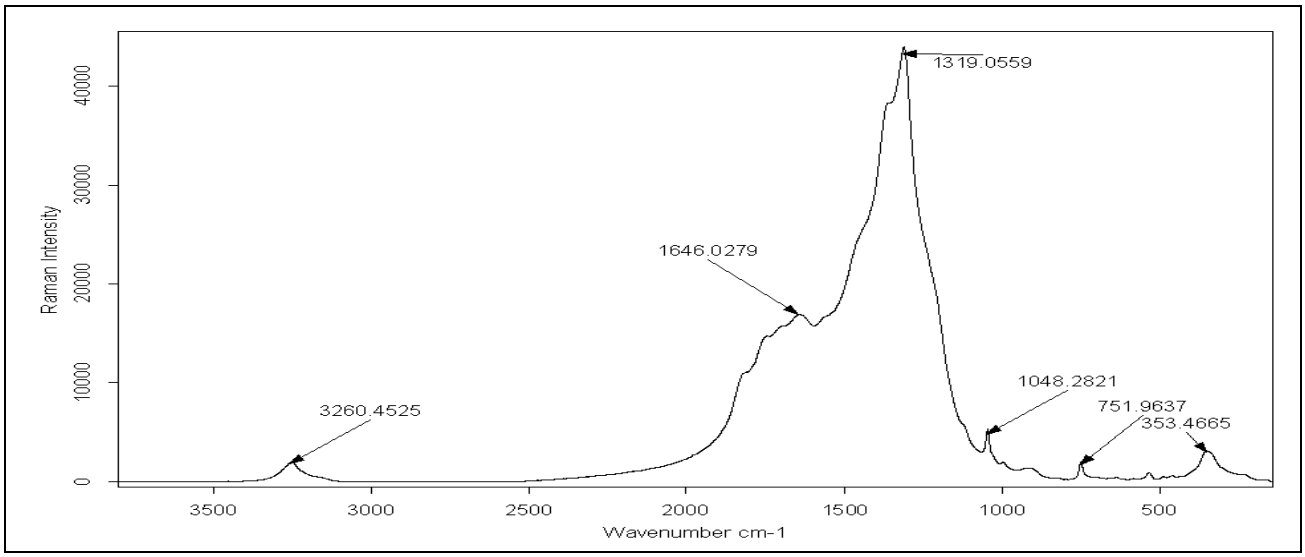

Figure8 Raman spectrum of glass-ceramic specimen containing 43 wt % P_2O_5, 30 wt%,Na_2O, 25 wt% CaO and 2 wt% TiO_2 melting at constant temperature 1050 °C .

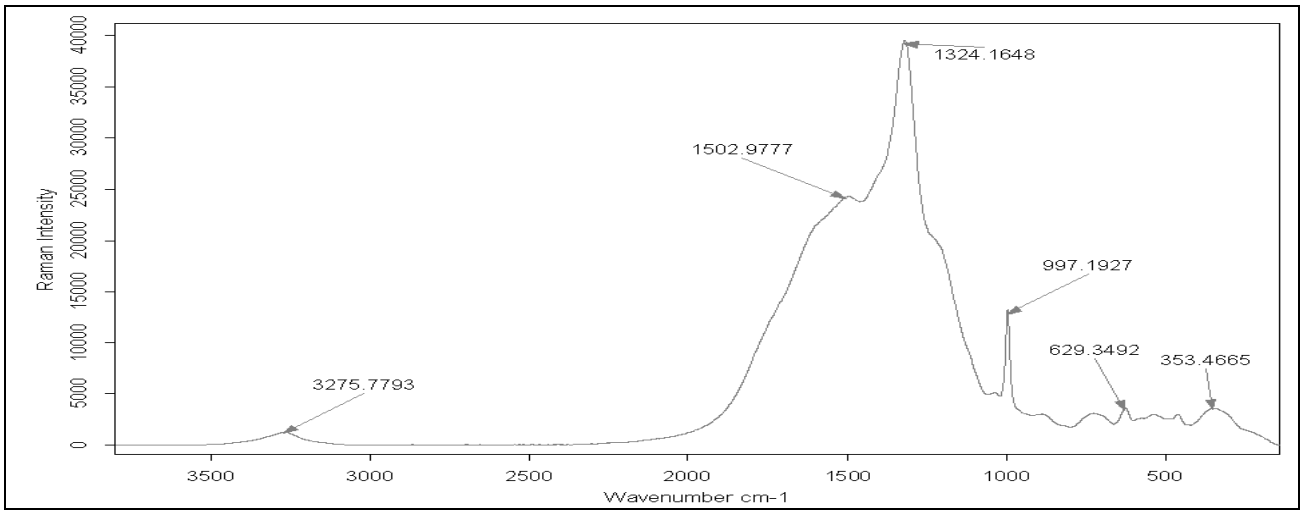

Figure 9 Raman spectrum of glass-ceramic specimen containing 41 wt % P_2O_5, 30 wt%,Na_2O, 25 wt% CaO and 4 wt% TiO_2 melting at constant temperature 1050 °C .

4. CONCLUSIONS

Structural properties,SEM and Raman spectroscopy of the glass ceramic contain, P_2O_5, CaO, and Na_2CO_3 with different TiO_2 content have been studied. The outcome of this investigation can be summarized as follows:

1. The XRD patterns of the prepared glass ceramics with different TiO_2 content show that the increase of the addition weight percent of TiO_2 lead to produce a peak related to this additive increased gradually with the increasing percentage.
2. It was founded from Raman spectroscopy investigation that the increase of TiO_2 shifting with new position. We have described here highly homogeneous for phosphate glass-ceramic investigation of Raman spectroscopy suggest.
3. The P_2O_5 is a glass former, where it was to get through this on the glass ceramic composite by adding titanium oxide with high density and also by slow cooling, which gives a longer period of the atom to lose energy gradually and get Crystal system. The work is included in this research is to study the effect of adding TiO_2 on the optical and spectroscopic properties of glass-ceramic get to special quality of the product and employed for scientific application.

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