

# **Sol-gel synthesis of glass-ceramics using rice husk ash and its gelcasting**

A Thesis Submitted in Partial Fulfillment of the  
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**Bachelor of Technology**

by

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## **CERTIFICATE**

This is to certify that the thesis entitled, “**Sol-gel synthesis of glass-ceramics using rice husk ash and its gelcasting**” submitted by Mr. **Raja Bipul Warjri** in partial fulfillment of the requirements for the degree of **Bachelor of Technology in Ceramic Engineering** at 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.

**Date:**

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# **Chapter 1**

## **Introduction**

Glass-ceramic materials have many properties similar with both glass and more traditional crystalline ceramics. It is first formed as a glass, and then crystallized partly by heat treatment [1]. Bioactive glasses and glass-ceramics are extensively studied because of their surface chemical reactivity when in contact with body fluids [2-4]. This property makes bioactive glasses and glass ceramics interesting candidates for applications in the field of small bone defects reconstruction, or as coatings on inert substrates.

Since the discovery of bioglass by Hench et al. [5] in the early 1970s, various types of ceramic, glass and glass-ceramic have been used as bone replacement biomaterials [6-8]. Specifically, these biomaterials have found clinical applications as coating for prostheses, bone filler, vertebral substitution and, in a porous form, as bone substitutes [9-16]. Most of them are based on the  $\text{SiO}_2\text{-P}_2\text{O}_5\text{-CaO-Na}_2\text{O}$  system. Bonding between bioactive glass or glass ceramic and the surrounding tissues takes place through the formation of a hydroxyapatite layer, which is very similar to the mineral phase of bone. When the bioactive glass is placed in contact with physiological fluids, this layer is formed through a complex ion-exchange mechanism with the surrounding fluids, known as bioactivity [1].

In the current study, rice husk ash is being used as raw material for synthesis of glass-ceramics. Rice husk ash has a high content of silica and being readily available, it becomes very economical to use silica of the ash. It is beneficial in two ways; first, it provides value addition and second, it takes care of ash disposal.

Glass-ceramic powder is gelcasted to fabricate scaffold. There are many ceramic forming techniques, namely slip casting, ceramic shell casting, injection moulding, hot wax moulding, gelcasting, etc. Among these gelcasting is a promising technique for shape forming of bulk dense or porous ceramic, metal structures [17, 18]. The process offers a number of advantages over processes such as slip casting, injection molding in forming complex ceramic shapes. Gelcasting has been used for a wide variety of materials including metals, ceramics, alloys and composites. Gelcasting has also been successfully used in making highly porous ceramics by direct foaming techniques. The foamed gelcasting suspensions are cast to form net shape porous ceramic shapes [18].

# **Chapter 2**

## **Literature Review**



## 2. (a) Sol-gel glass-ceramics

Thousands of years ago, human discovery of clay, irreversibly transformed by fire into ceramic pottery, revolutionized human history. During the last 100 years, tremendous developments have taken place towards the designing and fabrication of specially fabricated ceramics for repair and construction of diseased, damaged or worn out parts of body. Ceramics used for this purpose are called Bioceramics [1].

### 2.1 Composition of glass and glass-ceramics

Some of standard composition of bioactive glass and glass-ceramics are in Table1 [1].

**Table1 Standard composition of bioactive glass and glass-ceramics**

	Na <sub>2</sub> O	K <sub>2</sub> O	MgO	CaO	B <sub>2</sub> O <sub>3</sub>	P <sub>2</sub> O <sub>5</sub>	Al <sub>2</sub> O <sub>3</sub>	SiO <sub>2</sub>	ZnO
Name									
45S5	24.5	0	0	24.5	0	6	0	45	-
S53P4	23	0	0	20	0	4	0	53	-
13-93	6	12	5	20	0	4	0	53	-
4-Mar	5	15	6	22.5	0	1	0	50.5	-
18-04	15	0	4.5	20	2	4	0	54.5	-
23-04	5	11.25	4.5	20	2	1	0	56.25	-
H2-02	6	11	7	22	1	2	0.5	53	-

(\* All the above compositions are in wt%)

## **2. (b) Gel casting**

In the 20th century, it was discovered that ceramics produced in a controlled way from artificial raw materials—alumina, silicon nitride, zirconia—possess useful properties besides their resistance to heat. Some of these engineering ceramics achieve melting temperatures as high as 4000°F. They exhibit extreme mechanical hardness, are resistant to corrosive chemicals, are light and intrinsically strong. Unfortunately, like traditional ceramics, the use of engineering ceramics has been limited by their brittleness; but, thanks to recent developments in altering ceramic compositions, engineering ceramics are now much less brittle [17].

Gelcasting was originally developed at ORNL to make complex-shaped automotive parts such as turbines. Industrial and government support for its commercialization is increasing because this new process for making high-quality, complex-shaped ceramic parts shows promise for manufacturing ceramics at a lower cost than conventional forming techniques. In addition, gelcasting appears attractive for an increasing number of applications ranging from accelerator magnets to artificial bone [17].

Gelcasting is promising for lowering down costs of manufacturing ceramic parts by allowing the industry to reduce the use of diamond tools to cut, shape, and finish ceramic products and use gelcast ceramics instead [17].

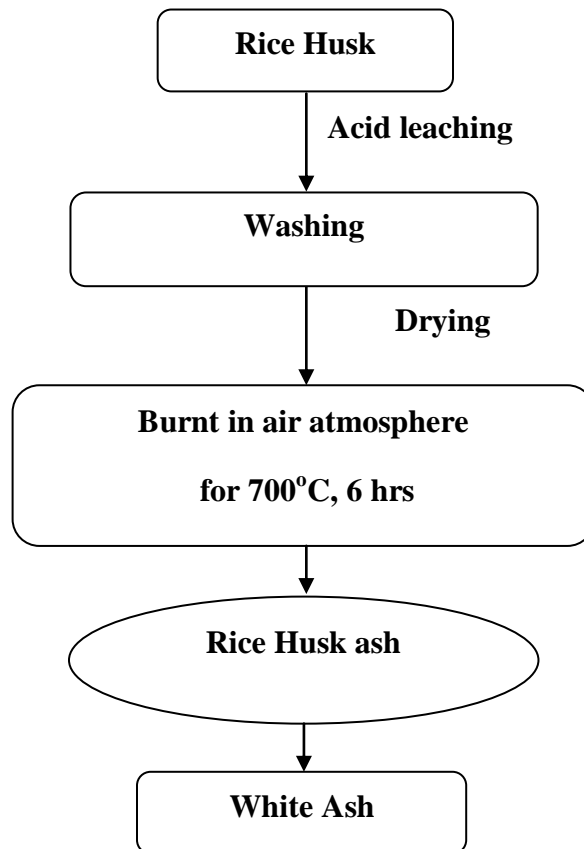
Gelcast ceramics can be formed in molds to get the precise shape desired because, unlike ceramics formed by other processes such as slip casting, gelcast ceramics shrink uniformly. Thus, the mold can be designed to compensate for shrinkage so that a ceramic part of the desired shape and size can be produced [17].

# **Chapter 3**

## **Experimental**

### 3.1 Synthesis of Amorphous silica from Rice Husk

Fig.1 shows the schematic process for extraction of silica from rice husk. The RH was separated from rice grain by air blowing and washed with tap water several times until all the impurities were completely removed. Then the water cleaned husk was treated with acid, i.e. acid leaching, for 1 h. Acid leached husk was cleaned repeatedly with hot distilled water to remove the acid portion which had adhered to the surface of the husk. Finally, the husk was dried overnight in oven at 110°C. The dried husk was burnt at 700°C for 6 h for complete combustion by which all volatile material is removed and ash was obtained. This ash contained more than 96% silica [1] and termed as white ash.



**Fig. 1. Flowchart for synthesis of amorphous silica from rice husk**

### 3.2 Synthesis of glass-ceramic powder

The composition of gel powder to be synthesized was taken as  $\text{SiO}_2$ - 50mol%,  $\text{Na}_2\text{O}$ -25mol%,  $\text{CaO}$ -25mol%. RHS was taken as source of silica whereas NaOH and  $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$  were the sources of  $\text{Na}_2\text{O}$  and CaO respectively. 100 ml of water was taken in a beaker and NaOH pellets weighing 3.326 gms was added to it. 5 gms of white ash powder( WAP) was added to the solution and the resulting solution was kept in boiling condition for 1 hr. 100 ml of  $\text{Na}_2\text{SiO}_3$  solution was then prepared. 9.84 gms of  $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$  was taken in 150 ml of  $\text{HNO}_3$  (conc) and a clear solution was prepared. The  $\text{Na}_2\text{SiO}_3$  solution was then added dropwise into the  $\text{Ca}(\text{NO}_3)_2$  solution. Turbidity appeared in the solution. After leaving the solution for 30 minutes the gelling process was complete. The gel was kept in a hot-water bath for drying.



**Fig. 2. Preparation of soda lime silica gel through sol-gel process; (a) addition of sodium silicate solution into calcium nitrate solution, (b) sol heated in hot water bath.**

After overnight drying, the gel was converted into powder. The powder was then grounded fine and placed in the furnace and fired at a temperature of 700°C for 4 hrs at a heating rate of 2°C per minute. Then slurry was prepared by pot milling technique. After a series of successive drying and grinding steps, the final BGC powder was obtained and it weighed 11.75 gms.

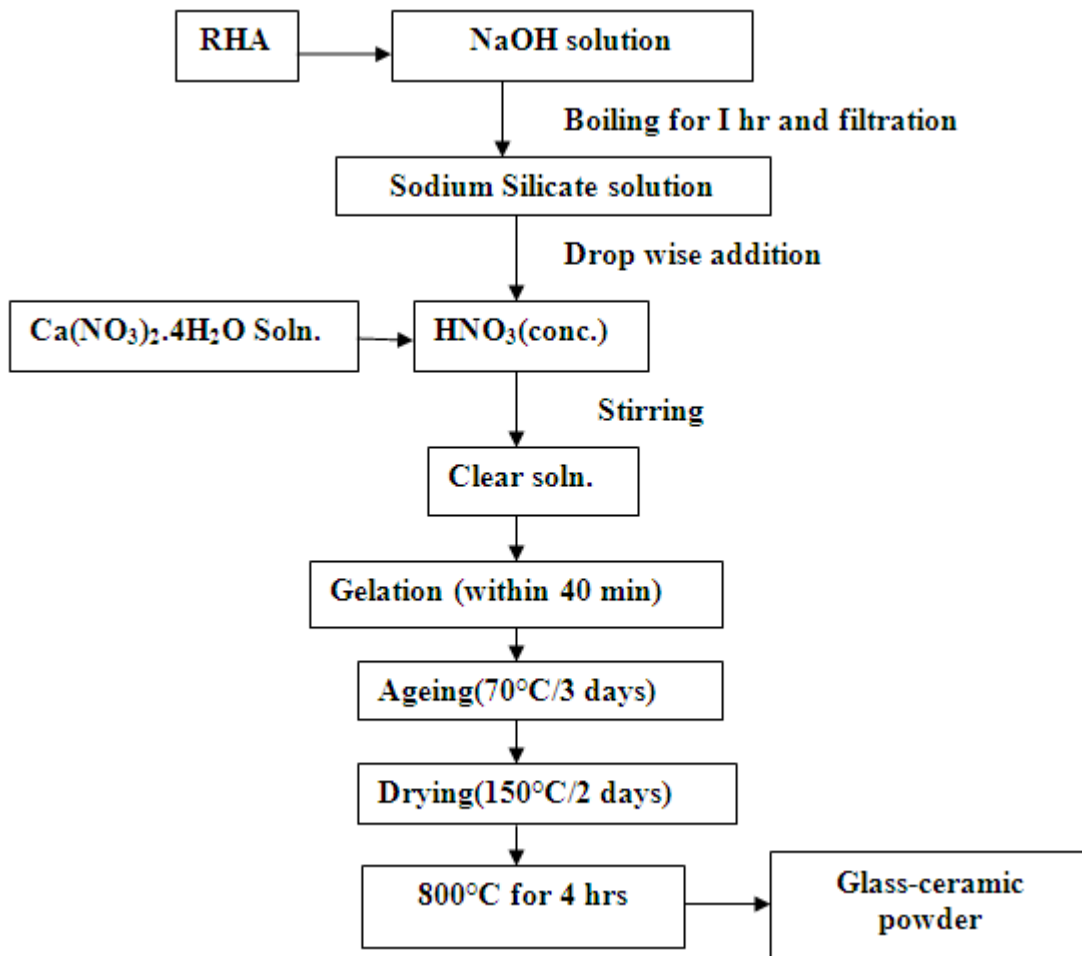
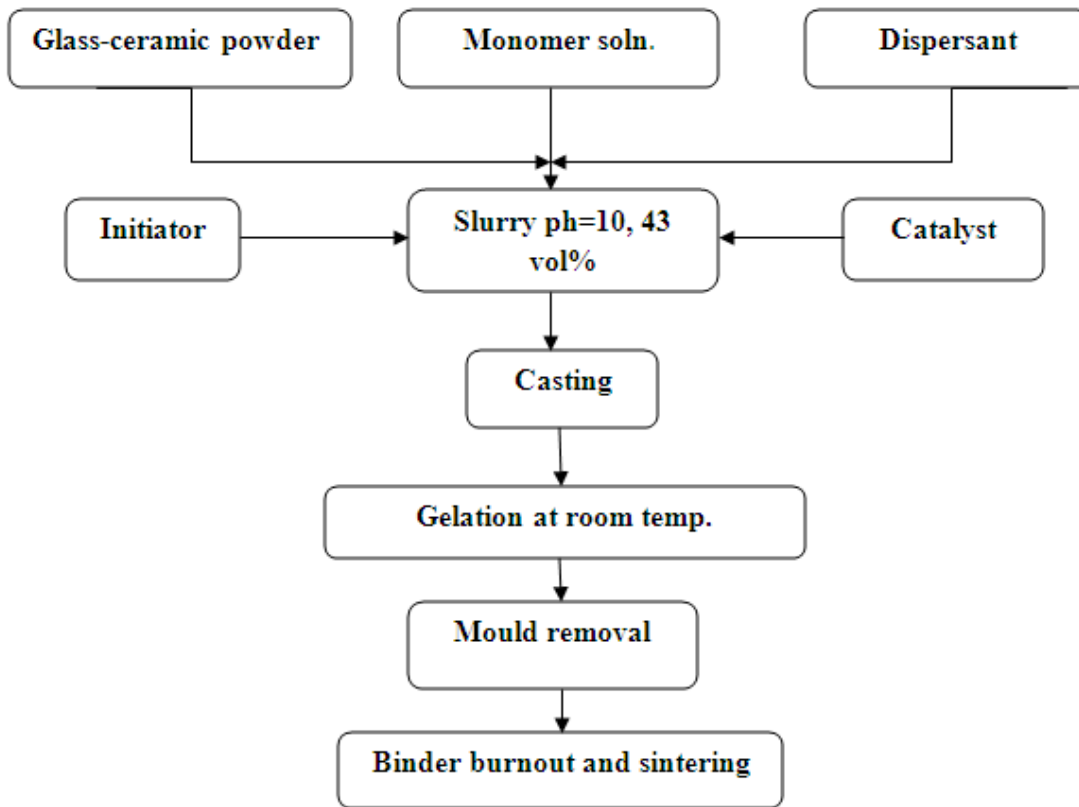


Fig. 3. Flow chart of detailed procedure for preparation of soda lime silicate glass powder.

### **3.3 Gelcasting of glass-ceramic powder**

First of all, 11.5 ml of distilled water was taken in a TARSON plastic bottle and kept on a stirring plate. 0.9375 gms of acrylamide (AM, Monomer) was added. After the AM was dissolved, 0.0625 gms of methylenebisacrylamide (MBAM, Crosslinker) was added. The solution was continuously stirred until to get complete clear solution of the monomer and the cross-linker. This solution was termed as premix solution. Lactic acid as dispersant with 0.01 wt% was added to the premix solution. Then calculated amount of glass ceramic powder (sol-gel 800°C calcined powder) was added into this above solution. pH of above solid-solution mixture was maintained at 10 by adding aqueous ammonium hydroxide solution. The mixture was pot-milled for 12 hours to get homogeneous slurry. Then slurry was deaired in vacuum condition. Ammonium per sulfate (APS), as initiator (0.01 wt.%, on the basis of ceramic powder) was added into the deaired slurry followed by addition of same weight percentage of catalyst, tetramethylethylenediamine (TEMED). The slurry was then mixed thoroughly again and poured into a non-porous PVC mold and left to complete the polymerization. All experiments were carried out at room temperature. The polymerized specimen was de-molded from PVC mold and was kept for drying in controlled atmosphere.



**Fig. 4.** Flow chart of detailed procedure for preparation of gel casted body

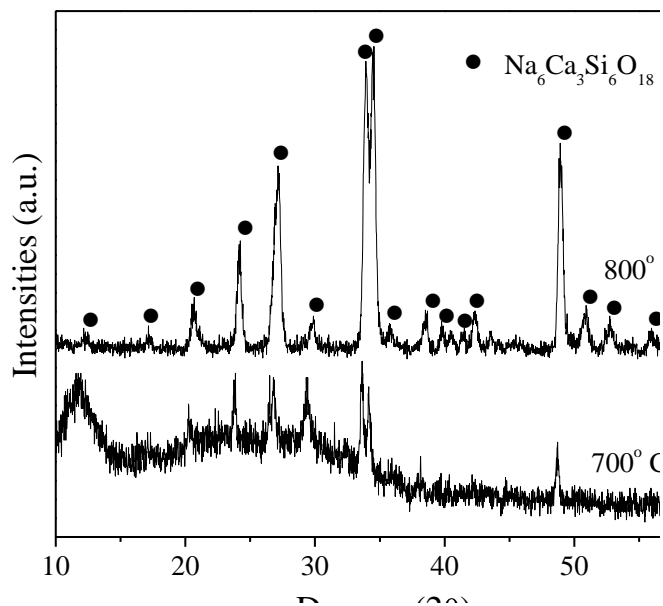


# **Chapter 4**

## **Results and Discussion**

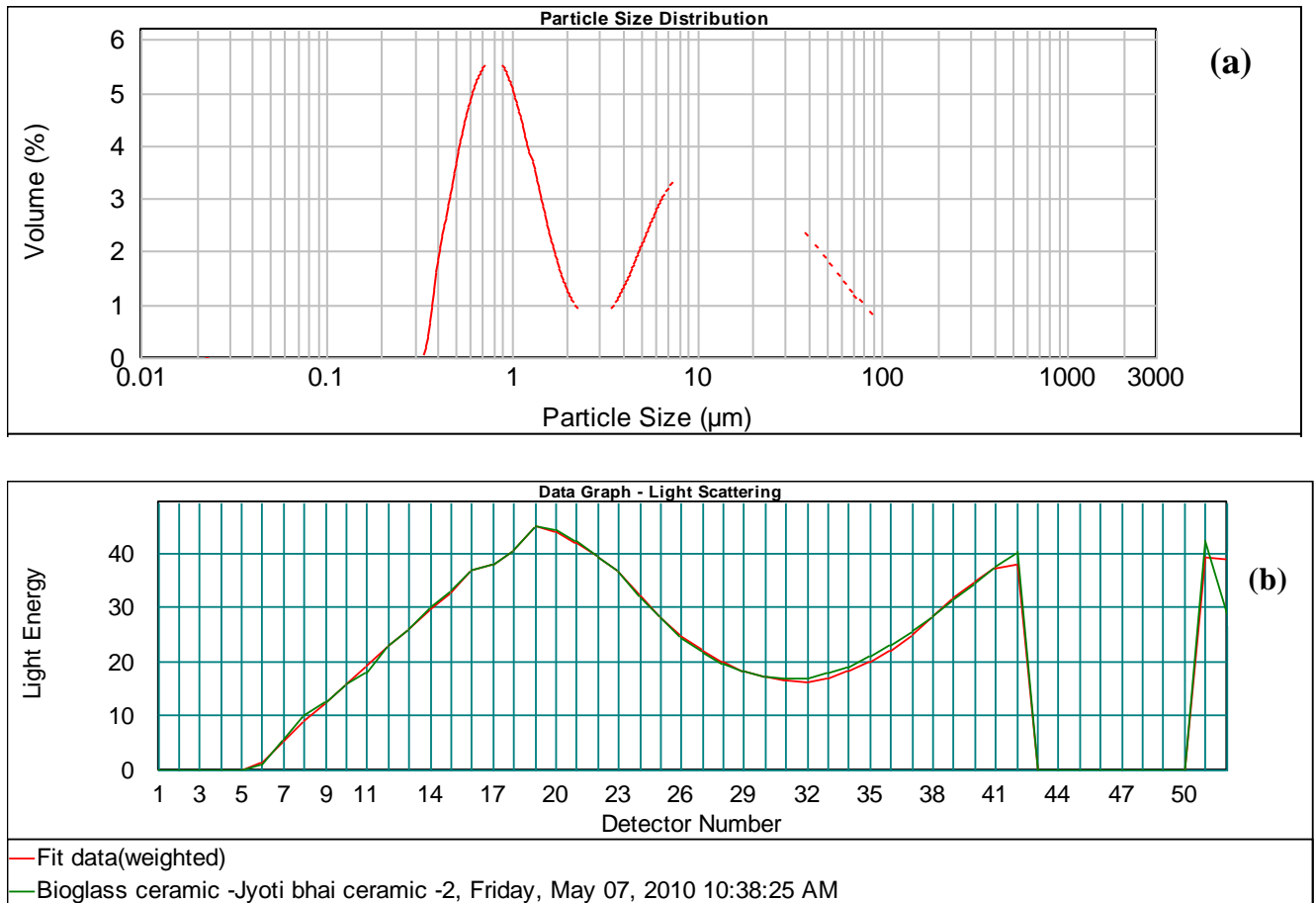
The white ash obtained from the acid leached husk was completely amorphous in nature as reported by several authors earlier [19]. This white ash contained ~ 99.5 wt% of silica.

White ash was used as silica precursor for preparation of bioglass-ceramics (BGC). By sol-gel technique, the glass powder was synthesized at room temperature. The dried gel powder was calcined at 700°C and 800°C for 4 hrs. Fig. 5 shows the XRD patterns of 700 and 800°C heat treated gel powders, which shows the presence of sodium calcium silicate phase ( $\text{Na}_6\text{Ca}_3\text{Si}_6\text{O}_{18}$ ) (JCPDS NO. 79-1089). The pattern shows an amorphous halo region in the range between 20-35° (2θ) including crystalline phases in 700°C calcined BGC powder. This halo region disappeared in 800°C calcined powder. Amorphous halo zone was speculated due to the presence of silica in the glassy matrix. Crystalline peaks were developed due to the decomposition of nitrates mainly along with calcium, sodium and silica. After heat treatment with higher temperature this halo region disappeared due to the growth phenomena of crystalline phases.



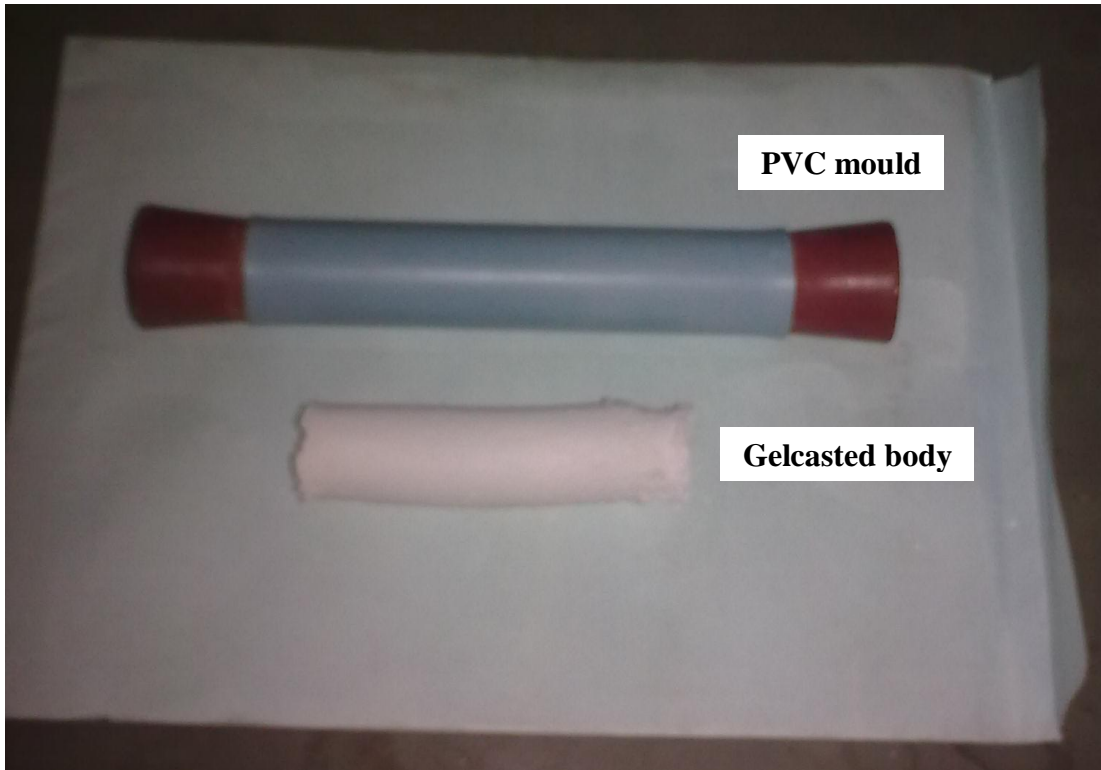
**Fig. 5. XRD patterns of BGC powder heated at 700 and 800°C.**

For gelcasting, particle size of ceramic powder is an important parameter to get near-neat shaped body. Hence, particle size of 800°C calcined powder was measured in Particle analyzer (Malverne Micro Analyzer). Fig. 6 shows the particle size distribution of BGC powder. Bimodal particle size distribution was obtained with average particle size ( $d_{50}$ ) of 5.5  $\mu\text{m}$ , as shown in Fig. 6 (a). Fig. 6 (b) is showing the fitting curve, which matched perfectly with distribution curve.



**Fig. 6. Particle size distribution of BGC powder.**

Fig. 7 shows the demolded gelcasted specimen, which was made with taking the BGC powder with 5.5  $\mu\text{m}$  particle size. Without any deformation or breakage, the specimen was demolded from the mould. Hence, it can be concluded that complete polymerization occurred in this BGC powder by taking the optimized monomer contents.



**Fig. 7. Gelcasted body prepared from BGC powder.**

# **Chapter 5**

## **Conclusions**

The rice husk ash was taken as a silica precursor for the preparation of glass-ceramics. Sol-gel route was opted for synthesizing glass ceramic powder. After calcination, the powder was used for preparation of body through gelcasting process. Hence, it can be concluded that rice husk ash can be used as a silica source for preparation of glass-ceramics and that glass-ceramics can be gelcasted to fabricate scaffold for bio-application.

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