

PREPARATION OF DIOPSIDE BY NOVEL SOL-GEL METHOD

USING RICE HUSK ASH AS SILICA SOURCE

A Thesis Submitted

In Partial Fulfilment of the Requirement

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BACHELOR OF TECHNOLOGY

By

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CERTIFICATE

This is certified that the work contained in the project entitled “**PREPARATION OF DIOPSIDE BY NOVEL SOL-GEL METHOD USING RICE HUSK ASH AS SILICA SOURCE**” by Rahul Nagar (Roll 107CR023) in partial fulfilment of the Bachelor of Technology Degree in Ceramic Engineering at the National Institute of Technology, Rourkela is an authentic work carried out by him under my supervision and guidance.

To the best of my knowledge, the matter embodied in the thesis has not been submitted to any other university / institute for the award of any Degree or Diploma.

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ABSTRACT

Diopside ($\text{CaMgSi}_2\text{O}_6$) was synthesised through a novel sol-gel synthesis. Sol-gel synthesis usually utilises silicon alkoxides (e.g TEOS) for the synthesis of Diopside. The material is costly and unstable in the air atmosphere. In the present investigation, rice husk ash (RHS) has been used for an alternative to TEOS raw material. RHS is cheap and contains amorphous silica which can be dissolved in the solution. RHS was dissolved in citric acid and metal nitrate solution. The gelling was performed. The gel was characterised for TG-DSC analysis. The phase formation behaviour with the application of heat on the gel was studied by calcining it at different temperatures upto 1050°C . XRD phase analysis showed the formation of diopside phase in the calcined product. The material was sintered at 1100°C and tested for bio-activity by incubating in SBF solution. The material induces apatite formation in its surface within 14 days of incubation. In conclusion, the Diopside bioactive material synthesised through this novel sol-gel processing, may be a cost effective material for bulk applications.

Chapter 1

Introduction

1.1 Background:-

Calcium silicate based biomaterials including bioglass are now a days a hot topic of research for bone tissue repair applications [1]. Diopside (CaMgSiO_6) belongs to the group of silicate biomaterials and they have the ability to release silicate ions at a definite concentration which helps osteoblasts to grow and differentiate [2]. Also CaSiO_3 and akermanite ($\text{Ca}_2\text{MgSi}_2\text{O}_7$) ceramics induce good in-vivo bone formation and better material degradation compared to β - tri calcium phosphate biomaterial. This suggests silicate ceramics have potential application in bone tissue regeneration [3]. Diopside is very similar to akermanite and CaSiO_3 . Only it has relatively slower degradation rate [4]. It has been reported that the diopside has ability to induce apatite formation in-vitro in SBF and bone formation in vivo [5]. Further it has been confirmed that the diopside possess good bioactivity and excellent bending strength, fracture toughness both in-vitro and in-vivo [6]. In that respect presently bioactive ceramics like HAP and β -TCP lack adequate mechanical strength which limits their application in load bearing area. On the other hand, calcium silicate and bio glass have relatively quick degradation rate. Considering all these, diopside could therefore be considered, to be potential biomaterial for artificial bone and tooth. Along with its other useful application like an immobilising agent of nuclear waste, as sealing material in solid oxide, gems and jewellery etc [7]. The structure of Diopside is monoclinic and the cell parameters are as follows:-

$$a = 9.76 \text{ \AA}, \quad b = 8.899 \text{ \AA} \quad c = 5.251 \text{ \AA} \quad \alpha = 90 \quad \beta = 74.17 \quad \gamma = 90$$

It has single chain of linked SiO_4 tetrahedra (**Fig. 1.1**).

Diopside is a pyroxene material found in SiO_2 -CaO-MgO system (**Fig 1.2**). The diagram shows that the diopside is surrounded by tridymite, pro-enstatite, fosterite, akermanite and pseudo-wollastonite [8].

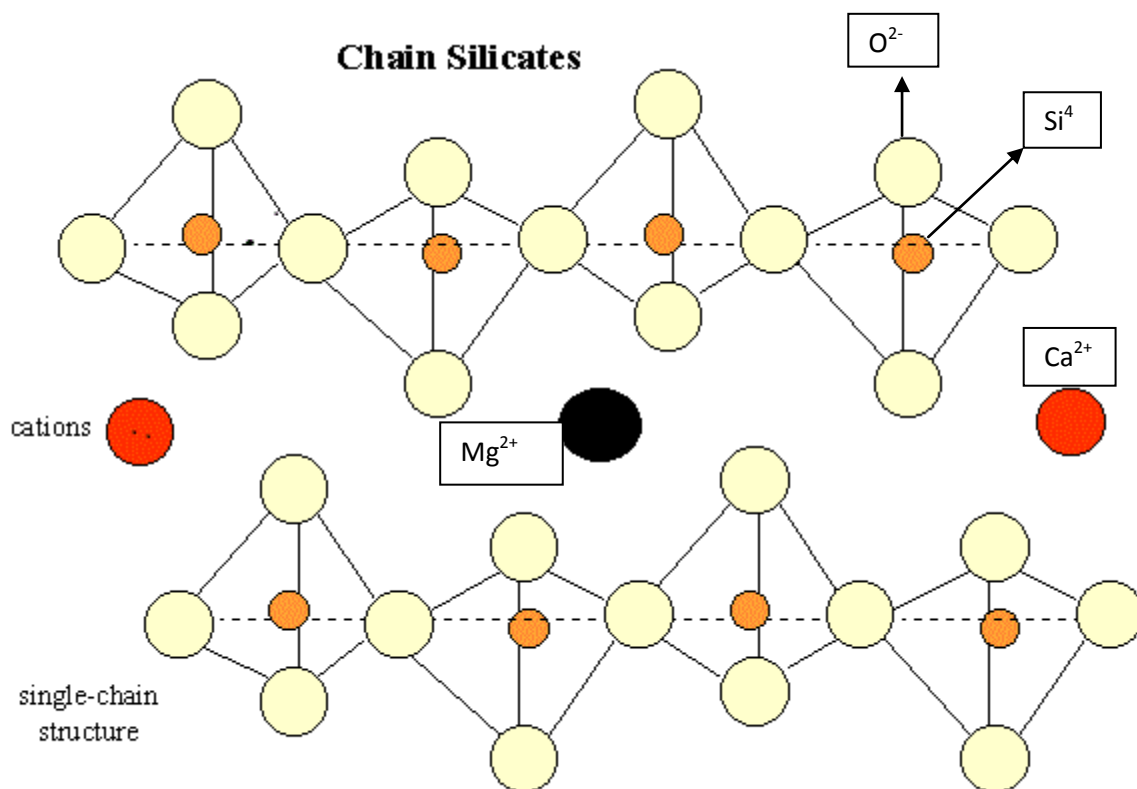


Fig. 1.1 Structure of Diopside

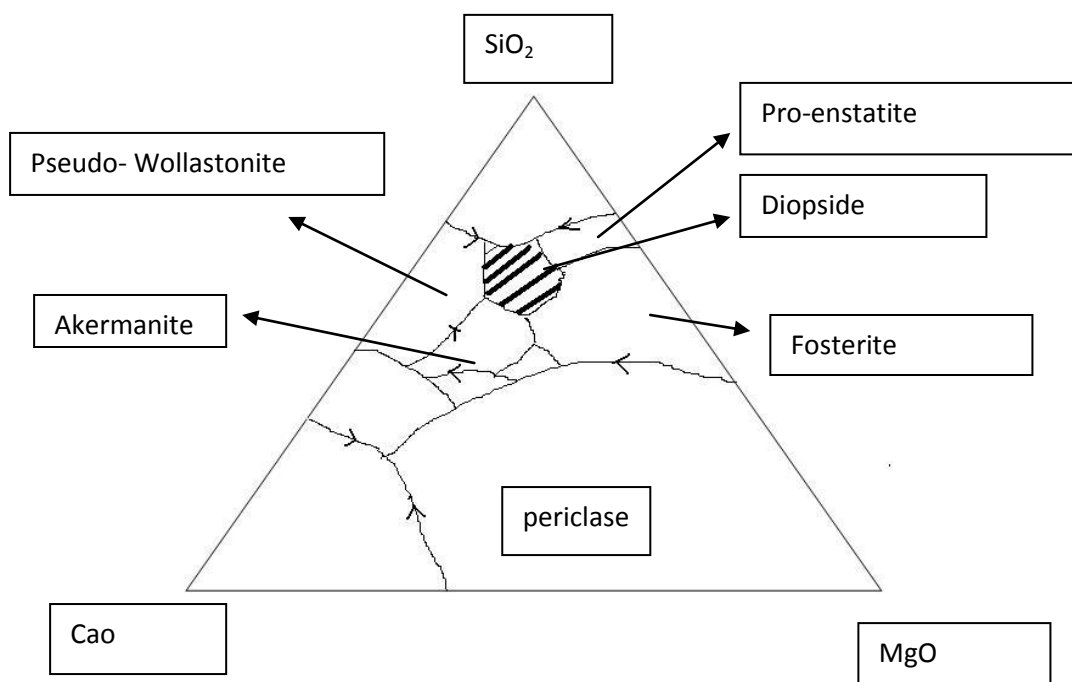


Fig. 1.2 Schematic CaO-SiO₂-MgO system showing Diopside zone.

1.2 Synthesis of Diopside

The various processes employed for the synthesis of Diopside are:-

1. Solid-State reaction
2. Sol-Gel process
3. Co precipitation process
4. Spray pyrolysis

With the exception of spray pyrolysis which is used for preparation of porous films [10], all other processes are employed for the preparation of dense bulk solids.

Solid-state reaction synthesis is the conventional ceramic processing, which has very simple processing steps but produces coarser particle size; require high temperature for phase formation as well as sintering, etc. On the other hand, sol-gel method has following advantages over other processes:-

- (a) Powder synthesised by sol gel process using solution retains the uniform mixing state of its component at molecular level, hence a homogenous product can be formed comparatively low temperatures.
- (b) Sol-Gel processed powder has very fine particles with high sinterability.

Sol-gel processed diopside showed approx. 1.7 times higher flexural strength than that of as reported diopside ceramics by solid state reaction [9].

In sol-gel process metal alkoxides are usually employed as raw materials for example tetra ethyl ortho silane (TEOS) are used as a source for silica [1, 10, 11]. However, almost all

metal alkoxides are quite unstable in air and can't be handled easily in the processing. It easily hydrates in presence of air by taking moisture from it. Additionally they are highly costly. So, an alternative non-alkoxide and cheap material will be very useful for the low cost production of diopside ceramics.

1.3 Scope of the present study:-

In the present study, the diopside has been prepared by sol-gel process using a non alkoxide and cheap raw material for silica. The rice husk ash (contains amorphous silica) has been used to synthesise the diopside ceramics through sol-gel process successfully.

Chapter 2

Experimental

2.1 Preparation of Diopside

The raw materials employed for the preparation of diopside are:-

1. Rice husk ash (RHS) as source for silica.
2. Magnesium Nitrate Hexahydrate ($\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$)
3. Calcium Nitrate Tetrahydrate ($\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$)
4. Citric Acid

Except RHS all other materials were of analytical grade. Rice husk ash was prepared by burning thoroughly cleaned rice husk at 700°C for 6 hours in flowing air atmosphere. The as prepared ash was used for the synthesis of diopside. The ash contains approx. 98.9% SiO_2 in amorphous state, rest were minor elements like calcium, potassium, aluminium, iron etc [12]. Citric acid was used as a chelating agent.

Two different molar ratios of citric acid were used:-

1. SiO_2 : Citric Acid = 1 : 2.5 (Sample CA2.5)
2. SiO_2 : Citric Acid = 1 : 6.25 (Sample CA6.25)

A typical 5 gm batch of diopside has the following amount of raw materials

Table 2.1

Amount of raw materials required for synthesis of 5 gm diopside sample

S. No	Material	Amount (in grams)
1.	Silica (Rice husk ash)	2.8
2.	Calcium Nitrate	5.45
3.	Magnesium Nitrate	5.9
4.	Citric Acid	(a) 22.37 (2.5 moles) (b) 55.94 (6.25 moles)

2.2 The powder synthesis and pellet preparation

The sol-gel process used for the synthesis is schematically shown in Fig. 2.1. Citric acid was added to the 100ml of deionised water under stirring conditions. Dissolution of citric acid took place and finally a clear solution was obtained. To this clear solution, required amount of RHS was added under stirring and boiling condition. Water evaporated during the process was compensated by addition of hot water to the solution and the water level of was constantly maintained at 100ml. For batch CA2.5, there was small residue of ash even after 4 hours of stirring and heating, whereas for batch CA6.25, the clear solution was obtained within 1 hour.

Now to this clear solution, Calcium Nitrate and Magnesium Nitrate were added under stirring and heating condition. No water was added after these nitrate salt additions. The viscosity of the solution increased slowly. The viscous solution was kept undisturbed for gelation. Within 1 hour, the gelation completed.

Gel was dried at 100°C in dryer. Dried gel was ground using agate mortar and was used for further characterisation.

Decomposition behaviour of dried gel was studied using TG-DSC analysis at a temperature range of 20-1100°C and at a heating rate of 10°C/min under argon atmosphere using NETZSCH STA 449 C.

To study the phase formation behaviour in the system, the dried gel was calcined at temperatures 600°C, 800°C, 1000°C and 1050°C respectively. After calcinations, each powder was characterised for its phase using XRD (PHILIPS PW-1843, Cu K α). Depending on the phase formation behaviour result, the gel was finally calcined at 1050°C for 2 hours to get the diopside phase. The calcined powder was ground using agate mortar and at the end of the grinding, 4% PVA solution was added as a binder. Then the powder was granulated using sieve. The granules were then pressed uniaxially at 3 Ton pressure with a dwelling time of 60 seconds. The cylindrical pellets with the dimension of 10mm diameter were pressed. Pellets were then sintered at 1100°C for 2 hours. Sintered pellets were characterised for density, phase analysis and bioactivity

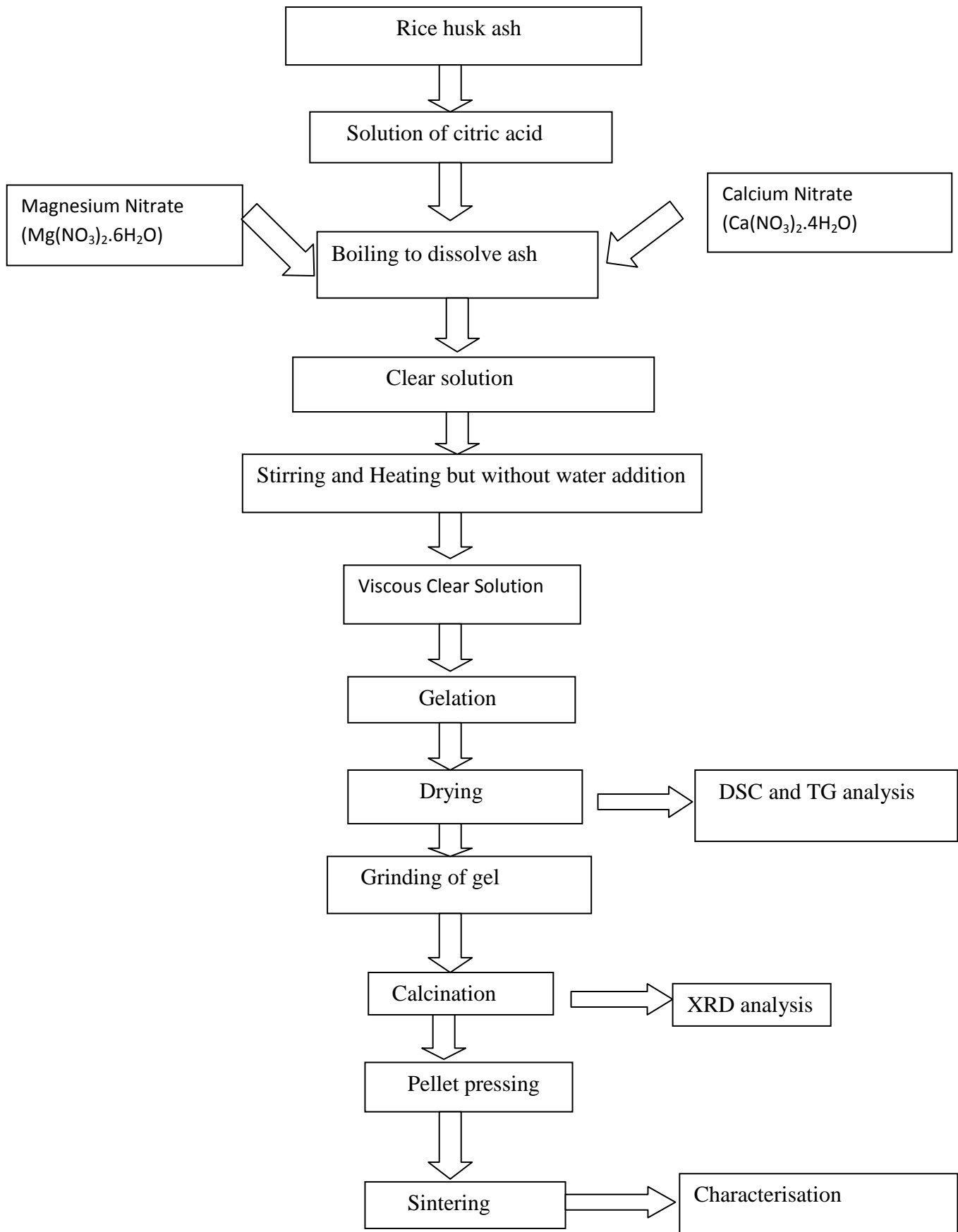


Fig. 2.1 Schematic Flow chart for sol-gel synthesis of Diopside

2.3 Characterisation of Sintered pellets

Evaluation of Bioactivity

Preparation of simulated body fluid

A simulated body fluid having inorganic ion concentrations similar to those in human blood plasma (Table 2.2) [11] was synthesised as per the process described by Kokubo et al [13]. The reagents for preparing SBF as shown in Table 2.3 were dissolved in 350ml of deionised water in tarson beaker. After complete dissolution of the reagent, the temperature of the solution was maintained at 36.5°C and PH of the solution was maintained at 7.4 by addition of 1M hydrochloric acid solution. Finally the solution was made into 500ml by the addition of deionised water.

Table 2.2

Ion Concentrations (m M) in SBF and Human Blood Plasma

Ion	SBF	Blood plasma
Na ⁺	142.0	142.0
K ⁺	5.0	5.0
Mg ²⁺	1.5	1.5
Ca ²⁺	2.5	2.5
Cl ⁻	147.8	103.0
HCO ₃ ⁻	4.2	27.0
HPO ₄ ²⁻	1.0	1.0
SO ₄ ²⁻	0.5	0.5

Table 2.3

Amount of reagents for preparation of 500ml SBF

S. No.	Reagent	Amount (in grams)
1	NaCl	4.081
2	NaHCO ₃	0.1759
3	KCl	0.1125
4	K ₂ HPO ₄	0.0879
5	MgCl ₂ .6H ₂ O	0.1556
6	CaCl ₂	0.1463
7	Na ₂ SO ₄	0.03585
8	(CH ₂ OH) ₃ CNH ₂	3.0591
9	1 M HCl	20 ml

Immersion of diopside pellets in SBF and characterisation

The CA6.25 pellets were immersed in SBF for a period of 7 days and 14 days in an incubator and the temperature was maintained at 36.5°C. The pellets were then taken out and washed with distilled water and then dried in vacuum.

The SBF treated pellets were investigated for its surface microstructure by using Scanning electron microscope (SEM, JSM-6480LV, JEOL ltd, Japan) and characterised for surface phase analysis by XRD.

Chapter 3

Results and Discussion

3.1 Thermal decomposition behaviour of gel powder

A good understanding of thermal decomposition behaviour of gel powder is essential for attaining the desired diopside phase in the ceramics. **Fig 3.1** shows the TG-DSC curves for CA 6.25 gel powder synthesised by Sol-gel process using RHS as a raw material. The total weight loss of the gel powder was 91.6%. Such a large weight loss is due to the decomposition of citric acid releasing CO_2 and H_2O from the gel and decomposition of nitrate salts releases nitrogen oxide gases.

DSC curve shows some endothermic and exothermic peaks. Endothermic peaks are due to the decomposition of nitrate and citric acid. Decomposition analysis reveals that the major decomposition and weight loss were completed by 600°C . The crystallisation peak for diopside is around 845°C [10]. The crystalline peak of diopside is not clear because there is crystallisation of many other phases like akermanite, montecellite, wollastonite and other calcium magnesium silicate phases overlapping with each other.

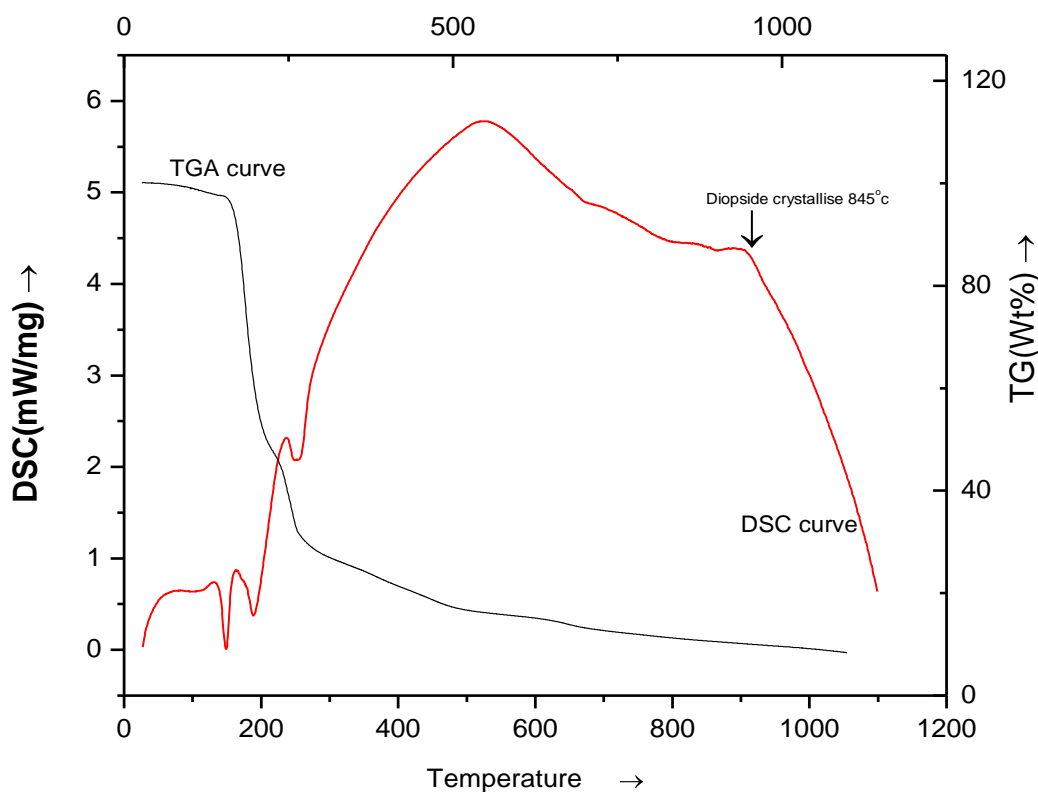


Fig 3.1 DSC and TGA curve of dried CA6.25 gel powder.

3.2 Calcination of gel

Fig. 3.2 shows the XRD pattern of CA2.5 powder calcined at 800°C, 1000°C and 1050°C. The various phase formed at respective temperatures are labelled in the diagram. The powder calcined after 800°C shows (Fig.4.2a) the formation of calcium carbonate, MgO and cristobalite phases due to the decomposition of gel and release of different metallic cations from the gel network. CaCO_3 is produced due to the reaction of calcium nitrate and citric acid. Citric acid releases CO_2 which reacts with calcium nitrate to form Calcium carbonate. However some un-burnt carbon was found in the specimen which increases in 1000°C calcined sample.

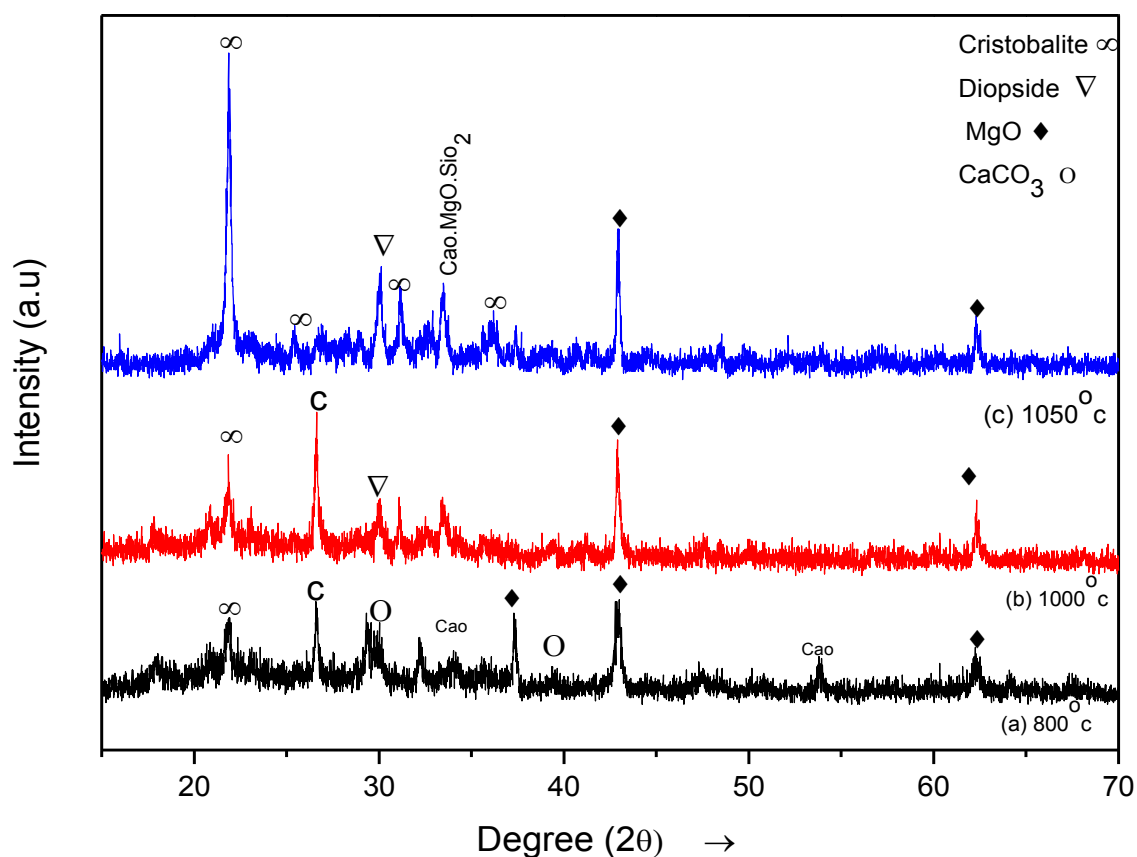


Fig. 3.2 XRD Pattern of CA2.5 calcined at temperature (a) 800°C (b) 1000°C (c) 1050°C

The Figure also shows that silica mainly separated from the gel as cristobalite phase which increases and maximised at 1050°C. This indicates that the CA2.5 specimen was not properly

prepared. It has already been mentioned that there were residue of RHS in the gelling process. That residue of ash converted to cristobalite when heat treated. However, the Figure shows the formation of some amount of diopside phase from 1000°C upwards. There was substantial amount of free MgO in calcined powder due to the separation of silica from the system as cristobalite. This investigation shows that CA2.5 batch was not proper for the synthesis of diopside through this sol gel process.

Fig. 3.3 shows the XRD pattern of CA6.25 powder calcined at 600°C, 800°C and 1050°C. The respective phases are labelled in the XRD pattern.

The XRD pattern shows that the gel after firing at 600°C produces mainly CaCO₃, MgO and amorphous silica phases. As stated above, CaCO₃ is produced due to the reaction of calcium nitrate and citric acid. The pattern also shows that the amount of CaCO₃ decreases when fired at 800°C. However some un-burnt carbon was found in the specimen and silica remains in the amorphous state.

After firing at 1050°C, the amorphous silica reacts with CaCO₃ and MgO to form mainly Diopside phase which is labelled in Fig. 3.3c. The analysis reveals that there is some separation of MgO and CaO phases during calcination. However, there was no separation of crystalline silica. Although, the diopside phase could be synthesised successfully by calcinations of the gel at 1050°C, it requires further improvement in the processing of the gel so that there will not be any phase separation of CaO and MgO.

Along with diopside some calcium magnesium silicate phases like Merwinite, Montecellite were also found. So this analysis reveals that the citric acid composition 1:6.25 was effective for the formation of diopside phase in this novel Sol- Gel route.

Citric acid composition 1:2.5 was insufficient to form diopside phases due to insufficient polymerisation between silica, calcium and magnesium in the gel network.

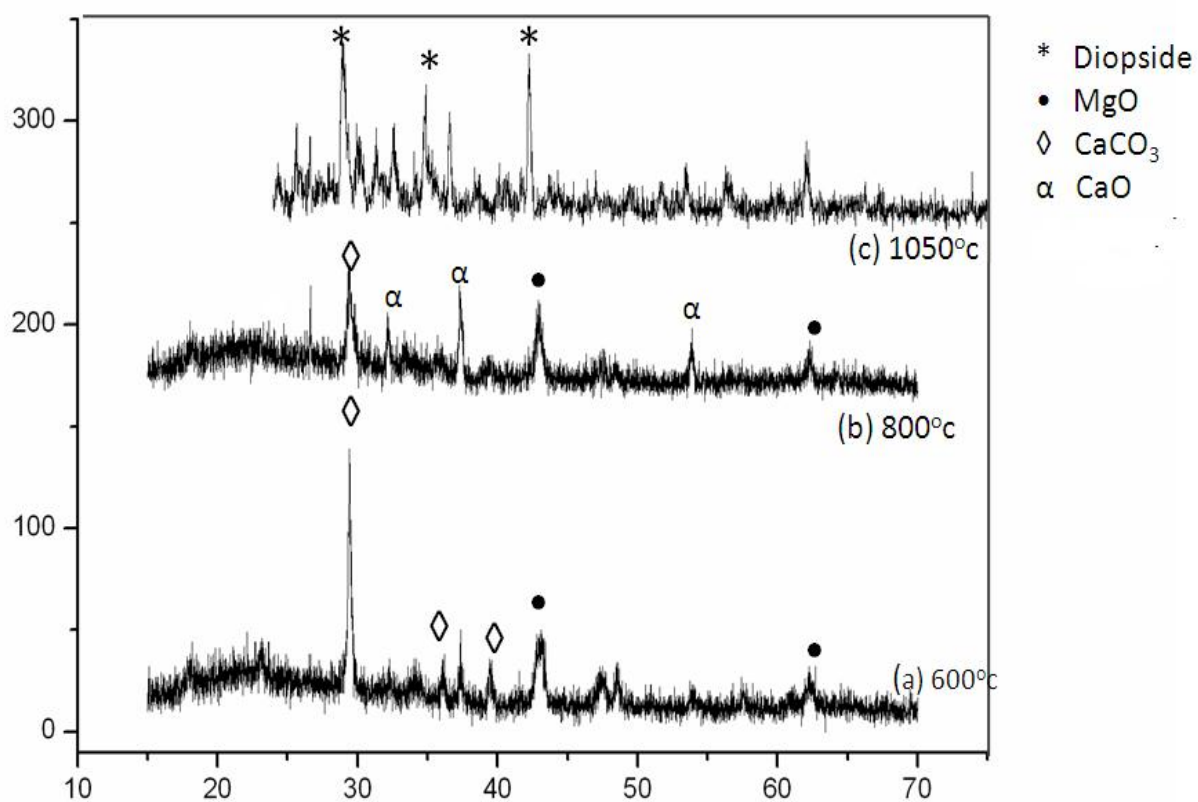


Fig. 3.3 XRD Pattern of CA6.25 calcined at (a) 600° C (b)800°C (c) 1050°C

3.3 Analysis of sintered diopside pellet:-

Fig. 3.4 shows the XRD pattern of Sintered CA6.25 pellet and only diopside peaks (Standard card no. 75-1577) were observed in the pattern indicating the formation of pure diopside after sintering. **Fig. 3.5** shows the SEM micrograph of the sintered CA6.25 pellet and crystals of diopside were clearly visible.

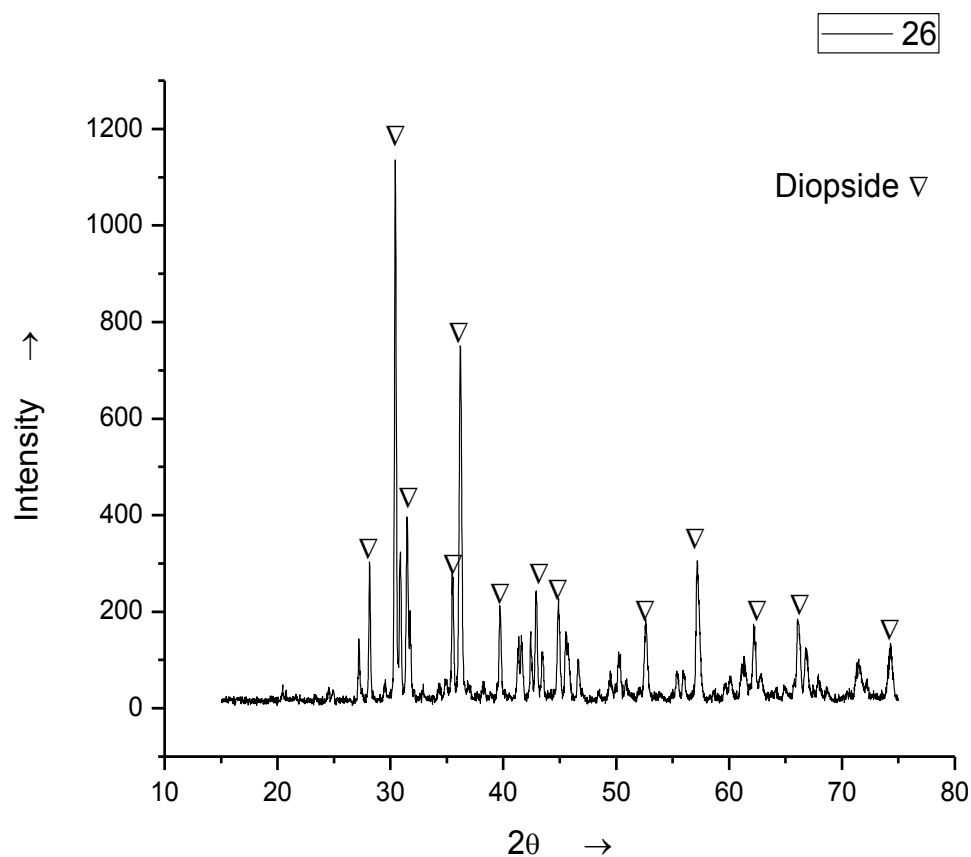


Fig. 3.4 XRD pattern of CA6.25 sintered pellet.

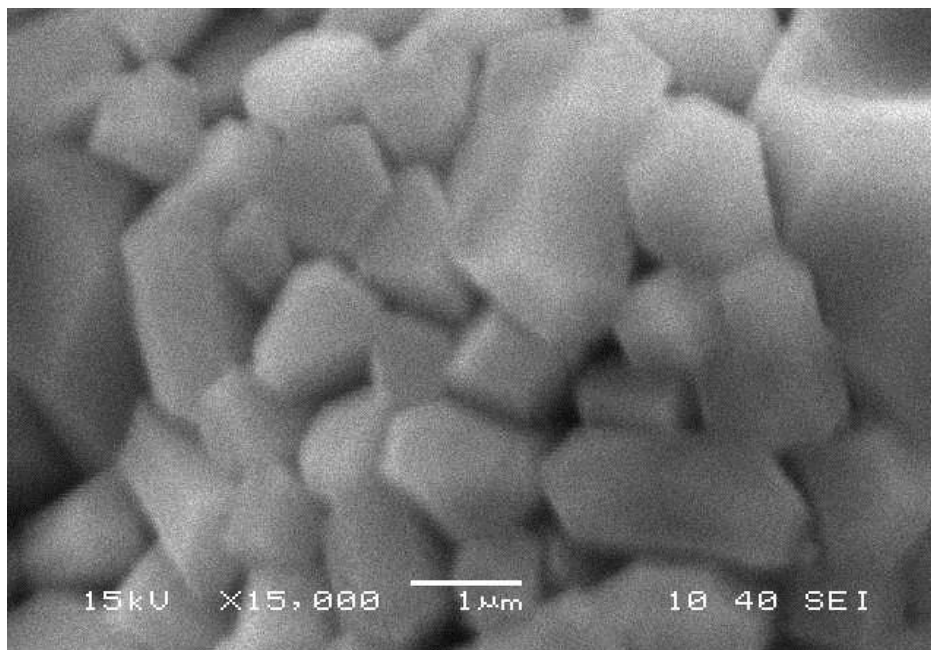


Fig. 3.5 SEM micrograph of CA6.25 sintered pellet before immersion in SBF.

Formation of apatite layer during SBF incubation:-

When a bioactive material is implanted in the living tissue such as bone, they combine with them with formation of bone like apatite layer on their surfaces. Hence the formation of apatite layer on the surface of Diopside is pre-requisite for the Bioactivity and its direct bonding property to the living bones. The bioactivity of this diopside material prepared by sol-gel process using rice husk as amorphous silica source was tested by immersion of sintered diopside pellets in the SBF (simulated body fluid) for 7 days and 14 days.

Fig. 3.6(a), 3.6 (b) and 3.6 (c) shows the SEM micrographs of diopside pellets surface after immersion in SBF for 7 days and 14 days. As seen in the Figure, there is the deposition of leaf like particles on the surface of diopside pellets. When compared with the results those reported by many authors [1, 10,11], this morphology resembles to the apatite formation. This could be confirmed by elemental analysis of the deposits. Due to some unavoidable circumstances elemental analysis by EDS (attached with the SEM) could not be performed. However, the Fig. 3.7 shows that the formation of an amorphous peak near 32° which is typically assigned to apatite [11]. So, comparing the results of XRD and SEM, it can be

concluded that the diopside prepared by this sol-gel process has the ability to induce apatite formation in the diopside surface in-vitro.

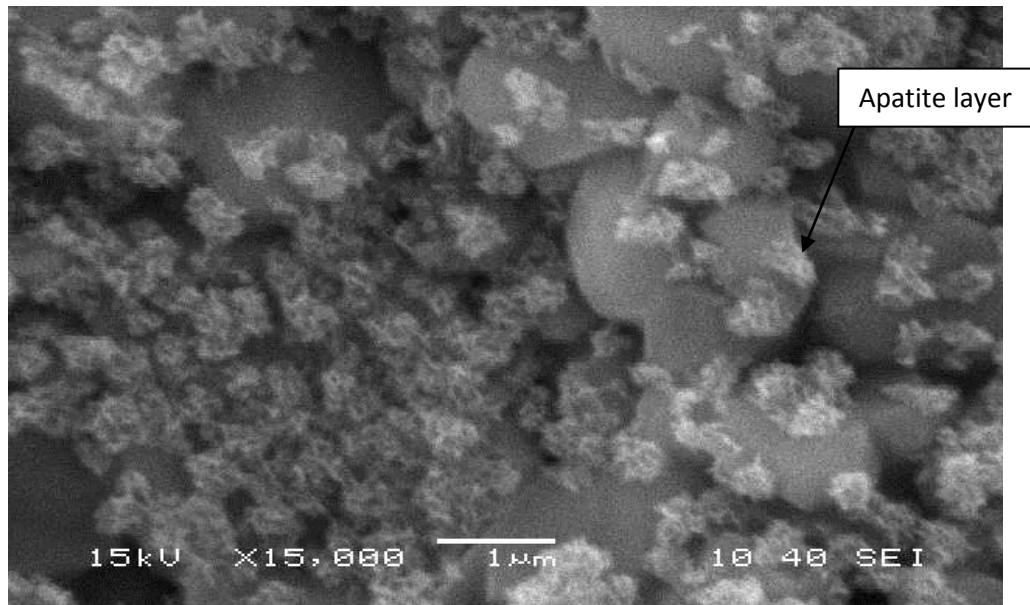


Fig. 3.6(a) SEM of sintered Diopside pellet immersed in SBF for 7 days

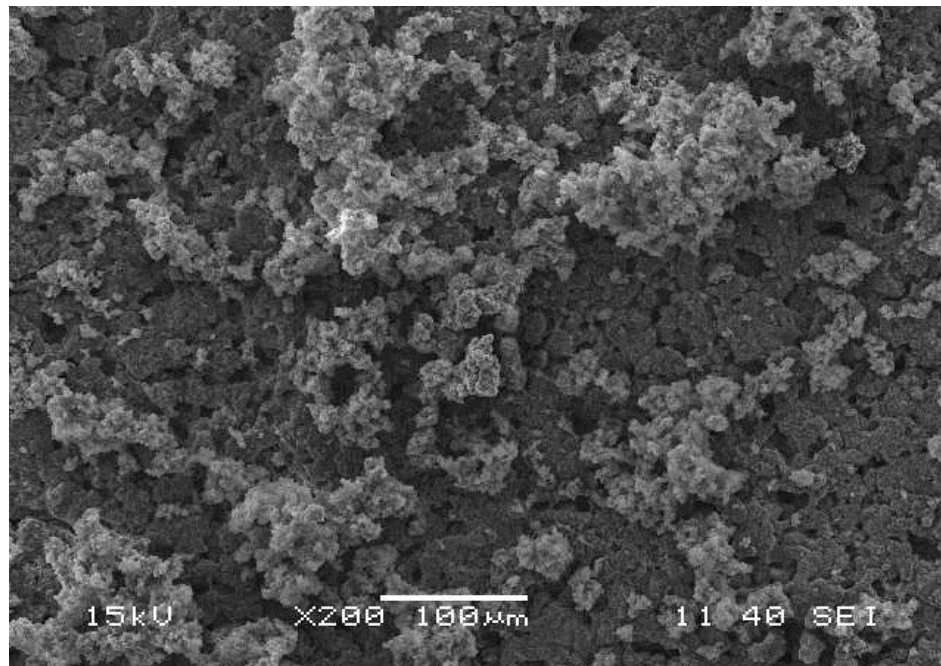


Fig. 3.6(b) SEM of sintered Diopside pellet immersed in SBF for 14 days

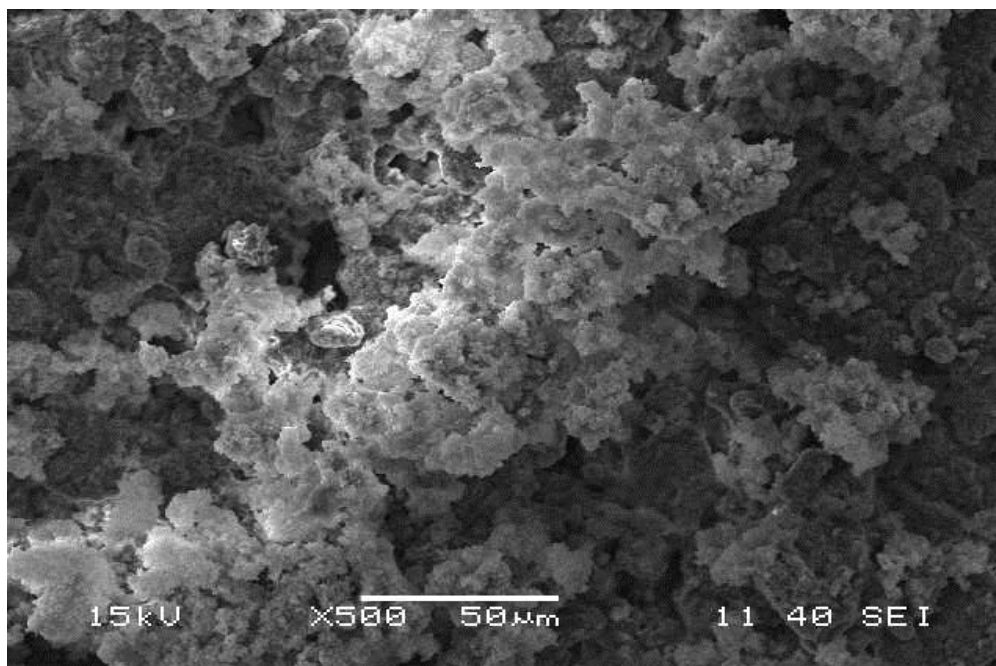


Fig. 4.6(c) SEM of sintered Diopside pellet immersed in SBF for 14 days

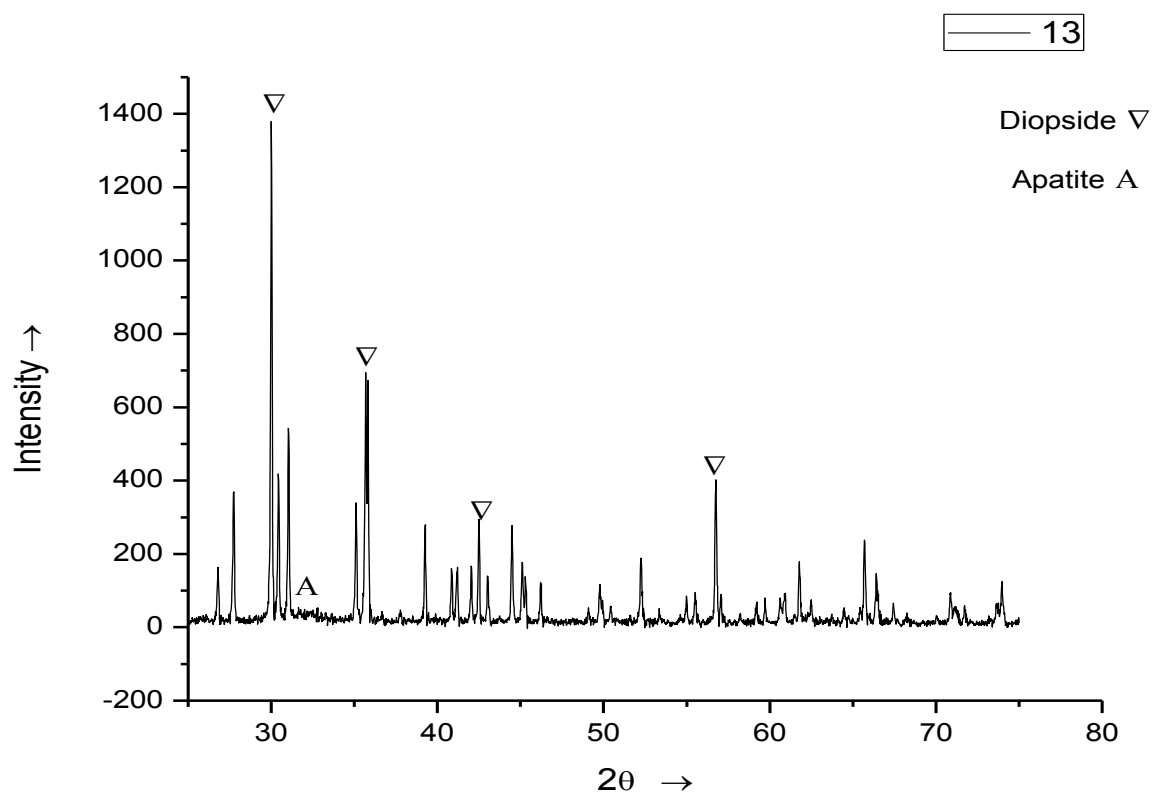


Fig. 3.7 XRD pattern of CA6.25 sintered pellet after immersion in SBF

The apatite forming mechanism on the diopside as proposed by Noriyuki Y et al. [10] is schematically represented in Fig. 3.8. As reported by the authors calcium, magnesium and silicon of diopside dissolve in SBF after immersion. Calcium has the highest dissolution rate which quickly supersaturates the SBF solution. After dissolution, diopside surface becomes negatively charged H_3O^+ , Ca^{2+} are attracted towards the silica rich surface. Next PO_4^{3-} group deposits on the surface and that is how apatite growth takes place.

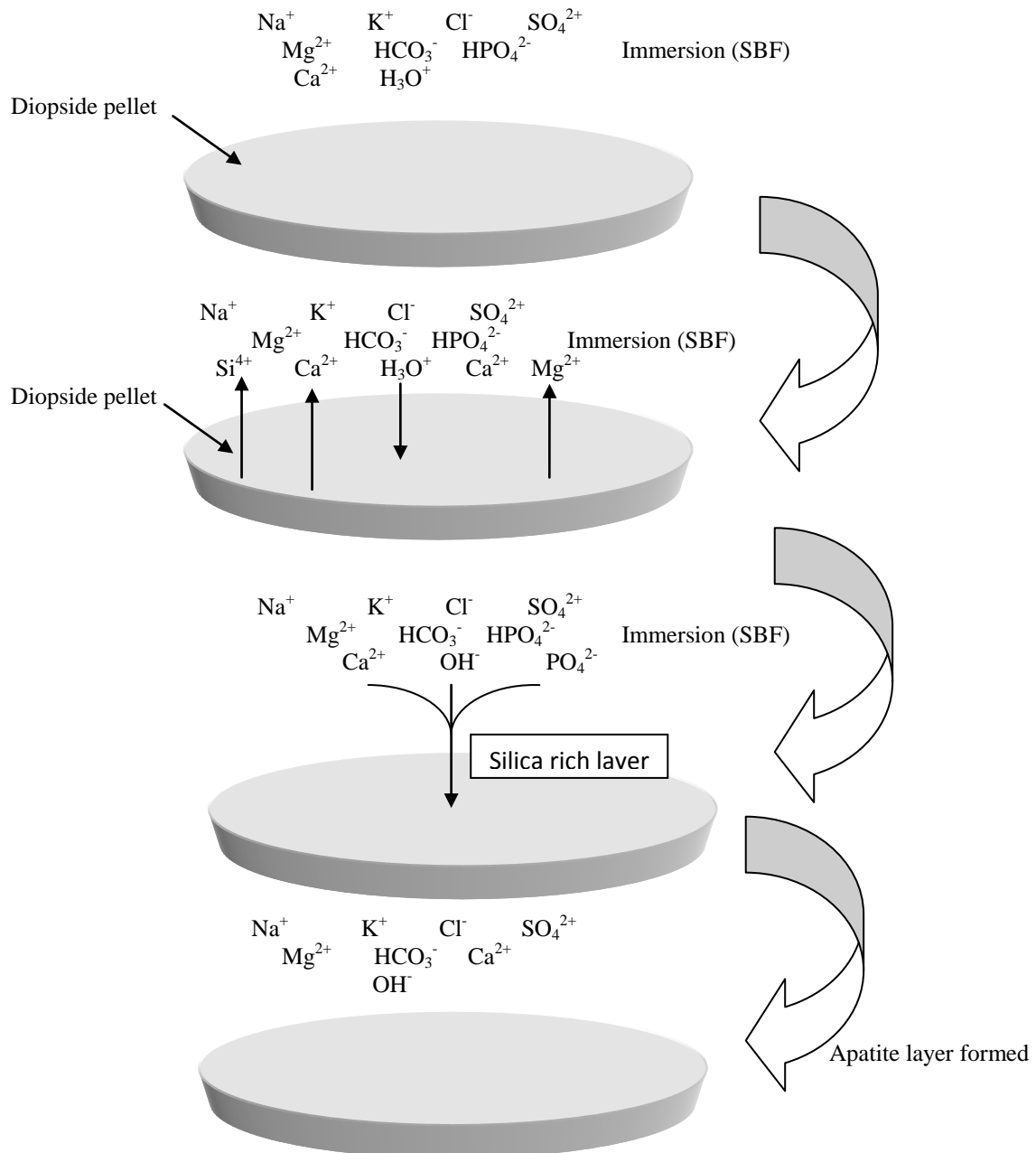


Fig. 3.8 Schematic flow chart showing formation of apatite layer.

Chapter 4

Conclusion

Major conclusions:

- Rice husk ash was completely dissolved in nitrate – citrate solution during the sol-gel synthesis of diopside.
- For the complete dissolution of amorphous silica, the SiO₂: Citric acid molar proportion should be 1:6.25 or above.
- The diopside phase could be synthesized from gel precursor by calcining at 1050°C.
- The diopside precursor thus formed could be sintered at 1100°C with high crystallinity.
- The diopside showed good bio-activity in-vitro that is formation of apatite layer in SBF solution within 14 days.

Future work:-

Further scopes:

- To improve the processing parameter so that during calcination, no phase separation takes place.
- Bio-dissolution characteristics of the ceramics.
- Bio-compatibility of the ceramics.
- Scaffold fabrication and mechanical strength measurement.

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