Formation and Crystallization Studies of Na_2O-CaO-SiO_2-P_2O_5 Glasses

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Summary: Calcium Phosphate based glasses and glass ceramics are known for their bio-active nature. In Na_2O-CaO-P_2O_5-SiO_2 system composition containing 40 %, 45 %, 51 % SiO_2 and 6 wt % P_2O_5 were studied with regard to ease of glass formation and crystallization. In the system large quantities of Calcium Oxide can be incorporated without significant increase in melting temperatures. Crystalization behaviour has been studied by iso-thermal heat treatment at 800 °C, 850 °C, 900 °C. Different crystallines phases developed during heat treatment were analyzed by X-ray Diffraction Method.

Introduction

In last two decades, remarkable advances in the field of bio-materials have led to the development of bio-glasses and bio-ceramics of various compositions for bone repair and teeth that do not cause damage in healthy tissue [1-2]. Synthetic ceramic materials based on calcium phosphate particularly in the composition of β–Tricalcium phosphate $Ca_3(PO_4)_2$, Hydroxyapatite $Ca_{10}(PO_4)_6(OH)_2$ and their composites are widely clinically used due to their good bio-compatibility [2-4] Calcium phosphate ceramics have attracted a great deal of attention for use as bonesubstitute due to their osteoconductivity and bio-activity [5-6]. Materials that are bio-active develop an adherent interface with tissues that resists substantial mechanical forces. In many cases the interfacial strength of adhesion is equivalent or greater than the cohesive strength of the implant material or the tissue bonded to the bio-active implant [7].

Bio-ceramics are compatible with the natural bone in a living man/animal, i.e. they do not have any adverse reaction when implanted. Bio-ceramics are of two types. They are bio-inert and bio-active ceramics. The former are useful for applications such as vertebrae – replacement. The later form a strong bond with the natural bone. It has been shown that these materials are firmly attached to the natural bone when implanted. Human bone is a composite material made up of collagen and calcium phosphate mineral. The mineral phase of bone comprises 60-70 % total dry bone weight. Bone mineral is an apatite calcium phosphate [8]. Sinja and Ingle have reported a Calcium Phosphate glass composition which was almost fully resorbable and was replaced, by new bone. The implant did not exhibit any kind of adverse effect to the surrounding tissues[5-6].

The mechanical properties constitute a limitation for load-bearing application. One solution for this problem is to cover metals (such as Ti, Ti alloys, Co-Cr alloys and stainless steel) which form the structural part of the implant, with a ceramic or a vitreous layer [9-11]. When it is imperative to avoid metals. For high mechanical strength the bio-ceramic should have fine and uniform grained micro structure [12]. The controlled crystallization of glasses involves proper heat treatment, crystal growth process not only highly critical to the production of micro-crystalline glass ceramics, but also of considerable importance in determining the morphology of the material produced. Crystal growth is dependent upon two factors:1 – The rate at which the irregular glass structure can be re-arranged into the periodic lattice of the growing crystal. 2 – The rate at which energy released in the phase transformation process [13]. In the present work the glass compositions given in Table-1, were melted and their thermal and crystallization behaviour have been studied by DT-40 Shimdzu, Thrmal expansion studied by Ortan Dilatometer Model-1600-D.

Table-1

Composition	Oxide (wt. %)				Temperature °C			
	SiO_2	CaO	Na_2O	P_2O_5	Melting	T_g	Tc	T_L
RA-1	40.00	26.34	27.67	5.99	1350	540	686	1090
RA-2	45.00	24.49	24.51	5.99	1350	519	1013	1115
RA-3	51.00	21.51	21.50	5.99	1350	536	935	1180

Results and Discussion

All the composition formed good clear glasses. Glass transition of these glasses determined by the dilatometery come out to be 540 °C, 519 °C and 536 °C respectively. Differential thermal analyses of the glasses under investigation are depicted in

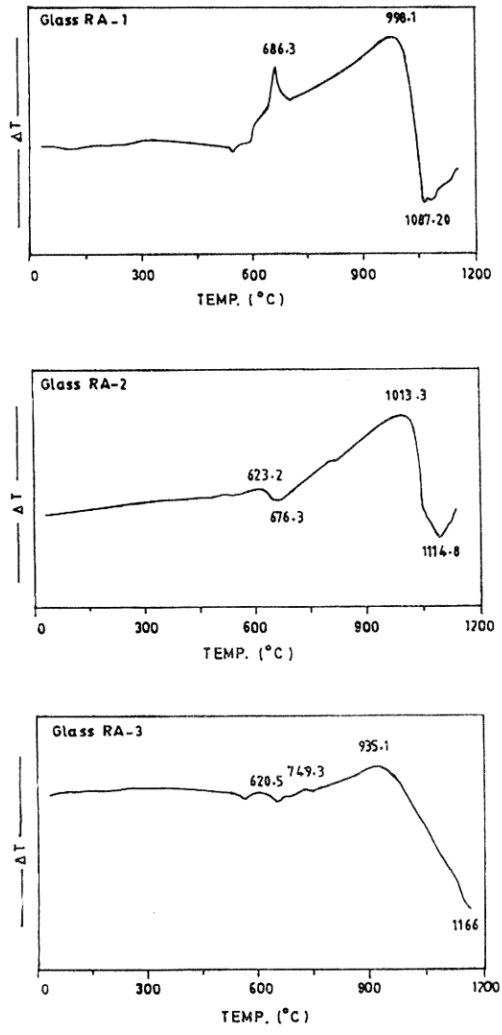

Fig. 1: Differential thermal analysis of calcium phosphate containing glass.

Fig. 1. RA-1 shows a endothermic peak at 580° C followed by a sharp exothermic peak at 686 °C, and a broad exotherm at 998 °C. These exothermic peaks indicate the formation of at least two different crystalline phases. Liquidus temperature (T_L) lies around 1088 °C. DTA of RA-2 shows a slight endothermic defection at 590 °C, an endothermic peak at 676 °C, and a broad exothermic peak at 1013 °C. T_L was found at 1115°C RA-3 has shown two small endothermic peaks at 581 °C and 665 °C a small exothermic peak at 749 °C and a broad exothermic peak at 935 °C with the liquidus tempera-ture was found to

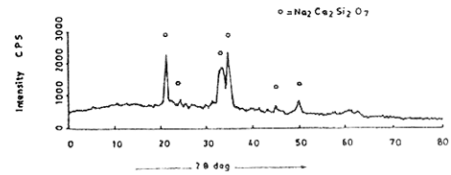

Fig. 2: XRD Patterns of RA-1 Glass heat treated at 680°C for 1 hour.

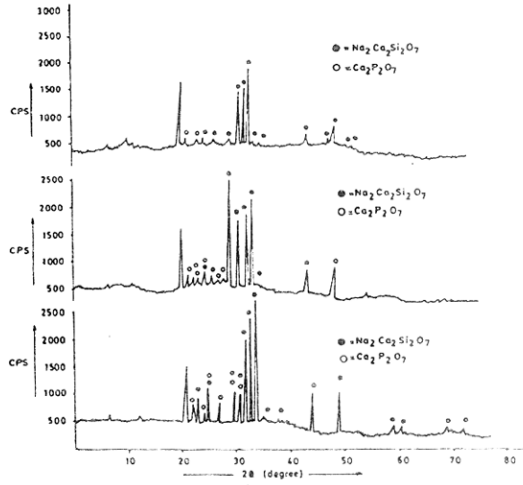

Fig. 3: XRD Patterns of RA-1 Glass heat treated at (a) 800 (b) 850 and (c) 900°C for 1 hour.

be 1181 °C. RA-2 seemed to be the most stable glass having highest crystallization temperature 1013 °C. It contains 24.5 wt % Na_2O and CaO. Visual observations also confirm that RA-2 is more resistant towards devitrification than the other two glasses. Heat treatment of three glasses was carried out at 800, 850 and 900 °C. RA-1 glass was also heat treated at 680 °C for 1 hour to ascertain the nature of DTA peak in their region. The XRD spectrum Fig. 2 revealed at low temperature 680 °C for 1 hour heat treatment only a single phase crystallize in RA-1 which is identify as $Na_2Ca_2Si_2O_7$ and is therefore, regarded as the primary phase. The X-ray diffraction spectra of heat treated glasses are given in Fig. 3 (a, b and c). Two crystalline phases were identified in RA-1. The major phase was $Na_2Ca_2Si_2O_7$ while $Ca_2P_2O_7$ was also present in appreciable amount. The observation is consistent with the thermal data of sample heat treated at 800 °C for 1 hour while shows significant proportion of glassy phase. This amorphous phase is reduced during heat treatment at

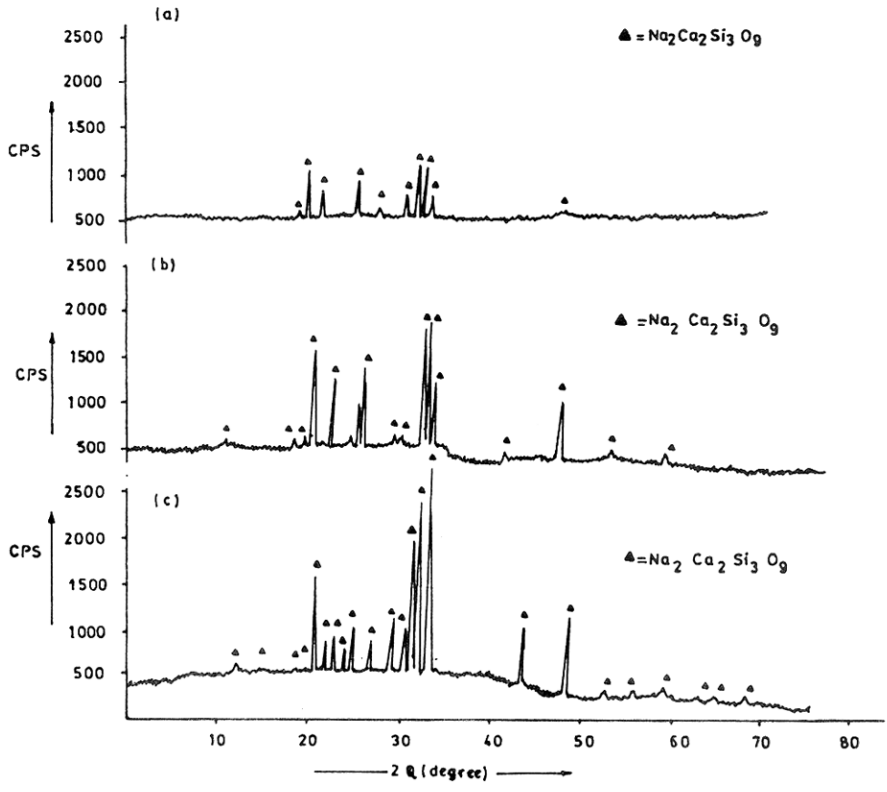

Fig. 4: XRD Patterns of RA-2 Glass heat treated of (a) 800 (b) 850 and (c) 900°C for 1 hours.

850 and 900 °C which can be observed in XRD patterns given in Fig. 3 (b & c). The samples heat treated at higher temperature were better crystallized. Only a single crystalline phase appeared during the heat treatment of RA-2 at these temperatures. The crystalline phase was identified as $Na_2Ca_2Si_3O_9$ as shown in Fig. 4. The peak intensity of the principal peak of the major phase appearing at 34.5° was 1600 cps. With the rise in the heat treatment temperature (680 °C- 900 °C) the intensity gradually rises to 2800 cps. At 800 °C the intensity of the principal peak was around 1000 cps and XRD spectrum shows predominantly glassy phase. The sample appeared as transulant. On further heat treatment at higher temperature the sample becomes opaque and glassy phase reduced significantly. Peak of intensity of the principal peak of the sample heat treated at 850 °C was 1880 cps and 3000 cps for the sample heat treated at 900 °C. RA-3 has shown the highest crystallization at 800 °C. The peak identified was $Na_2Ca_2Si_3O_9$. At higher temperatures the peak intensity of the principal gradually increases but the difference is not very large as compared RA-2. Although, it is not possible to compare the crystal growth rate of all three glasses, owing to appearance of different phases in RA-1 yet visual observation coupled with general thermal stability criteria i.e. larger the Tc-Tg gap more stable the glass would be, the RA-2 seems to be more stable glass.

Experimental

High purity silica (99 %), reagent grade calcium carbonate, sodium carbonate and phosphorous pentaoxide were weighed and mixed in a ball mill to obtain three glass compositions studied (Table-1). The glasses were melted in a gas-fired furnace at 1350 °C for 3 hrs, and poured in to a mould to form (10 mm x 2.5 mm) discs. The glass discs were annealed at 520-540 °C for 2 hrs. Differential Thermal analysis was carried out by using Shimadzu DT-40 Thermal analyzer. Glass powder samples (20-25 mg) were heated to 1200 °C at a rate of 10° C/min in air. The reference cell

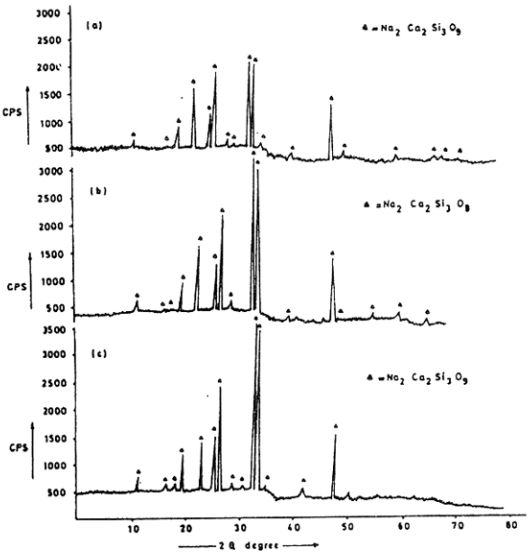

Fig. 5: XRD Patterns of RA-3 Glass heat treated at (a) 800 (b) (c) 900°C for 1 hour.

contained α-alumina powder. For stable Glass it is difficult to determine glass transition temperature from DTA curve. For this purpose Orton Dilatometer 1600-D was used. The samples were prepared by cutting Glass slabs of 24.5mm x 3mm x 2.5mm dimension. Glass transition temperature was determine as the point where the thermal expansion straight line exhibits a different slope. For crystallization studies iso thermal heat treatment was carried out in an electric furnace. One half of the cast disc of each composition was taken and placed on a platinum lid and then put into a pre-heated furnace in a region of uniform temperature of furnace. The temperature of furnace was maintained at 800 ^{o}C, 850 ^{o}C and 900 ^{o}C for one hour. Heat treated samples were ground until all samples were passed through 150 BSS mesh. Different phases developed during iso-thermal heat treatment were identified by XRD method. A Rigaku X-rays Diffractometer D Max-2 of wave length of radiation 1.5405 of Cu Kα was used, where d is atomic spacing in the crystal. Scan angle (2θ) ranged from 10-80°. 2θ and λ are related by Bragg's equation i.e. $\lambda = 2d \sin \theta$. The spectra obtained were matched with the standard data to identify the crystallization phases.

Conclusions

Present investigation has revealed that glasses containing 40-50 % SiO_2 with high concentration of CaO and Na_2O form good clear glasses. Thermal studies showed that RA-1 is least stable glass and crystallizes at lower temperature. XRD studies at high temperature heat treated samples identified two crystalline phases in RA-1 glass i.e. $Na_2Ca_2Si_2O_7$ and $Ca_2P_2O_7$ while a single phase $Na_2Ca_2Si_3O_9$ in other heat treated glasses.

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