FABRICATION AND CHARACTERIZATION OF GLASS-CERAMICS IN THE SYSTEM CaO-SiO_2-ZrO_2-CaF_2

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ABSTRACT : *This research work is focused on the fabrication and characterization of glass-ceramics in the system CaO-SiO_2-ZrO_2-CaF_2. Zirconia was selected due to its well-known mechanical stability and biocompatibility as bone implant material. Glasses were prepared by melt-quenching technique and by using two-step heat treatment these were converted to glass-ceramics. Differential Thermal Analysis (DTA) was performed to find, the glass transition temperature (Tg) and the glass crystallization temperature (Tc). X-Ray Diffraction (XRD) analysis was carried out to identify different crystalline phases developed during heat treatment. Scanning Electron Microscopy (SEM) was used to study the surface morphology of the samples. ZrO_2 addition showed remarkable effect on the DTA, which resulted in the shift of endothermic and exothermic peaks. Wollastonite ($CaSiO_3$), calcium zirconium silicate ($Ca_2ZrSi_4O_{12}$) and ZrO_2 were the major crystalline phases observed. High content zirconia (15.5 wt. %) glass-ceramic showed high mechanical strength. The results indicate that high mechanical strength glass-ceramics can be prepared from the system CaO-SiO_2-ZrO_2-CaF_2.*

Keywords: Glass-ceramics, Differential Thermal Analysis, X-Ray Diffraction Analysis, Compressive Strength.

1. INTRODUCTION

Glass-ceramics are polycrystalline materials, produced by controlled crystallization of glasses having special compositions [1]. These materials have higher mechanical strength, toughness, refractory properties and lower thermal expansion coefficient than glasses. Other advantages of the glass-ceramics are their lower density and resistance to chemical effects, temperature variations and wear as compared to metals as implants [2].

Ceramic materials that are implanted in the living body are known as bioceramics. These materials are now being designed not only to replace damaged bone but also to repair and regenerate defective tissue in vivo [3]. Some glasses and glass-ceramic materials, when implanted in the human body make a bond with natural bone and are known as glass bones. A number of glasses and glass-ceramics implants have been prepared after Hench et al. research [4] that some silicate glasses can chemically bond with living bone.

The use of bioceramics is revolutionizing the biomedical field in its deployment as implants for humans. Many implant materials made of ceramics have been used for the past three decades. In the search to improve the biocompatibility and mechanical strength of implant materials, attention has been directed towards the potential use of load bearing ceramics. The ceramic-based biomaterials have been accepted after biological evaluation through several in vivo and in vitro tests.

Some hard tissues require very high strength. Among various structural ceramics, zirconia containing ceramics have been widely researched during the last three decades; because of their better toughness and strength properties. Addition of an appropriate amount of zirconia can increase the strength of the material while keeping it as bioactive. The addition of zirconia to hydroxyapatite ceramics notably increases the mechanical stability of ceramics. Thus it can enhance the application possibilities of such ceramics [5]. Apart from providing a toughening phase, ZrO_2 is also well known for its biocompatibility traits [6]. It is also known that among the bioceramics, bio inert materials like alumina and zirconia are candidate materials for load bearing implants e.g. total hip replacement (THR), knee joints etc. [7]. The use of zirconia in the ball heads of total hip replacements (THR) was first introduced in 1988. This method still persists as one of the current main applications of zirconia. Zirconia and yttria stablized zirconia have wider applications as hip joint heads, temporary supports, hip and knee prostheses, dental crowns, tibial plates. A study of in vitro drug release from zirconia ceramics has also been carried out [8]. Although zirconia is considered a bio-inert ceramic because when implanted, it only shows a morphological fixation with the surrounding tissues without any chemical or biological bonding [9] but now research is going on glass-ceramics containing appropriate amount of zirconia along with other oxides to be used as bioactive material [10, 11,12]. A recent research has been done by hydroxylation of yttrium stabilized zirconia and studying it in vitro bioactivity by examining the formation of bone-like apatite on its surface in the simulated body fluid [13].

In the present work three glass-ceramics in the system CaO-SiO_2-ZrO_2-CaF_2 have been fabricated and characterized for their properties with a view to be used as high strength bioactive and bioinert implant materials.

2. MATERIALS AND METHODS

Analytical grade (99.9 %) calcium oxide, silicon oxide, zirconium oxide and calcium fluoride were weighed and thoroughly mixed in an agate mortar and pestle to obtain glass compositions as given in Table 1. CaF_2 was added to the initial composition in order to facilitate glass processing. The mixed powders were then melted in a platinum crucible in a preheated muffle furnace (Model 51314 Lindberg USA) at a temperature of 1550 ° C for 1 hour duration and then were poured on a stainless steel plate to form glasses.

Table 1 Glass Compositions in wt. %

Glass sample	CaO wt. %	SiO_2 wt. %	ZrO_2 wt. %	CaF_2 wt. %
BG- Z_1	44.5	44.5	10.5	0.5
BG- Z_2	44.5	41.5	13.5	0.5
BG- Z_3	44.5	39.5	15.5	0.5

Glasses were pulverized to fine powders of grain size less than 45 µm and compacted to circular pellets of diameters, 14 and 10 and 7 mm by hydraulic press (Model Carver 4350, USA) while exerting a pressure of 196 MPa. Some powder of each composition was used for DTA analysis.

Differential thermal analysis (DTA) of these glass samples was carried out to determine the glass transition temperature (Tg) and crystallization temperature (Tc). For this purposes thermal analyzer model [Simultaneous DSC/TGA SDT-Q-600, Germany] was used. DTA was carried out on powdered glass samples which were examined up to temperature range from room temperature to 1200ºC at a heating rate of 20ºC / min. From DTA results suitable heat treatment program was established for the conversion of glasses to their corresponding glass-ceramics. The DTA curves of glass samples were recorded.

Two-stage heat-treatment was used for conversion of glasses to glass-ceramics. Glass pellets were heat treated at the nucleation temperatures for 1 hour and at crystallization temperatures for 2 hours. Some pellets were crushed into fine powders for XRD analysis performance. Identification of crystalline phases was carried out by X-ray diffractrometer (Model Bruker D8 Discover, Germany) performed at 40 kV and 40mA, by using a step size of 0.3º, scan rate of 3º/ min. The XRD patterns were also recorded in a 2θ scan range 10º- 80º with Copper Kα 1 radiations.

Compressive strength of glass-ceramics was measured by using Universal Testing Machine (Model 1000 Win wdw 100, China) at a crosshead speed of 0.5 mm/min. The samples were circular in shape and of diameter 14 mm. The compressive strengths of the samples were calculated by using the equation: σ_c = Compressive strength= F/area = F/ πr^2 where r = d / 2 . d is the diameter of the specimen (mm) and "F" is the maximum compressive load during the test (N) [14]

The surfaces of the glass-ceramic samples were then examined by a Scanning Electron Microscope (SEM) (Model JEOL JSM-6480 LV, JAPAN) - equipped with Energy Dispersive Spectroscopy (EDS).

3. RESULTS AND DISCUSSION

Clear transparent glasses were prepared from all these glass compositions containing, 10.5, 13.5 and 15.5 wt % zirconia.

3.1. Differential Thermal Analysis

DTA was carried out to determine the glass transition temperature Tg and crystallization temperature Tc of the glasses. It was observed that addition of ZrO_2 had a prominent effect on the DTA results, which is evident by the shift in the endothermic and exothermic peaks. Figs.1 [(a), (b), (c)] show the DTA curves of the BG-Z_1 (base glass), BG-Z_2 and BG-Z_3, respectively

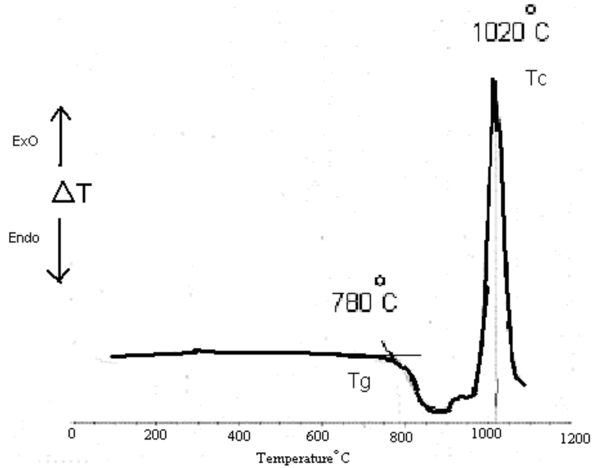

Fig. 1 (a) DTA curve of BG- Z_1 showing Tg (780°C) and Tc (1020°C).

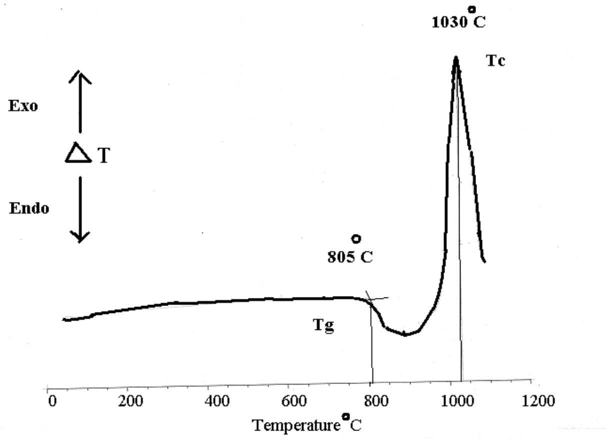

Fig 1, (b) DTA curve of BG- Z_2 showing (805°C) and Tc (1030°C).

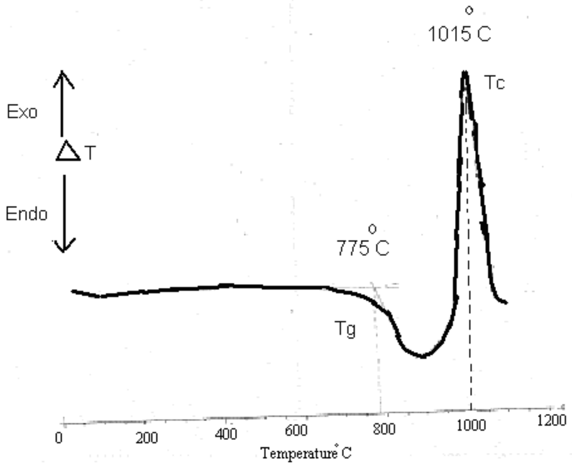

Fig.1(c) DTA curve of BG-Z_3, showing Tg (775°C) and Tc (1015°C)

Fig 1, (a) (b) (c) showing DTA curves of Z_1, Z_2 and Z_3.

The DTA curve of BG-Z_1 depicted an endothermic peak at 780°C corresponding to glass transition temperature Tg and an exothermic peak at temperature 1020°C, which

represents crystallization temperature Tc. The glass crystallized in the temperature range (950°C-1060°C). Fig.1b shows the DTA curve of BG-Z_2. This glass contains 3 wt. % more ZrO_2 and 3 wt. % less of SiO_2 than the base glass. Glass transition temperature Tg was found at 805°C and crystallization temperature Tc at 1030ºC. These data indicate that an increase of ZrO_2 content up to 3 wt % had increased the endothermic and exothermic peak temperatures. This has already been investigated by Maragha F. M *et al.* [15] that addition of ZrO_2 shifts endothermic and exothermic peaks towards higher temperatures. The glass crystallizes in the temperature range (1000°C-1050°C). Fig.1c shows the DTA curve of BG- Z_3 containing 5 wt. % more ZrO_2 at the expense of SiO_2 than the base glass. In this curve glass transition temperature was found at 775ºC and crystallization temperature at 1015ºC and glass crystallized in the temperature range (975°C-1075°C). The results indicated that an increase of the zirconium oxide content beyond 5 wt. % decreased both the glass transition and crystallization temperatures. It was also observed that not only, both the temperatures decreased below the base glass (BG-Z_1) temperature, but also the major crystalline phase (wollastonite) was converted into ZrO_2 phase.
These results have also been summarized in Table 2.

Table 2 Characteristics Temperatures of Glasses

Glass sample	Glass Transition Temperature T_g (°C)	Glass Crystallization Temperature T_c (°C)
BG - Z_1	780	1020
BG – Z_2	805	1030
BG – Z_3	775	1015

3.2 X-Ray Diffraction (XRD) Analysis

Figs. 2a, 2b and 2c show the XRD patterns of BGC-Z_1, BGC-Z_2 and BGC-Z_3, respectively.

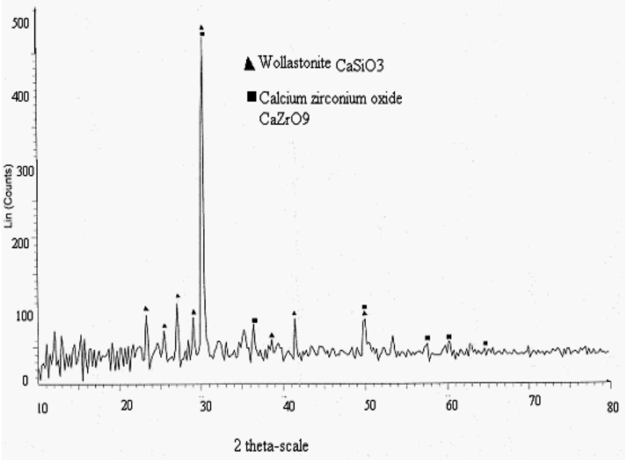

Fig. 2a XRD pattern of BGC- Z_1 showing phases ▲wollastonite, ■ calcium zirconium oxide.

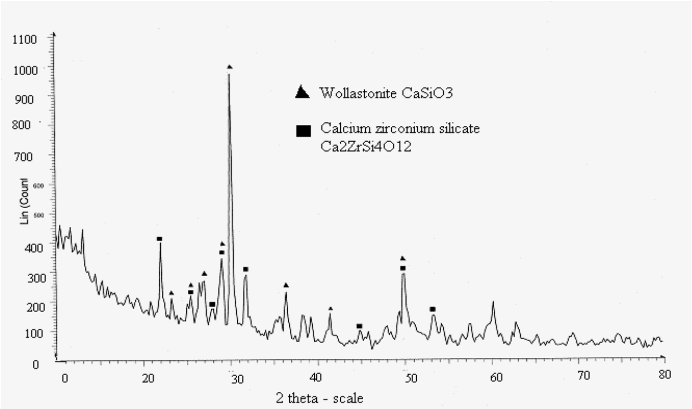

Fig.2b XRD pattern of BGC-Z2 showing crystalline phases▲Wollastonite■Calcium zirconium silicate

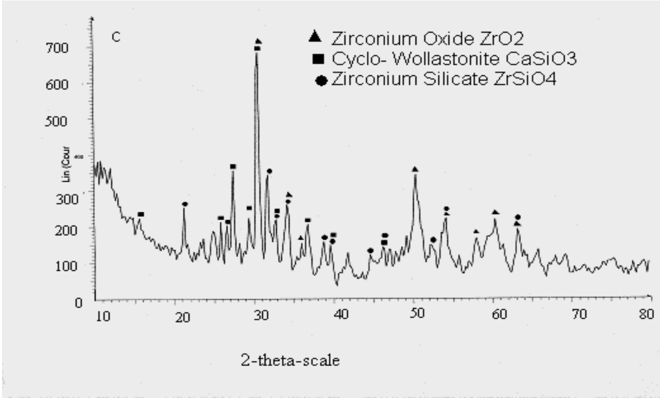

Fig. 2 c XRD pattern of BGC-Z_3 showing phases,▲ zirconium oxide,■ cyclo - wollastonite,● zirconium silicate.

Fig 2, (a) (b) (c) XRD patterns of BGC-Z_1, BGC-Z_2 and BGC-Z_3

Regarding the compositions of the samples, BGC-Z_1 containing 10.5 wt % of ZrO_2 showed two crystalline phases namely wollastonite ($CaSiO_3$) (card number: PDF# 29-372) and Calcium zirconium oxide ($CaZrO_9$) (card number: PDF# 28-887). A glass-ceramic in the system SiO_2.CaO-ZrO_2 processed with same technology also has been investigated by De Aza et al. [16], and wollastonite ($CaSiO_3$) was observed as the major crystalline phase in the system. Fig. 2b shows the XRD pattern of sample BGC-Z_2 containing 13.5 wt. % ZrO_2. The glass showed two crystalline phases wollastonite ($CaSiO_3$) (card number: PDF# 29-372) and Calcium zirconium silicate ($Ca_2ZrSi_4O_{12}$) (card number: PDF# 15-164). K.J. Hong et al. have also prepared and studied a glass-ceramic in the system CaO–ZrO_2–SiO_2 under a single stage heat treatment schedule. In the sintered glass-ceramic the same two phases, wollastonite ($CaSiO_3$) and calcium zirconium silicate ($Ca2ZrSi_4O_{12}$) were identified [17]. These results show that by increasing the ZrO2 content in the composition, glass crystallizes at higher temperature and different phases are observed. At this temperature, calcium zirconium oxide ($CaZrO_9$) phase was dissolved and a new phase of calcium zirconium silicate ($Ca_2ZrSi_4O_{12}$) appeared with the persistent of wollastonite phase. Wollastonite phase remained the major crystalline phase in BGC-Z_1 and BGC-Z_2. The wollastonite phase was observed above 950°C. Fig. 2c shows XRD pattern of sample BGC-Z_3 containing 15.5 wt. % ZrO_2. The behaviour of sample BGC-Z_3 was quite different, by increasing zirconium oxide content up to 15.5 wt. %, glass transition temperature (775°C) and crystallization temperature (1015°C) both were decreased and zirconium oxide (ZrO_2) (card number: PDF# 34-I084) appeared as the major crystalline phase. Wollastonite ($CaSiO_3$) and calcium zirconium silicate ($Ca_2ZrSi_4O_{12}$) phases were dissolved at this temperature and cyclo-wollastonite and zirconium silicate were the new phases observed. The over all results of XRD analysis for these samples showed that for this particular system wollastonite phase was observed as the major crystalline phase for 10.5 and 13.5 wt. % addition of zirconia and with the addition of 15.5 wt % zirconia; ZrO_2 was observed as the major crystalline phase.

Different crystalline phases, which developed during the heat treatment, are summarized in Table 3.

Table 3 Crystalline phases identified in glass-ceramics

Glass Ceramic Sample	Phases Identified
BGC – Z_1	Wollastonite, Calcium zirconium oxide
BGC – Z_2	Wollastonite, Calcium zirconium silicate
BGC – Z_3	ZrO_2, Cyclo Wollastonite, Zirconium silicate

3.3 Mechanical Testing

Mechanical testing was carried out on samples BGC-Z_1, BGC-Z_2 and BGC-Z_3 to determine their compressive strength. The strength curves are given in figure 3.

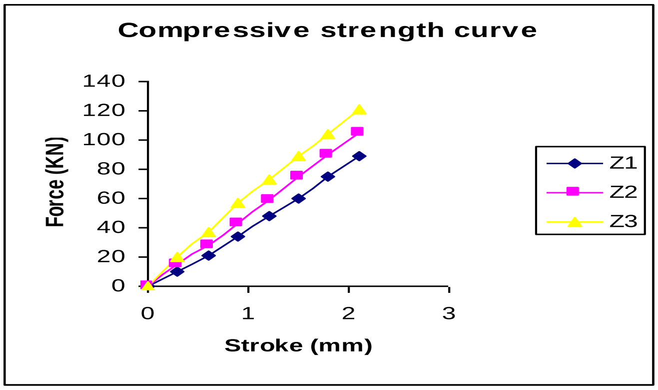

Fig. 3 compressive strength of BGC-Z_1, BGC-Z_2 , BGC-Z_3

The stress-strain curves had a positive slope until a maximum stress is reached. This maximum stress causes the samples to crush and shows the maximum compressive strength.

Compressive strengths of BGC-Z_1 BGC-Z_2 and BGC-Z_3 determined by compression test are illustrated in Table 4. It showed that by increasing zirconium oxide content compressive strength also increased.

Table 5 Compressive Strengths of Samples

Glass Ceramic Sample	Compressive strength MPa
BGC – Z_1	585.9
BGC – Z_2	691.2
BGC – Z_3	791.6

3.4.2 SEM analysis

SEM analysis was carried out to study the surface morphology of the samples. Fig. 4 a, b show SEM images of the surfaces of BGC-Z_1 and BGC-Z_2..

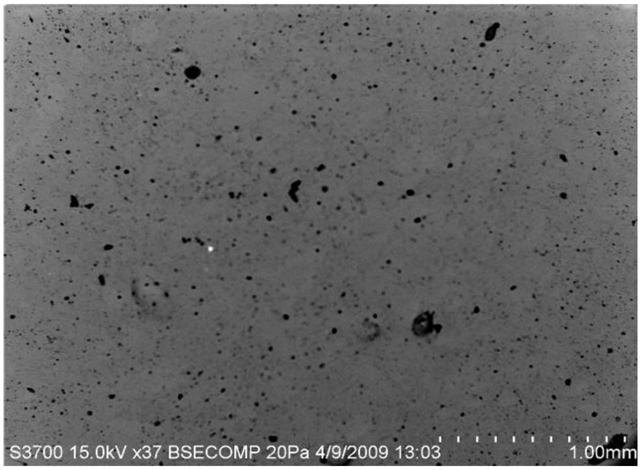

Fig. 4 a SEM image of BGC-Z_1

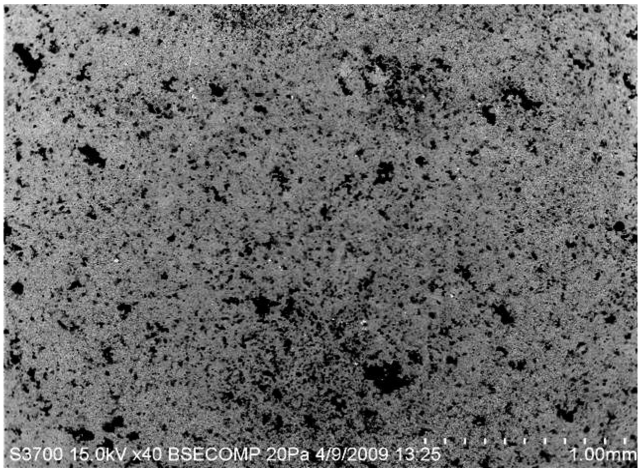

Fig.4 b SEM image of BGC-Z_2.

The SEM image of Fig. 4 a, shows the main crystalline phase as wallostonite ($CaSiO_3$) and small phase of calcium zirconium oxide ($CaZrO_9$). SEM image of Fig. 4 b shows the two phases Wollastonite ($CaSiO_3$) and calcium zirconium silicate ($Ca_2ZrSi_4O_{12}$).

4. CONCLUSIONS

In the present work clear transparent glasses have been fabricated from the system CaO- SiO_2 -ZrO_2 -CaF_2. Differential thermal analysis showed that by increasing the amount of zirconia content up to 13.5 wt. % at the expanse of silica, glass transition temperature and crystallization temperatures both were increased whereas further increase of zirconia content up to 15.5 wt. %, decreased both temperatures. XRD analysis revealed that with the increase of zirconia up to 13.5 wt. %, wollastonite ($CaSiO_3$) was observed as the major crystalline phase while higher percentage addition of zirconia resulted in zirconium oxide (ZrO_2) being the major crystalline phase. Intensity of wollastonite major peak was greater in composition containing 10.5 % zirconia. Mechanical testing proved that by increasing ZrO_2 content the compressive strength increased

REFERENCES

1. .Yao K, Zhang L, Yao X, Zhu W: Controlled Crystallization in Lead Zirconate Titanate Glass-

Ceramics Prepared by the Sol-Gel Process. *J Am.Ceram. Soc.*, **81**(**6**): 1571–1576, 2005.

2. Cekli C, Goller G: The Crystallization behaviour and Machinability of Sodium- potassium, Mica and Fluorapatite containing glass-ceramics. *J. Aust. Ceram. Soc*.,**43** [1],: 9-17, 2007 .
3. Coleman Nichola J, Nicholson John W: Feature, Glass bones, RSC | advancing the chemical sciences. 1-8, 2006.
4. Hench L.L, Splinter R. J,Allen W.C, Greenle T.K: J. Biomed . Mater. Res. Symp. No.2, 1972.
5. Enrica Verne, Roberto Defilippi, Chiara Vitale Brovarone, Gunter Carl, Jurgen Vogel:Glass-Ceramics Matrix/ZrO_2 Particles Biocompositis, Materials for Medical Engineering, 2005**.**
6. Salama S.N, Darwish H, Abo-Mosallam H.A: HA forming ability of some glass- ceramics of the $CaMgSi_2O_6$-$Ca_5(PO_4)_3F$-$CaAl_2SiO_6$ system. Ceram. Int.32:357-364, 2006.
7. M.Srinivas, G.Buvaneswari, International Conference on Design of Biomaterials, Indian institute of Technology, 2006.
8. S. Nath, N.Sinha, B. Basu, Ceramics International, 2007)
9. Xuanyong Liu, Anping Huang, Chuanxian Ding and Paul K. Chu, Bioactivity and cytocompatibility of zirconia (ZrO_2) films fabricated by cathodic arc deposition, 2006.
10. Polaska U, Berger G, Sahre M: Investigation of the Influence of Zirconium content on the formation of Apatite on Bioactive glass-ceramics, Key Engineering Materials, Volume 254-256, 2003**.**
11. De Aza P.N, De Aza S: Bioactivities of a SiO_2-CaO-ZrO_2 Glass in Simulated Body Fluid and Human Parotid Saliva, Key Engineering Materials, Volume 254-256, 2003.
12. Toshihiro Kasuga, Masahiro Yoshida, Akira J Ikushima: Bioactivity of Zirconia -Toughened Glass-ceramics, J. Am. Ceram. Soc., 75 [7], 1992:1884-1888.
13. R. Velmurugan, S. Kanagesan, S. Jesurani, T.Kalaivani, European Journal of Scientific Researc Vol.41 No.3 (2010) 430-436.
14. David W. Richerson, Modern Ceramic Engineering, properties, processing and use in Design, (2006) Taylor and Francis, CRC Press.
15. Fatma Hassan Margha, Salwa Abdel-Hameed Mohamed Abdel-Hameed,Nagwa Abd El-Shafy Ghonim, Saadia Ahmed Ali, Shigeru Kato, Shigeo Satokawa, Toshinori Kojima, Crystallization behaviour and hardness of glass-ceramics rich in nanocrystals of ZrO_2, *Ceramics International*, **35**, pp 1133-1137, 2009.
16. De Aza PN, Luklinska ZB, Effect of glass-ceramic microstructure on its in vitro bioactivity, *J Mater Sci. Mater Med*., **14** (10), 2003, 891-8.
17. Hong K.J, Kim J.M, Kim H.S, Microstructure and properties of CaO–ZrO_2– SiO_2 glass ceramics prepared by sintering, *Journal of the European Ceramic Society*, **23** : 2193–2202, 2003.