



Structural Investigations on Na₂O – CaO-V₂O₅- SiO₂ Bioglass Ceramics

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Authors' contributions

This work was carried out in collaboration between all authors. Authors GED and HK designed the study, performed the statistical analysis, wrote the protocol, wrote the first draft of the manuscript and managed literature searches. Authors AKH, MA and SL managed the analyses of the study and literature searches. All authors read and approved the final manuscript.

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ABSTRACT

All as obtained glasses in the system 24.5 Na₂O-24.5 CaO-6 P₂O₅- xV₂O₅ (45-x) SiO₂ (x ranges from 0-15 mole %) are transparent and have an amorphous network structure. Glasses containing up to 6 mol% V₂O₅ still transparent upon heat treatment at 660°C for 4 hours. On the other hand, heat sintered glasses containing higher V₂O₅ concentration are transformed to opaque white glass ceramic characterized by their highly crystalline network structure. Crystalline apatite (calcium phosphate, Ca₃(PO₄)₂), wollastonite (calcium silicate, CaSiO₃), and sodium vanadate (Na₂VO₃) are the main well-formed crystalline species played the major role in material bioactivity. The advantage of V₂O₅ containing glasses is that it can easily be crystallized, since the high crystallinity is obtained by lowering sintering temperature when compared with that of glasses free from V₂O₅. Crystalline clusters containing vanadate species and both apatite and wollastonite phases are evidenced to be present. A hydroxyapatite (HA) formation is confirmed by the *in vitro* test of bioactivity. Processes of degradation and ion exchange between sample and phosphate solution and HA precipitation are evaluated. It is found that V₂O₅ can speed up the rate of reaction between the tested sample and phosphate solution. Glass ceramics containing V₂O₅ is highly active than that of vanadium free silicate glasses.

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1. INTRODUCTION

Bioglass ceramic (BGC) is considered as a most useful one among several types of biocompatible materials [1]. BGC is characterized by its high interfacial reaction rates between the host tissue and the implanted material in the body [2]. BGC has a great interest in medical and materials engineering applications [3]. There are some important requirements for materials to be used as biomaterial. These include suitable mechanical properties, low fabrication cost, increasing rate of reaction with body tissues and reducing the temperature of synthesis and crystallization [4]. Most types of these materials are based on amorphous silicate with a composition based on silicon dioxide 45S5® that was developed by Hench et al. in 1969 and has been demonstrated to be bioactive and osteoconductive [5,6].

In the production of bio-glass or glass ceramics, nucleating agents (NAs) such as TiO_2 , Cr_2O_3 and V_2O_5 can be used in order to induce bulk crystallization of the apatite phases [7,8]. Furthermore, the introduction of nucleating agents to the main glass can decrease the crystallization temperature and time [9]. The effects of NAs have appeared in improving both nucleation and growth rates of apatite by decreasing the surface energy between crystal and glassy phases [6]. Sintering of glasses is usually performed (between 500-800°C) to induce positive transformation processes in the glass matrix [10]. The sintering method gives clear guidelines to control the crystallization kinetics of the major phase ($Na_2CaSi_2O_6$) [11].

The bioactivity was reported to be enhanced by increasing surface areas and pore volume of bioglass (BG) [12]. Increasing of the latter may greatly accelerate the deposition process of hydroxyapatite. Moreover, it is revealed that increasing surface area of biomaterial could stimulate the reaction between material and living tissues or cells. i.e. the biomaterial is professionally prepared in nanopowders to form and enhance its surface area [13].

Previous studies have revealed that the vanadium-containing borate glasses are characterized by their high degradation rates [14]. The high in vitro HA forming ability of materials containing V^{+5} therapeutic ions makes the materials as promising candidates for bone

tissue applications [15]. To our knowledge, these characteristics didn't evaluate in vanadium containing silicate glasses. Therefore, this work is devoted to shedding some light on the effect of V_2O_5 on bioactivity behaviors of modified silicate glasses in terms of compositions. In this context, this paper reports a systematic study on the thermal evaluation of crystalline phases and microstructure of vanadium silicate bioglasses. For this aim, results of different characterization techniques are presented to determine the state of material activity upon V_2O_5 addition, since there is no previous studies concerning the effect of V_2O_5 on the bioactivity of modified silicate glass ceramics have been reported.

2. EXPERIMENTAL PROCEDURES

2.1 Preparation of Bioactive Glasses

Glass samples were prepared by using chemically pure SiO_2 , $CaCO_3$, Na_2CO_3 , and V_2O_5 . Using nominal composition $24.5Na_2O$, $24.5CaO$, $6 P_2O_5$ - xV_2O_5 and $(45-xSiO_2)$ mol% (where $x = 0, 3, 6, 9, 12$ & 15 mole %), the glasses were prepared and investigated. The batches were accurately weighed out and then melted in alumina crucibles using an electric furnace at temperature 1250°C for 2 h and the melts were shocked well several times to achieve homogeneity. Each melt was stirred by rotating the crucible several times every 30 mins. The homogeneous melts were cast after 2 h of melting into preheated stainless steel molds.

2.2 Preparation of Phosphate Solution

The phosphate solution used in the reaction was prepared by dissolving K_2HPO_4 (Reagent grade; Fisher Scientific, St. Louis MO) in deionized water (pH = 5.5 ± 0.1) to obtain a solution with a 0.02 M concentration of K_2HPO_4 and with a pH value of 7.0 ± 0.1 .

2.3 FTIR Measurements

Fourier transform infrared absorption spectra of the studied HAp samples were measured at room temperature in the wavelength range 4000-400 cm^{-1} using a computerized recording FTIR spectrometer (Mattson5000, USA). Finely powdered samples were mixed with KBr in the ratio 1:100 for quantitative analysis and the weighed mixtures were subjected to a load of

5t/cm² in a sample cell i.e. to produce clear homogenous discs. Then, the IR absorption spectra were immediately measured after preparing the discs to avoid moisture attack.

2.4 X-ray Diffraction Analysis

The structure of glass samples was assessed using an X-ray powder diffract meter (a Philips PW1390 X-ray diffract meter) with Cu K α target (Ni filter), wavelength (λ) = 1.54 Å. C/S was used. The Bragg's angle (2θ) in the range of 4–70°, step size = 0.02 and step time 0.4s at room temperature. Crystallographic identification of the phases of synthesized apatites was accomplished by comparing the experimental XRD patterns to standards compiled by the Joint Committee on Powder Diffraction Standards (JCPDS).

2.5 Differential Scanning Calorimetry

DSC/TG analysis was carried out using a NETZSCH STA 409C/CD instrument. Known mass (\approx 30 mg) of crushed samples was placed into an aluminum pan then sealed with a crimped lid and heated from 25°C to 1000°C at a rate of 5°C/min with argon as carrier gas at a flow rate of 30 cm³/min.

2.6 Transmission Electron Microscope (TEM)

Transmission electron microscopy (TEM) and electron diffraction pattern (EDP) were performed on a JEOL-JEM-2100, Japan model with an electron acceleration voltage of 160 kV to examine the internal microstructure of the bioactive glass samples.

2.7 Scanning Electron Microscope (SEM)

Surface modifications and microstructure of the samples were examined using a scanning electron microscope (SEM). The scanning micrographs were obtained using a Model JEOL-JSM-6510 LV attached with EDAX unit, operated at accelerating voltage 25 KV, with a magnification up to 300.000X. For the SEM study, the pieces were gold plated.

3. RESULTS AND DISCUSSION

3.1 As Prepared Glasses

NMR and FTIR results suggested a relationship between the concentration of non-bridging oxygens (NBO) which are formed in silicate

network and the development of clustering process in highly modified glasses (silicate glasses rich with modifier). These results provide evidence for a presence of a specific type of bridging oxygen BO which has the good ability to bridge two sodium atoms to form sodium clusters [8,16]. The concentration of this type is found to increase with increasing the total concentration of NBO atoms in the silicate glass network. Then glasses rich with a modifier and consequently rich with NBO would contain a specific type of structural species which are required for building up some type of crystalline phases. Formation of the aggregated species was reported to play an important role in enhancing the bioactivity of the materials [17].

FTIR spectroscopy is applied to probe the structure of Na₂O-CaO- SiO₂-V₂O₅ glasses in terms of formation crystalline apatite (calcium phosphate), wollastonite (calcium silicate, CaSiO₃) and Na₂VO₃ species. The well-formed species are considered as the most effective type required playing the major role in material bioactivity [18].

Fig. 1 represents FTIR spectra of all as obtained glasses as a function of V₂O₅ content. The most important criteria noted in the FTIR spectra is the presence of well-defined absorption peak appeared around 1600 cm⁻¹ in all spectra of investigated glasses. The area of this band is found to increase with increasing V₂O₅ content. In contrary, the band area and intensity of FTIR absorbance band centered at about 540 cm⁻¹ are clearly decreased upon increasing V₂O₅ contents. Decreasing of the relative area of peaks centered around 540 cm⁻¹ and increasing of resolved peak around 1600 cm⁻¹ lead to suggest that the concentration of modifier ions is reduced in silicate network and its content is increased in vanadate network structure [19]. These observed bands are assigned to asymmetric vibration of Na-O or Ca-O in calcium (sodium) phosphate, calcium and sodium silicate phases. Both formed apatite (CaPO₄) and wollastonite (CaSiO₃) and sodium or calcium vanadate phases are the most required species for promoting the compatibility and bioactivity of the studied material [20].

It is evidenced from x-ray diffraction (XRD) and TEM &EDP, Figs. 2 & 3, of the as-prepared glasses that the well-formed structural species are constructed in its amorphous state which has drawback effect on bioactive properties of the glasses [8,21]. Therefore, controlled heat

treatment process is important method to control the formation of crystallized or sub crystallized species [22]. The latter is desired to be obtained for both their bioactive and dental applications since the bioglass ceramics are preferred to contain some crystalline or polycrystalline phases. The type, size and morphology of the crystalline phases are dependent on the glass composition.

vanadium silicate glass-ceramic, microstructures consisting of fine-grained phase crystals has to still much desire. A more controlled crystallization of the glass may, therefore, be a useful way to control the crystal size, volume fraction and morphology of these materials, which can influence not only bioactive properties but also the mechanical properties. For these purposes, the sintered process (treating the glasses at the temperature higher than T_g) should be applied to transform the glass to glass ceramic which contains crystalline bio clustered phases.

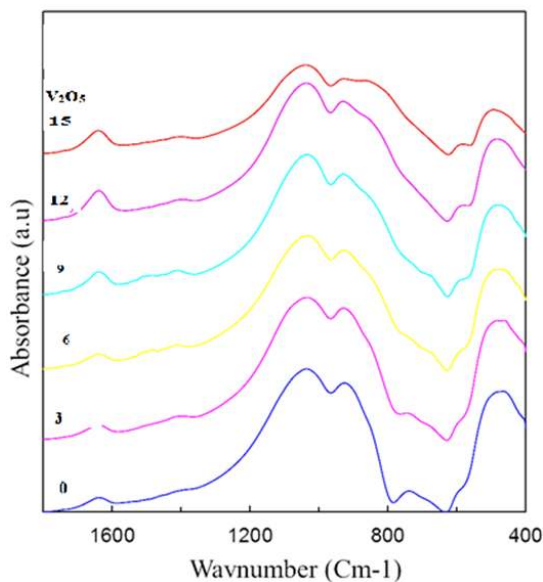


Fig. 1. FTIR spectra of as prepared glasses as a function of V_2O_5 concentration which changed from 0 to 15 mol%

In addition, the stoichiometry of the crystal phases and crystallization heat treatment time and temperatures are found to have some effects. Therefore, to produce biocompatible

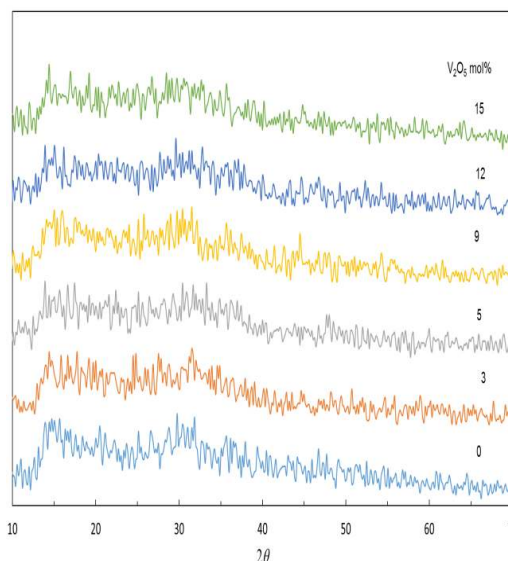


Fig. 2. XRD patterns of selected as prepared glass samples containing (0, 3, 6, 9, 12 & 15 mol%) V_2O_5

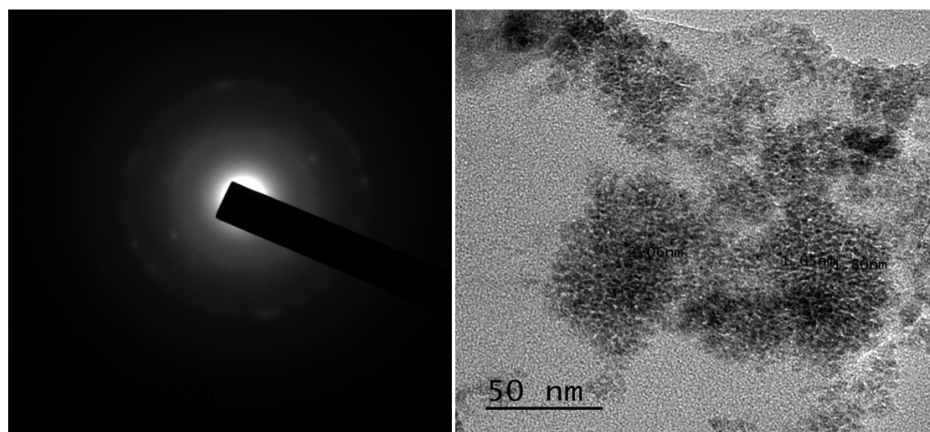


Fig. 3. TEM & EDP for a sample containing 15 mol% V_2O_5

3.2 Heat Treated Glasses

Treating as prepared glasses thermally can limit the most effective drawbacks related to poor crystallinity of both apatite and wollastonite phases of the biomaterials [23]. The heat treatment process can vary the properties of the originally amorphous matrix of the glass by converting it to glass ceramic which characterizes by its higher crystallinity, bioactivity and mechanical strength.

Fig. 4 shows the differential scanning calorimetry (DSC) curve of the studied bioglass ceramics containing 15 mol% V_2O_5 . It is noticed that there are exothermic peaks, with the top or maximum at about 450°C and 660°C, indicating that the amorphous structures can be highly crystallized by treating them around the crystallization temperature. Therefore, 660°C is applied as the proper chosen controlled crystallization temperature since the glass is transformed to glass ceramic by the effect of this temperature to 4 hours.

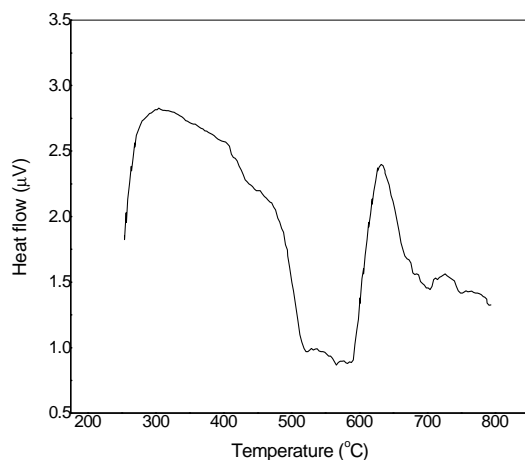


Fig. 4. Differential scanning calorimetry (DSC) curve of bioglass ceramics containing 15 mol% V_2O_5

XRD pattern of the initial glass confirmed its amorphous nature, see Fig. 2. On the other hand, enhancement of crystallinity is achieved by treating the glass thermally at 660°C, Fig. 5. This indicates that the amorphous structure is the dominant phase characterized the as prepared glass. On the other hand, the XRD peaks become sharper and the amorphous hump nearly disappears after treating the glass at 660°C as clarified in Fig. 5, resulting in crystallinity of 71%. Increasing degree of

crystallinity to 71% with increasing temperature, may lead to conclude that the initial amorphous matrix is well crystallized by the effect of heat treatment. The angular location and intensity of nearly all the peaks closely match the standard JCPDF database (76-0186), which indicates that the major crystalline phases are wollastonite ($CaSiO_3$) and sodium calcium silicate ($Na_2Ca_2Si_3O_9$), JCPDF database (22-1455) [8,24]. Besides, some extra XRD peaks can be observed in Fig. 5 which should be attributed to the crystalline apatite phases that is assigned to tricalcium phosphate $Ca_3(PO_4)_2$ (JCPDS 86-1585) produced in the material's network [25]. In addition, angular location peaks closely match the standard JCPDF-520649 which indicates that the crystalline sodium or calcium vanadate phases ($Ca_{10}V_6O_{25}$) are present [26]. Then both apatite (A) and wollastonite (W) crystalline phases could be formed by the effect of the heat treatment process. These phases are considered the essential phases required for bone construction in phosphate solution.

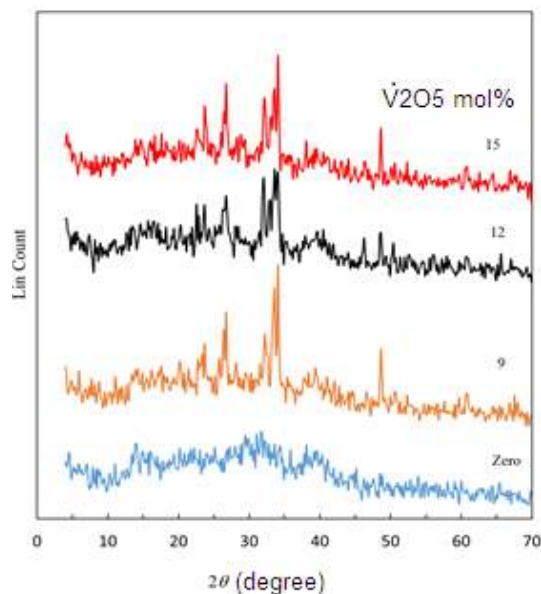


Fig. 5. XRD patterns of glasses containing (0, 9, 12 & 15 mol% V_2O_5) and treated thermally at 660°C for 4 hours

3.3 Structural Role of V_2O_5

Vanadium oxide gives the ceramics good advantages toward improved properties like extremely resistant to thermal shock, high mechanical strength, chemical stability bioactivity etc [27]. The advantage of the present glasses is that it can easily be crystallized by an effect of

V_2O_5 since the high crystallinity is obtained by lowering temperature when compared with glasses free from V_2O_5 . The optimum crystallinity is achieved at 660°C for 4 hours as treating time instead 1000°C for 10 hours in glasses free from vanadium. This difference is considered due to the role of vanadium which can act as an effective agent for crystallization when the glasses are thermally treating. XRD sharper peaks (Fig. 5) that correspond to the presence of crystalline apatite - wollastonite, and vanadate crystalline species are consistent with V_2O_5 .

The glasses containing up to 6 mol% V_2O_5 are still transparent upon heat treatment temperature of 450°C or even sintering at temperature, 660°C . On the other hand, glasses containing higher V_2O_5 concentration are transformed to opaque glass-ceramic under the effect of thermal treat treatment. The color is changed from transparent brown to opaque white color. This transformation is considered as a result of changing the nature of the material structure. e.g. transformation of the amorphous glass to crystallized glass-ceramics is considered as the main reason for changing material color as well as its microstructure.

SEM showed also some clear changes upon controlled heat treatment processes, see Fig. 6. As a consequence, the main formed crystalline phase appears as needle-like shaped as shown in SEM of the investigated material, Fig. 6b. Then, heat treatment temperature leads to a considerable change of microstructure, since SEM of an as-prepared sample (Fig. 6a) is shown to have differed from that of treated samples. EDX spectra (Fig. 7) of the heat treated glass showed that both crystalline vanadate and wollastonite species are present. The ratio of Ca to Si is found to around unity, which leads that the good wollastonite phase is found in its crystalline form.

Figs. 1 & 8 showed FTIR patterns of both as-prepared and heat-treated glasses at 660°C for 4 h. The main envelop in the spectrum of heat treated glass splits into two or more peaks at 920cm^{-1} and 1100cm^{-1} . The peak at 920cm^{-1} is assigned to Si-O-Si stretching vibration and the peak at 1100cm^{-1} corresponds to P-O asymmetric stretching vibrations [27,28]. Moreover, the peak centered at 480cm^{-1} in the as-prepared glass is assigned to vibrations of Si-O and P-O in the miscible phosphate and silicate network. Growing and intensification of the IR peak at about 450cm^{-1} , assigned to Si-O vibration in silicate phase, in the heat treated

sample was attributed to phase separation and crystallization [28]. The peak at 620cm^{-1} corresponds to P-O or V-O vibration in crystalline apatite. Moreover, the broadband around 1400 and 1600cm^{-1} in as- prepared glass appears to be more intensive in the heat treated glass. It is assigned to vibrations of OH, and Ca-O in both calcium silicate and calcium phosphate groups present in dicalcium phosphate (DCP) phase [28,29]. Thus based on these data, it can confirm that heat treatment results in a phase separation and crystallization of both the silicate and phosphate phases. As a result, clusters containing vanadate species and both apatite and wollastonite crystalline phases are concluded to be present. These phases are important for carrying out the reaction between the material and the body fluids.

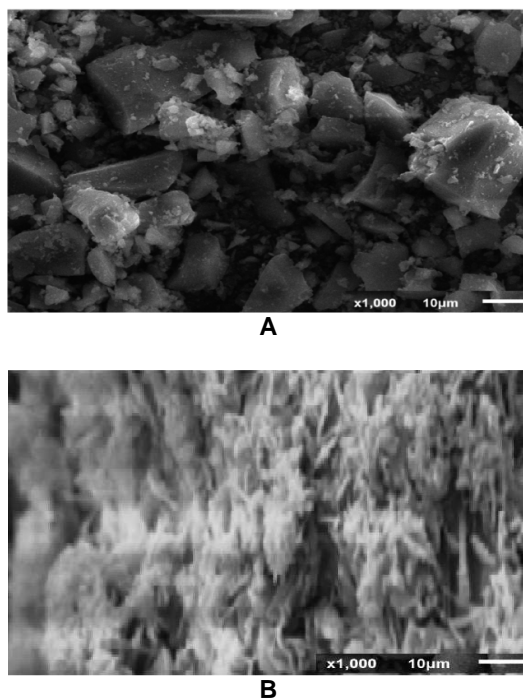


Fig. 6. SEM for as obtained (A) and thermally treated (B) samples

3.4 Bioactivity Assignment

When the powdered sample is dipped in a phosphate solution, some chemical reaction may be carried out as a result of the formed active species. This reaction is known to depend on the type of the active phases found in the sample and on the time of dipping [29]. The chemical reactions result in the formation of CaPO_4 and CaSiO_3 layers precipitated on the surface of the

immersed samples. The reaction of the sample and phosphate solution clearly leads to participation of hydroxyapatite layer which can be indicated by pH measured values [29]. Based on these measurements, it is very simple to conclude that leaching from samples plays an important role to form hydroxyapatite layer. Change of pH of the phosphate solution after immersion as a function of time is considered as a guide of reaction to occur. In this case, a small variation in pH from 7.31 to 7.45 in 16 days is carried out. These changes are considered as a result of the presence of species such as H^+ , H_3O^+ and OH^- from the solution which attacks the glass network and is exchanged with Na^+ and Ca^{2+} ions from the glass network [29]. Leaching of these ions from glass to solution leads to the increase of pH. In the later stage of the pH measurement, the pH value decreases to 6.65 due to the formation of Hydroxyapatite layer.

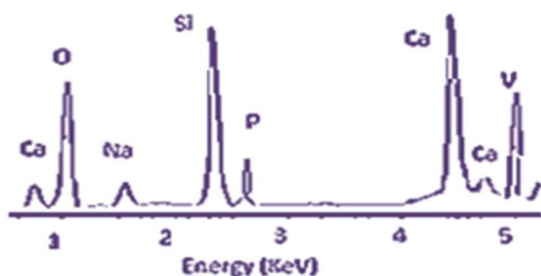


Fig. 7. EDX spectra for sintered glass at 660°C for time of 4 hours

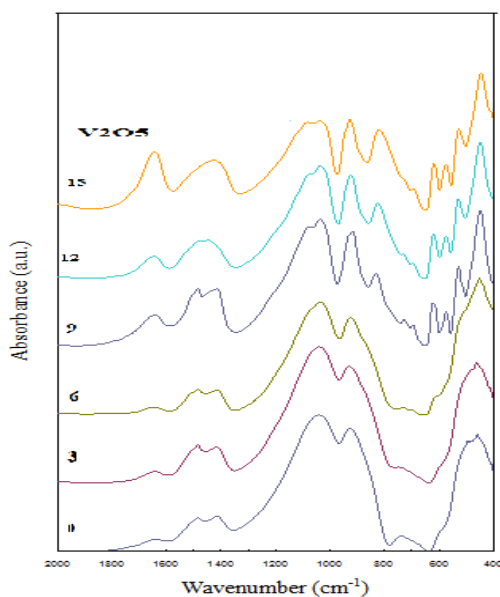


Fig. 8. FTIR of thermally treated glasses at 640°C for time interval of 4 hours

4. CONCLUSION

Different glass samples containing a different concentration from V_2O_5 (0-15 mole %) has been prepared. All the as-obtained samples are transparent and possessed an amorphous network. The latter is transformed into opaque white colored crystalline structure (in glasses containing more than 6 mol% V_2O_5) by the effect of sintering at 660°C. In this situation, the glassy material is transformed to glass ceramic which is characterized with its higher controlled crystallinity. Networks of glasses with lower V_2O_5 contents (<6 moles %) remained amorphous and transparent even upon thermal treatment. Apatite (A), wollastonite (W) and modified vanadate phases are the major formed separated crystalline phases under the sintering process. The structure and morphology of phases formed in sintered glasses are differed from that found in as prepared glasses. Needle-like structure is the dominant feature of the well-formed species formed in thermally treated glass ceramics. Bioactive properties are found to depend on the type and concentration of the apatite and wollastonite formed phases. The presence of vanadium in the network of the glass played the role of agent for crystallization which in turn can speed up the reaction of the material when immersed in body fluids.

COMPETING INTERESTS

Authors have declared that no competing interests exist.

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