Raman Spectroscopic Studies of Bioactive Materials

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ABSTRACT: *Bioactive materials including glass and glass-ceramics are nowadays used as medical implants for orthopedic applications. In this study several samples of glass-ceramics have been prepared using both heat treatment and sol-gel processes. The structure and bioactivity of these samples based on their interaction with simulated body fluid (SBF) have been determined, in-vitro, using the Raman spectroscopic technique. It is found that most samples exhibit bioactivity when they are soaked in SBF. It is also concluded that Raman spectroscopy is a powerful technique in such studies.*

KEY WORDS: *Raman Spectroscopy, Bioactive Materials, Glass-Ceramics, Hydroxyapatite.*

INTRODUCTION

Bioactive materials are a group of inorganic compounds which have the ability of forming a bond with the living tissues of the human body. These materials are used to improve the properties of medical implants for the replacement of tooth and bone. Medical implants which are made from metals have the disadvantage of having corrosion, wear and negative tissue reactions in the human body. Almost all metallic implants are encapsulated by a dense fibrous tissue which prevents proper function of the implant and results in the loosening of the implant [1]. To overcome these problems and to have a clinical success of the implant, there must be a stable biocompatible interface connection between the implant and tissue. This can be achieved by using a bioactive material which provides a chemical bond at the bone/implant interface [2]. Although medical and surgical implants have been used for many years, the major developments in the use of bioactive materials have taken place over the last 25 years[3].

Bioactive materials include certain compositions of glasses, ceramics and glass-ceramics. The first bioactive glass was discovered by Hench *et al* in 1971[4]. Since then several glasses and glass-ceramics have been known to have bioactivity and can form chemical bonds to bone [2].

A common feature of bioactive materials is that a calcium phosphate known as hydroxyapatite is formed at their surrfaces after implantation in bone tissues. It is this apatite layer that bridges the non-living materials and living bone. Because of their poor mechanical properties, most bioactive materials can not substitute the metallic part of the implant, and they are hence used as a coating for metallic prostheses.

Several techniques including X-ray diffraction (XRD) [5,6], energy dispersive X-ray analysis (EDXA)[7], infared spectroscopy (IR)[8] and Raman spectroscopy (RS) [9] have been used to determine the structure and function of bioactive materials. In the present study we have

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prepared a number of glass-ceramics and used Raman spectroscopy to determine the structure and properties of these materials, in particalar their bioactivity in simulated body fluid (SBF) solution.

EXPERIMENTAL

Materials

All materials were obtained from commercial sources (Merck, Riedel-de Haen, Baker and Hopkin) and were used as received. Two series of glass-ceramics were prepared using heat treatment and sol-gel processes. The first one was a batch composition of the following compounds in wt% as: SiO_2 (65.7-45), P_2O_5 (12-2.6) CaO (24.4-12.1), Na_2O (28.9-15) and CaF_2 (10.8-0.5). The batch was melted at 1500°C for 3h in an electrical furnace and allowed to cool on a platinium plate.

The second group of glass-cercmic samples were prepared using a sol-gel process.This process started from tetraethoxysilane (TES) which was prepared by the reaction of ethanol with $SiCl_4$. To a solution of TES in ethanol, nitric acid and water were added and then the required amount of materials to produce the desired glass-ceramics were added as nitrate salts. Solutions were kept for 10 days and then were heated at 200°C for 140 h. The dried gel was then crushed and calcined at 800-1000°C for 5 h.

Simulated body fluid (SBF) was prepared by dissolving the desired amount of sodium chloride, potassium chloride, sodium bicarbonate, calcium chloride, magnesium chloride and dibasic potassium phosphate in deionized water. This solution which, contains the concentration of ions equivalent to human blood plasma, was buffered at pH=7.5 with hydrochloric acid and Tris buffer [10].

Bioactivity of the glass-ceramic samples was investigated *in-vitro* by soaking the samples in the SBF solution for up to a few weeks.

Instrumentation

X-ray diffraction analysis was performed using a Philips X-ray instrument Model x-pert.

Raman spectra were recorded using a Bomem combined FT-Raman/FT-IR spectrometre Moded NB-Series equipped with a Te-cooled indium-gallium-arsenide detector.Excitation wavelength at 1064 nm was obtained from a Nd/YAG laser. Lasear power was estimated to be in the range of 300 - 350 mW at the samples.

RESULTS AND DISCUSSION

X-ray analysis of both series of samples showed a broad background with a few peaks which indicates a glassy phase containing crystalline components. The samples therefore were identified as glass-ceramics.

Fig.1 shows a typical Raman spectra of four samples prepared by the heat treatment method in the wavenumber shift range 200-1700 cm^{-1}.The composition of these samples has been given in table.1. Fig.2 shows a typical Raman spectra of three samples prepared by the sol-gel method in the wavenumber shift range 400-1200 cm^{-1}. The composition of these samples is given in table.2.

In the four Raman spectra shown in Fig.1 three bands are observed; a strong band at 950-960 cm^{-1}, a medium to strong band at 590-620 cm^{-1} and a medium (shoulder) band at 1070-1080 cm^{-1}. In some spectra a weak band at 420-440 cm^{-1} is also observed. In the Raman spectra of phosphates, normally there are four bands namelyν_1 = 960 cm^{-1} ν_2 = 435 cm^{-1}, ν_3= 075 cm^{-1} and ν_4 = 590 cm^{-1}

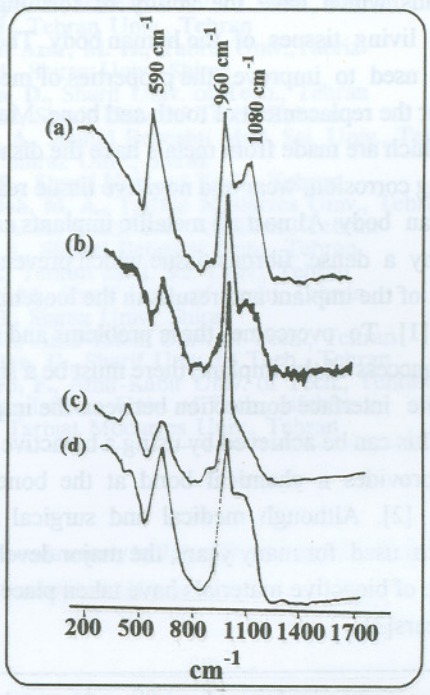

Fig.1: Raman spectra of four glass-ceramic samples pre-pared by the heat treatment method in the wavenumber shift range 200-1700 cm^{-1}.

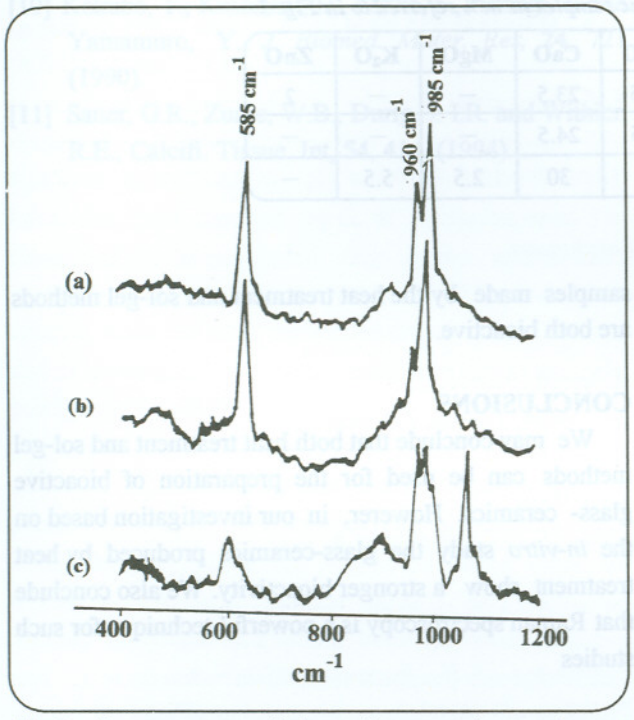

Fig.2: Raman spectra of three glass-ceramic samples prepared by the sol-gel method in the wavenumber shift range 400-1200 cm^{-1}.

Table 1: Composition of four glass-ceramic samples in wt% referred to in Fig. 1

Labels on Fig.1	SiO_2	P_2O_5	Na_2O	CaO	CaF_2
(a)	46.1	2.6	24.3	16.2	10.8
(b)	39.6	12	8.4	39.5	0.5
(c)	57.3	1.7	28.9	12.1	–
(d)	45	6	24.5	24.5	–

[11], whereas the Raman spectra of silicates show only two weak bands at 1080cm^{-1} and 521 cm^{-1}.The 1080 cm^{-1} is much stronger than 521 cm^{-1} band. The 1080 cm^{-1} band in our spectra is in near coincidence with the 1075 cm^{-1} band of the phosphate group and the 521 cm^{-1} band is too weak to be observed. Comparing these data it seems reasonable to assume that in the heat treatment method, a network of SiO_4 and a phosphate has been formed. Furthermore, the phosphate phase is expected to have an apatite structure similar to hydroxyapatite (HAP) or tricalcium phosphate (TCP)[11]. as expected from the position of 960 cm^{-1} band.

In the Raman spectra shown in Fig.2, there are three bands; a strong doublet band at 985 and 960 cm^{-1} and a medium to strongin intensity band at 585-600 cm^{-1}. In spectrum(c) there is also a strong band at 1060 cm^{-1}. The position of the 960 cm^{-1} and 985 cm^{-1} bands suggest the existence of a phosphate phase which in this case the 960 cm^{-1} band represents either a hydroxyapatite or tricalcium posphate. The 985 cm^{-1} band is assigned to the ν_1 vibration of dicalcium phosphate dihydrate (DCPD) [11]. The Raman band at 1060 cm^{-1} which appears in spectrum (c) only, is lover than the ν_3 vibration of phosphate and can not be assigned to silicate vibration too. Based on these assignments, we may assume that in the sol-gel method a phosphate phase has been formed.

Fig.3 shows the Raman spectra of a sample of glass-ceramics prepared by the heat treatment method before (a) and after (b) immersion in SBF solution in the wave-number shift range 200-1700 cm^{-1}.

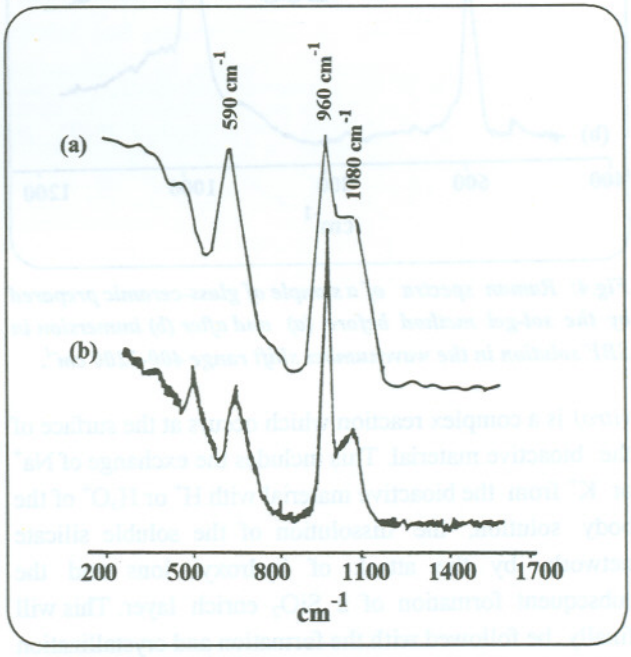

Fig.3: Raman spectra of a sample of glass-ceramic repared by the heat treatment method before (a) and after (b) immersion in SBF solution in the wavenumber shift range 200-1700 cm^{-1}.

Fig.4 shows the Raman spectra of a sample of glass-ceramic prepared by the sol-gel method before (a) and after (b) immersion in SBF solution in the wavenumber shift range 400-1200 cm^{-1}.

According to Hench and Wilson [12,13], the interaction between bioactive glass-ceramics and a living cell *(in-vivo)* or a biological solution suchas SBF (in-

Table 2: Composition of three glass-ceramic samples in wt% referred to in Fig. 2

Labels on Fig.2	SiO_2	P_2O_5	Na_2O	CaO	MgO	K_2O	ZnO
(a)	45	6	23.5	23.5	–	–	2
(b)	45	6	24.5	24.5	–	–	–
(c)	45	10	7	30	2.5	5.5	–

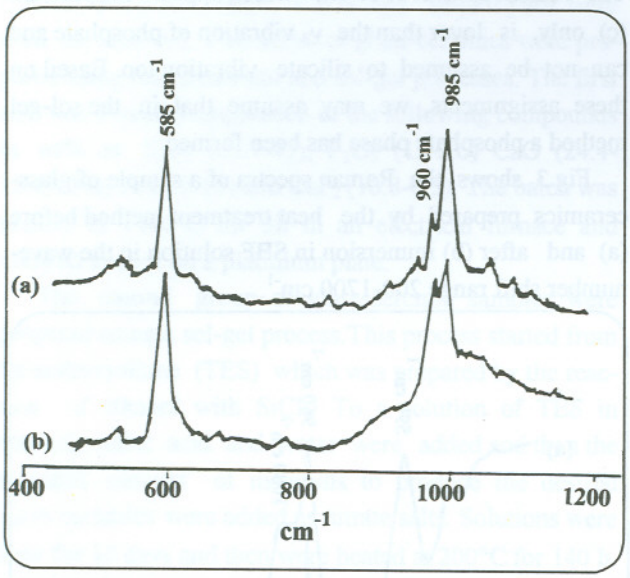

Fig.4: Raman spectra of a sample of glass-ceramic prepared by the sol-gel method before (a) and after (b) immersion in SBF solution in the wavenumber shift range 400-1200 cm^{-1}.

vitro) is a complex reaction which occurs at the surface of the bioactive material. This includes the exchange of Na^+ or K^+ from the bioactive material with H^+ or H_3O^+ of the body solution, the dissolution of the soluble silicate network by the attack of hydroxyl ions and the subsequent formation of a SiO_2 enrich layer. This will finally be followed with the formation and crystallization of a polycrystaline layer of apatite on the surface of the bioactive material.

It can be seen from Fig.3 and Fig.4 that in both cases the intensity of the Raman band at 960 cm^{-1} has increased considerably after being soaked in SBF solution (spectrum(b) in both Figs). This band is assigned to the ν_1 vibration of hydroxyapatite and it therefore shows that a rich layer of apatite has been formed on the surface of glass-ceramic samples. Similar behavior more or less was observed for other samples. This indicates that the samples made by the heat treatment and sol-gel methods are both bioactive.

CONCLUSIONS

We may conclude that both heat treatment and sol-gel methods can be used for the preparation of bioactive glass- ceramics. Howerer, in our investigation based on the *in-vitro* study the glass-ceramics produced by heat treatment show a stronger bioactivity. We also conclude that Raman spectroscopy is a powerful technique for such studies

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