

*Effect of additives on the decomposition, densification and phase  
analysis of zircon*

**A THESIS SUBMITTED IN PARTIAL FULLFILLMENT AS A REQUIREMENT FOR THE  
DEGREE OF BACHELOR OF TECHNOLOGY**

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**CERTIFICATE**

This is to certify that the thesis entitled, **“Effect of additives on the decomposition, densification and phase analysis of Zircon sand”** submitted by **Miss Anupama Baskey** in partial fulfillment of the requirements of the award of Bachelor of Technology Degree in Ceramic Engineering at the National Institute of Technology, Rourkela is an authentic work carried out by her 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**

The present work deals with the densification, decomposition and phase analysis of zircon flour in presence of different additives sintered at three different temperature of 1500<sup>0</sup> C, 1550<sup>0</sup>C and 1600<sup>0</sup> C for a soaking period of 2hours. The study has been done for five different batches, prepared with four different additives – alumina, iron oxide, magnesium oxide, and titanium oxide and fifth batch is without additive. Additives were used at 1 wt% level. Zircon sand and the additives were mixed, pressed and sintered.

The sintered samples were then characterized for the physical properties like, bulk density, apparent porosity, water absorption and shrinkage. Results reveal that the additives used are beneficial for sintering of zircon showing better properties then the reference sample without additives. Phase analysis showed decomposition of zircon and formation of zirconia at high temperature and the phase intensity of zirconia is found to be increased with increasing temperature.

# Chapter 1~~ INTRODUCTION

**Chemical Formula:  $ZrSiO_4$**

## 1.1 Background

**Zircon or zirconium silicate** ( $ZrSiO_4$ ) is an interesting ceramic and refractory material due to its excellent thermo-physical properties like low thermal expansion, low thermal conductivity, as well as a good corrosion resistant material. Zircon or zircon sand can be used as a source of many industrially used zirconium compounds of which zirconia is a major product.

Zirconium sulphate, oxychloride, oxynitride, tetrahalides and pure or doped zirconium oxide are some of the products that are produced from zircon [1]. It is a coproduct or byproduct of the mining and processing of heavy mineral sands for titanium minerals like ilmenite and rutile or tin minerals [1].

## 1.2 Structure

Zircon is chemically very stable compound, this is due to the high coordination of the bisdisphenoid  $ZrO_8$  in the tetragonal structure with  $SiO_4$  tetrahedra [9]. This structure of zircon make it very stable against mineral acids and no acid other than hydrofluoric acid can attack zircon and very aggressive reaction conditions are required to break the strong binding between zirconium and silicon parts in the compounds [1].

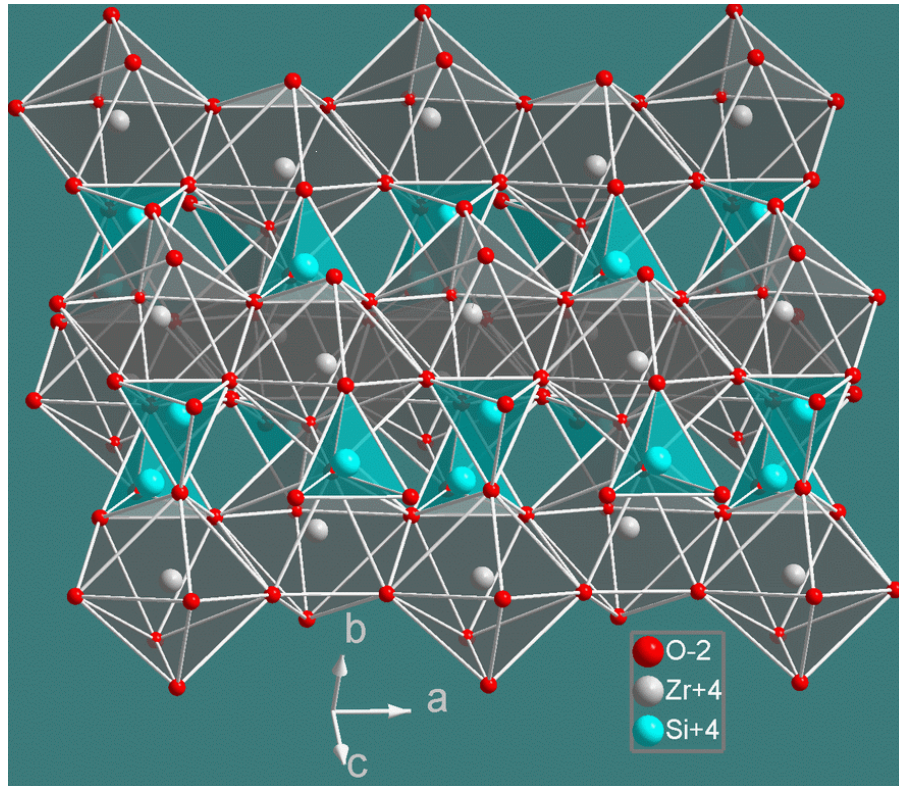


Fig. 1 Structure of zircon

### 1.3 OCCURENCE:

It is found world wide as an accessory mineral in igneous and metamorphic rocks. Occurrences include the Ural Mountains; Monte Somma, Trentino and Vesuvius Arendal; Ratanakiri, Camabodia; the Kimberley mines (south africa), India, Sri Lanka and Madagascar, Renfrew County, Grenville, Ontario, Quebec. In United States, it occurs in Litchfield, Maine; Chesterfield, Massachusetts; Essex, Orange, and Saint Lawrence counties, New York; Henderson County, North Carolina; the Pikes Peak district of Colorado; and Llano County, Texas [2].



## **1.4 Application**

- Mainly consumed as an opacifier in the decorative ceramics industry.
- Zircon is used as the principal precursor to for metallic zirconium and many other zirconium compounds.
- Zircon also found used in the refractory industries. Zircon or zirconia is used in the fabrication of tundish nozzles. These tundish nozzles are manufactured having zirconia percentage as high as 58% to 95%.

Zircon is an extremely refractory material which when heated decomposes to form zirconia which is also a highly refractory material.

## **1.5 Zirconia**

Zirconia is chemically inert to chemical and corrosion well above the melting point of alumina.

Properties :

- It has a very high melting point of 2750 °C and can be used upto 2400 °C.
- It has a high density of 5.68gm/cc
- Has a low thermal conductivity (nearly 20% of alumina)
- Chemically inert
- High fracture toughness and hardness
- Wear resistant

## CHAPTER 2~~ LITERATURE REVIEW

There are many research works available on the zircon system. Abdelkader and others worked on a novel decomposition method for zircon, they observed the fusion of zircon with the equimolar ratio of KOH-NaOH [3]. It was proved that using alkalis mixture reduces the energy requirements than the using of individual alkali by reducing temperature and the time required for heating the reactant. 20% excess of alkali mixture at 550°C with only 60min reaction time have been selected as the optimum reaction condition such conditions succeed to obtained 96% decomposition of zircon.

Maitra and others synthesized a precursor for zirconia–mullite composite by co-precipitation in aqueous medium taking inorganic salts of zirconium, silicon and aluminium in requisite amount and studied the role of two additives, namely magnesium oxide and chromium oxide, on the densification of compacted powder at different elevated temperatures like 1300–1500 °C [4]. It was observed that the batch with only magnesium oxide as an additive showed a progressive and steady increase in the specific gravity and bulk density while the batch containing both chromium oxide and magnesium oxide as sintering aid contained more glassy phase compared to only magnesium containing batch. Mechanical properties like flexural strength, compressive strength and fracture toughness of the batch containing both chromium oxide and magnesium oxide was found to be better than others. This may be probably because the Cr<sup>+3</sup>doped expanded the mullite crystals giving a better interlocking matrix with reinforcement from t- and m- ZrO<sub>2</sub>, and MgO containing liquid phase is also a reason for this. All the batches contained corundum, cristobalite, mullite, monoclinic, tetragonal and cubic zirconia and some amount of glassy phase[4].

Halder and others observed that the addition of yttrium oxide improves the thermo-mechanical properties and physical of the composites [5]. Composites of mullite -zirconia with 2–6 mol% yttrium oxides sand, alumina and zirconia. The Yttrium oxide used helps in the grain growth of the samples. It was observed that the higher porosity is may be due to the exaggerated grain growth as the temperature increases but there is a downtrend observed in the porosity in the composites with no yttrium oxide with rise in temperature.

Moya and co-workers demonstrated that the microstructure of alumina-zirconia and mullite-zirconia composites can be modified by the use of additives [6]. It was observed that the additives like magnesium oxide and calcium oxide that do not form a solid solution with the matrix encourages the rate of sintering by a transitory liquid formation while titania additive that has a considerable amount of solubility in the matrix affects the densification either by the formation of a transitory liquid phase or by creation of defects, depending on the amount of additives used. It was also shown that the addition of titania results in an improved effect on the mechanical properties of the composites because the zirconia grain growth is been controlled by this.

Ebadzadeh and Ghasemi prepared composites of mullite–zirconia by sintering reaction of  $\alpha$ -alumina and aluminium nitrate as the sources of alumina, and zircon powder [7]. The results indicated that  $\text{TiO}_2$  addition to mullite- $\text{ZrO}_2$  composites formed from different alumina sources leads to a change in the sintering reaction, densification and microstructure which can change the formation temperature and retention of t-  $\text{ZrO}_2$  phase in these composites. No tetragonal phase was detected in the mixture of  $\alpha$ -alumina and zircon when sintered below  $1500^\circ\text{C}$ , while by adding  $\text{TiO}_2$  showed t-  $\text{ZrO}_2$  peaks appeared at low sintering temperature (e.g $1400^\circ\text{C}$ ). It was observed that the composites derived from aluminium nitrate have a higher t-  $\text{ZrO}_2$  concentration

than when alumina was used (with and without  $\text{TiO}_2$ ). Introducing  $\text{TiO}_2$  in aluminium nitrate derived composites has decreased concentration of t-  $\text{ZrO}_2$ .

Bose and co-workers found that the presence of tetragonal phase is either due to the dopant effect or the grain size effect [8]. The formation of the tetragonal solid solution of  $\text{NiO-ZrO}_2$  is believed to be due to the smallness of the grains, hence, the enhanced surface reactivity and diffusion of the atoms at the surfaces. Usually, stabilization of the tetragonal/cubic phase of  $\text{ZrO}_2$  has been found to be dependent on many parameters such as valence, electro negativity, ionic size of the dopant etc. However, the extent of the tetragonal solid solution is dependent on the dopant concentration (here the  $\text{NiO}$ ). The maximum volume percentage of the tetragonal phase is observed for 20 vol%  $\text{NiO}$  at an annealing temperature of  $800^\circ\text{C}$ . The reasons for the reduced fraction of the tetragonal phase in 30 mol%  $\text{NiO-ZrO}_2$  may be the following: The increased concentration of the dopant  $\text{NiO}$  helps nucleation of crystallites and enhances grain growth. The higher the grain size, the lesser the surface area and hence, reduced reactivity of the surface atoms. Thus, the diffusion of  $\text{Ni-O}$  atoms from the nearby  $\text{NiO}$  clusters into the lattice of  $\text{ZrO}_2$  crystallites in touch with them will be reduced. The formability of the metastable tetragonal solid solution of  $\text{NiO-ZrO}_2$  has been observed by  $\text{NiO}$  doping and reduction in grain size.

Bradecki and Joans observed the solid state reactions between  $\text{ZrSiO}_4$  and a  $\text{Al}_2\text{O}_3$  with X-ray and electron scanning microscopy with disperse X-ray analysis [9]. The results indicate that  $\text{ZrSiO}_4$  and  $\text{Al}_2\text{O}_3$  react and form crystalline  $\text{ZrO}_2$ , crystalline mullite and non-crystalline silicon-alumina phase. At  $1660^\circ\text{C}$  the fastest stage of reaction is dissociation of  $\text{ZrSiO}_4$ . Results show that dissociation of zircon is a first order reaction. The dissolution of  $\text{Al}_2\text{O}_3$  particles and diffusion of  $\text{Al}$  into non-crystalline phase seem to be the slowest step of the reaction.

Haldar prepared zirconia–mullite composites with 4-8mol% magnesium oxide from Indian coastal sillimanite beach sand, zirconia and alumina in the temperature range of 1500–1600°C [10]. The XRD study showed all that the raw materials were crystalline in nature. Varying amount of magnesia the bulk density of the sintered samples decreased with increase in temperature. The sintered samples have linear shrinkage which increases with higher content of magnesia. The sintered materials showed a comparatively higher value of fracture toughness than the pure mullite.

Kaiser and others, **studied the thermal stability of zircon ( $ZrSiO_4$ )** based on annealing experiments with natural and synthetic raw materials of known grain size, impurity level as well as single crystals by noting the temperature of thermal dissociation of  $ZrSiO_4$ [1]. Zircon decomposes by a solid state reaction releasing silica in the form of discrete metastable intermediate phases with super stoichiometric silica content. Even small amounts of impurities can influence on the decomposition temperature and kinetics which is explained by the formation of low melting liquid phases resulting in the favoured dissociation of solid silica immediately after release from zircon structure.

This study reveals that “100%” purity zircon based commercial products start to decompose at 1600°C and no soaking time forming zirconia and an amorphous  $SiO_2$  phase. The decomposition rate accelerates significantly at temperature above 1650°C. The zircon formed is most often tetragonal phase in agreement with the thermodynamic stability range. Large particles, i.e. > 2-5micron may transform spontaneously to monoclinic during cooling and thus cause some confusion when detected by X-ray diffraction at room temperature.

Both purity as well as the grain size strongly influences the temperature and rate of zircon decomposition. According to the XRD study, the reaction for 98%  $ZrSiO_4$ , <3 micron starts between 1450°C and for 100%  $ZrSiO_4$ , <1 and <4 micron it starts at 1660°C. The results revealed at higher temperature the decomposition is faster and slow at temperatures below 1650°C. The zircon decomposition is controlled by the liquid phase formed due to natural or processing inherent impurities. Thus more or less all experimental data suffer from the problem that the peritectoidal dissociation of zircon is super imposed by the kinetic of liquid phase-driven dissolution of the solid silica generated as dissociation product. As the amount of liquid phase increases with temperature and the decomposition rate accelerates with the increase in temperature and time. The significant influence of even a very small amounts of impurities also influences the grain size sensitivity of the decomposition temperature: as a larger surface area are created, lattice defects are generated and diffusions distances are lowered- facts enabling fast nucleation, an easy release of silica, and providing an excellent contact with liquid impurities. This is particularly important for natural zircon because these crystals usually contain very small inclusions of rutile, magnetite, garnet, spinels, xenotime, apatite and others releasing a local melting.

For the case of pure single crystals it is worth while noting that the release of  $SiO_2$  in the solid state occurs along certain crystallographic planes by local accumulation of  $SiO_2$  with  $ZrO_2$  neighborhood. The formation of intermediate metastable zirconium silica  $ZrSi_2O_6$  is most likely. This again needs further experimental proof.

## CHAPTER 3 ~~ EXPERIMENTAL WORK

### 2.1 Raw materials used:

- Zircon flour
- Alumina
- Iron oxide
- Magnesium oxide
- Titanium dioxide

### 2.2 Powder Preparation

- A 30 gram batch of five different compositions is prepared with zircon sand as the main constituent and 1wt% of the additives. The additives used are alumina, iron oxide, magnesium oxide and titanium oxide. The batches were named as Z, M , A, T and F containing zero, 1wt% magnesia, 1 wt% alumina, 1 wt% titanium oxide and 1 wt% iron oxide respectively.

Composition:

Z: 100wt% Zircon flour

M: 99wt% zircon flour + 1wt% MgO

A: 99wt% zircon flour + 1wt% Al<sub>2</sub>O<sub>3</sub>

T: 99wt% zircon flour + 1wt% TiO<sub>2</sub>

F: 99wt% zircon flour + 1wt% Fe<sub>2</sub>O<sub>3</sub>

- Zircon flour and the additives are weighed accurately and then mixed in an alcohol medium for uniform mixing as well as easy drying.

- It is then naturally dried in air and again mixed with 6% PVA solution (3% concentration) which acts as a binder during pellet formation.

### **2.3 COMPACTION**

- These powders are then weighed and are pressed uniaxially to form pellets.
- Dry pressing was done to form pellets of 12 mm dia using a Hydraulic Press (**Carver press USA**) at a pressure 2 ton with a dwelling time of 60 sec. Stearic acid is used as lubricant.

### **2.4 SINTERING**

After the pellets are formed it is then sintered at three different temperatures ie 1500, 1550 and 1600°C in a workshop furnace

- Rate of heating is 5°C/min upto a temperature of 650°C for all the three temperatures and 1hour soaking.
- Next, heating it at a rate of 3°C/min till it reaches the required temperature followed by 2 hours soaking.
- Then cooling it to the normal temperature.

The samples are taken out when they are at room temperature and then characterized.



## 2.5 CHARACTERISATION

### **Bulk Density and Apparent Porosity of pellets:**

The bulk density and apparent porosity of the sintered pellets were determined by Archimedes principle using the mass in air and the mass when immersed in water. For Dry Weight the sample is weighed in air. Then the sample is kept in a beaker filled with water and vacuumed for about 1 hour so that all the pores present in it are filled with distilled water and when no more air bubbles evolve the vacuum pump is turned off. Then measurements for suspended weight is done using apparatus in which pellet is suspended in water. After taking suspended weight, soaked weight is taken by wiping off the excess water present on its surface using a wet cloth. Once the dry weight, soaked weight and suspended weight were measured, bulk density and apparent porosity were calculated by the formulas:

**Bulk Density-** it is defined as the mass of a material including the volume of the pores.

$$\text{B.D} = \text{dry weight} / (\text{soaked weight} - \text{suspended weight})$$

**Apparent porosity-** apparent porosity is the ratio of open pores to the total volume of the material.

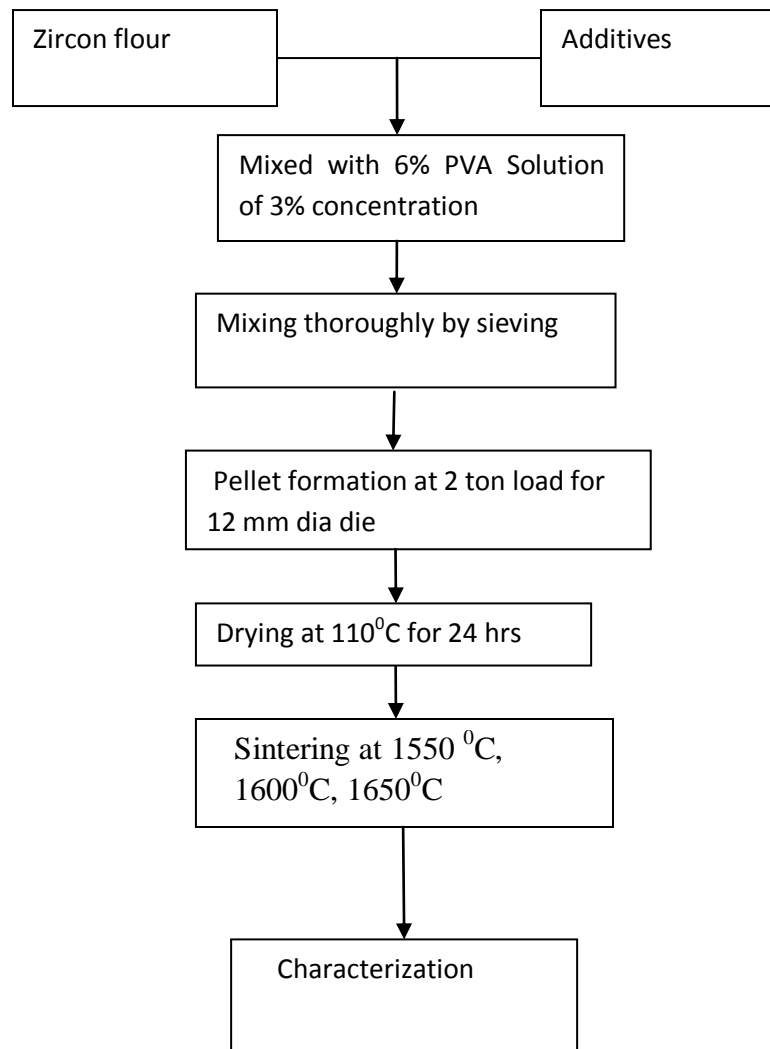
$$\text{A.P} = (\text{soaked weight} - \text{dry weight}) / (\text{soaked weight} - \text{suspended weight}) \times 100$$

### **Water Absorption:**

$$\text{W.A} = (\text{soaked weight} - \text{dry weight}) / \text{dry weight} \times 100$$

## PHASE ANALYSIS

The sintered pellets were subjected to phase analysis by X-ray diffractometer (PW1830 D, Phillips, and Netherland) using a Cu k alpha radiation and Ni filter. The angle range was 20°-60°.



**Flow chart of the whole procedure**

## CHAPTER 4 ~RESULTS AND DISCUSSION

### Raw material characterization

Raw Zircon flour :

Chemical composition :

**%ZrO<sub>2</sub>=64.45**

**Fe<sub>2</sub>O<sub>3</sub> content: 0.16%**

**SiO<sub>2</sub> : 34.35%**

**Fineness: -325# -100%**

**Colour: white**

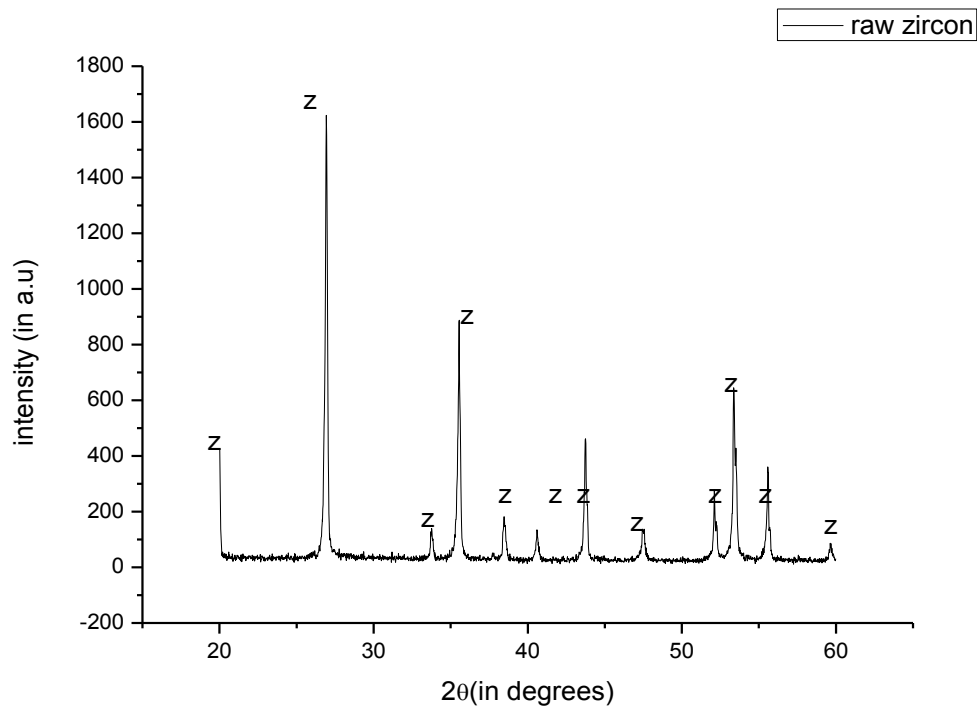


Fig .1 Raw unfired zircon sample.

b)

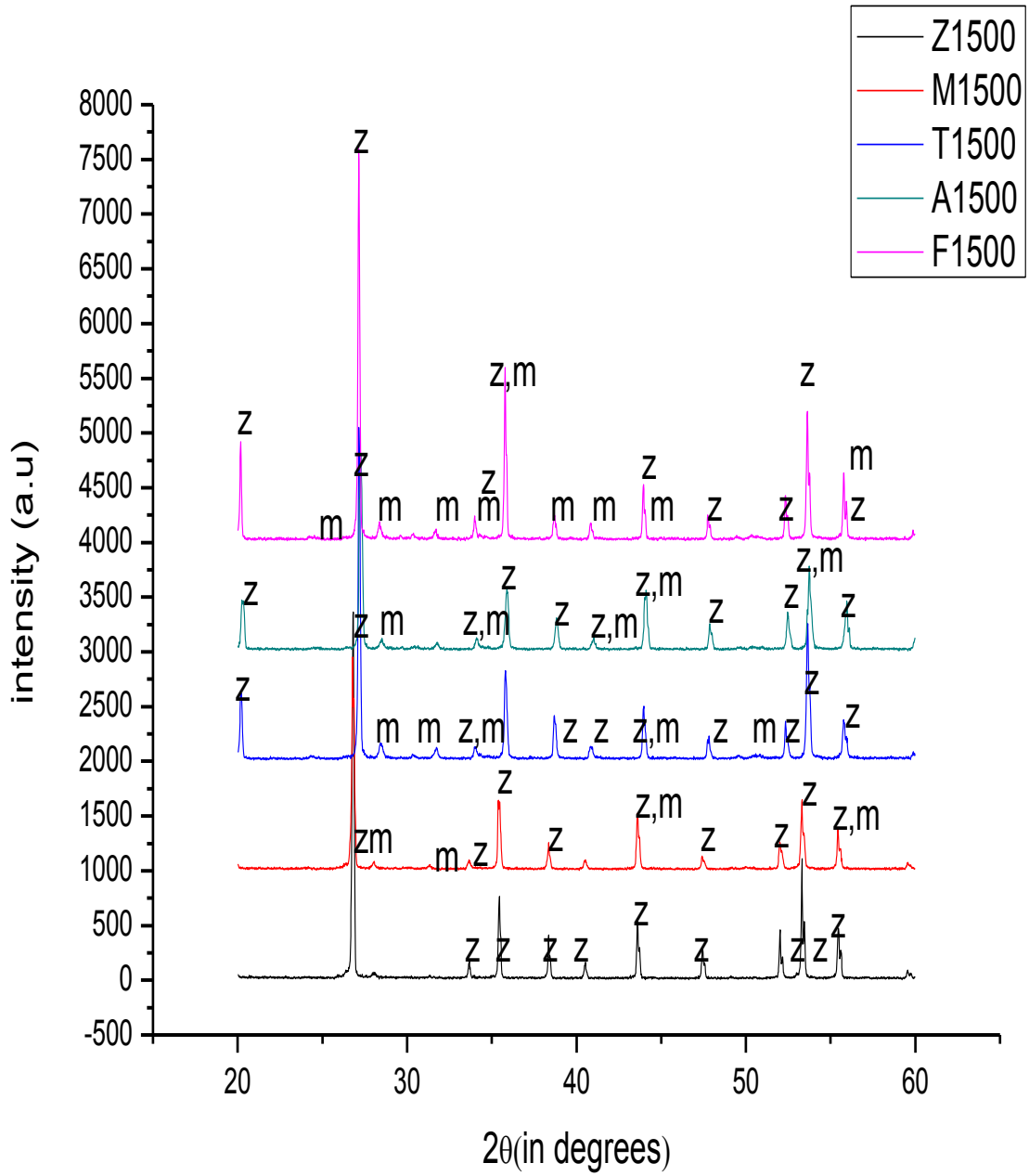


Fig.2 Comparison of XRD plot of different samples at 1500°C.

c)

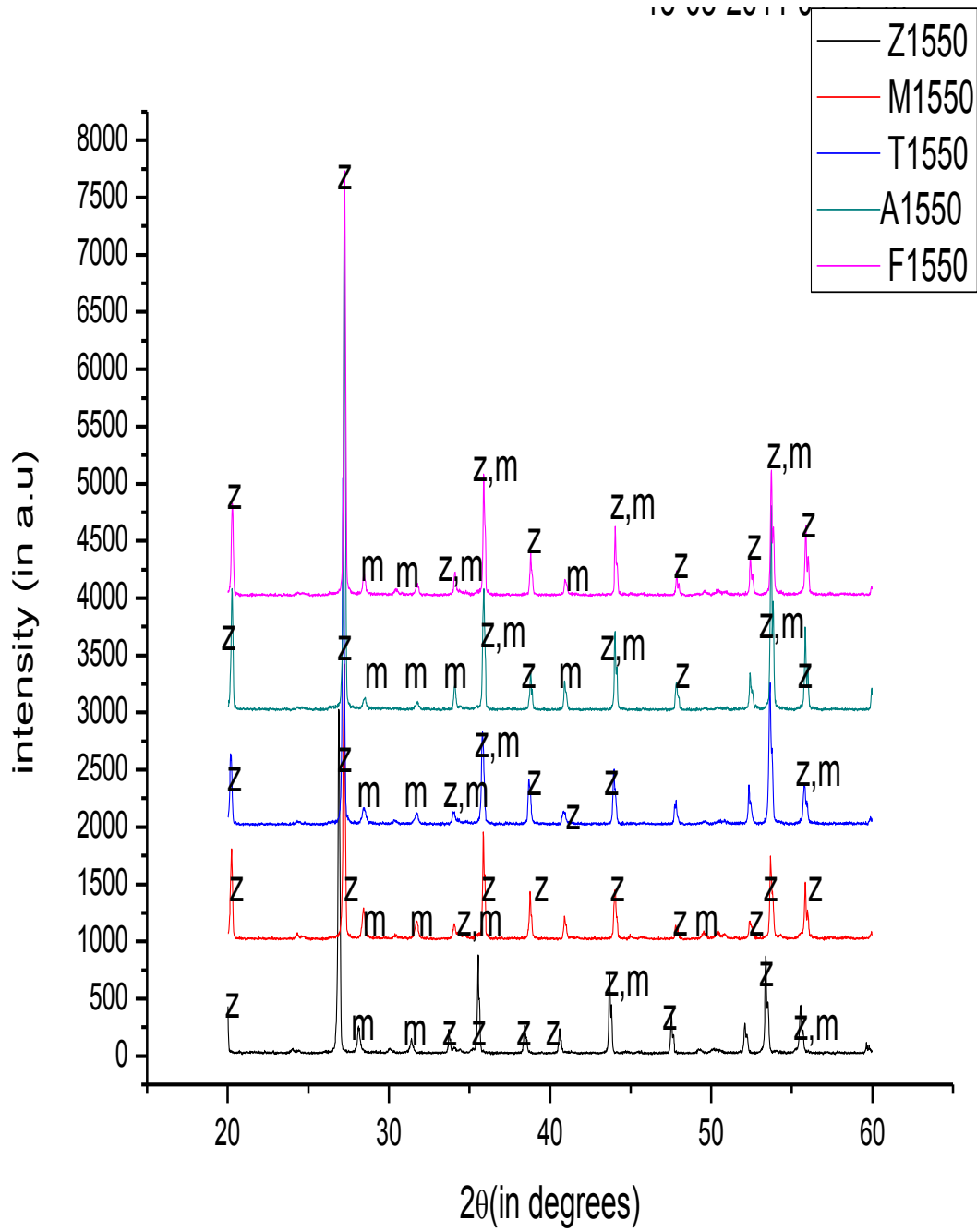


Fig.3 Comparison of XRD plot of different samples at 1550°C.

d)

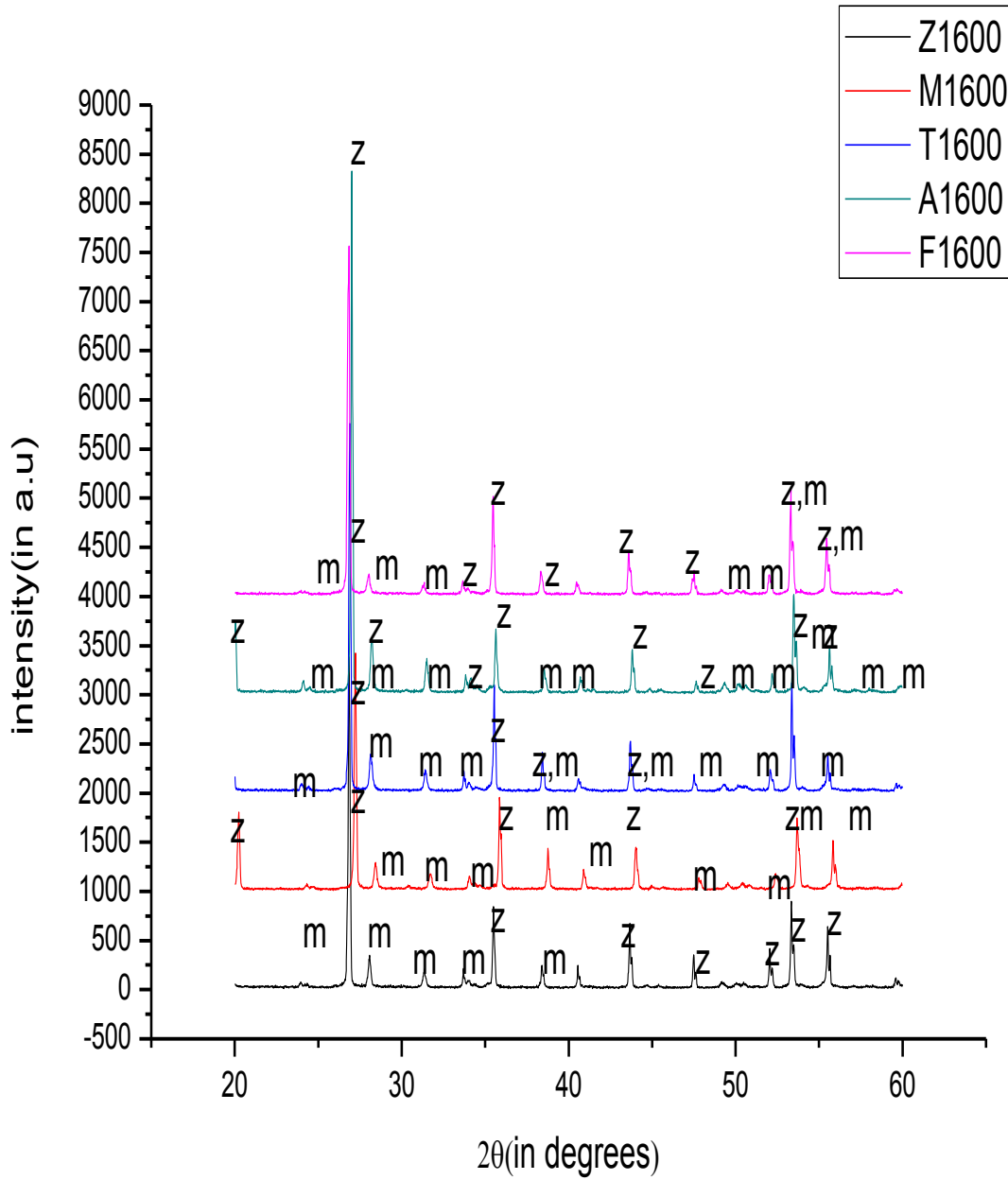


Fig.4 Comparison of XRD plot of different samples at 1600°C

X ray diffraction plots of all the samples showed that even at a temperature of 1500°C zircon dissociates and form free zirconia phase. But the presence of free zirconia peak was not strong , but in presence of iron oxide and titania, free zirconia phase shows stronger peaks. But at higher temperatures there is little difference was observed in the free zirconia phase intensity with different types of additives. More or less without additive and all the different additives showed similar phase distribution and their intensities. However titania, iron oxide and magnesia showed little stronger peak intensity of zirconia phase after sintering than that of the without additives one. Thus the additives show little effect on the decomposition behaviour of zircon sand. But there is an increase in zirconia phase intensity with the increase in sintering temperature, which indicates that the dissociation of zircon increases further with increasing temperatures. But hardly any difference in also observed for the zirconia peak intensity with different additives. Only zircon and zirconia phases were observed in the phase analysis of the sintered products and no free silica phase was found, may be due to the presence of free silica as glassy phase. This phase analysis study indicates that hardly there is any effect of different additives at 1 wt% level on the dissociation and phase content of the sintered zircon.

**TABULATION FOR BULK DENSITY, APPARENT DENSITY AND WATER  
ABSORPTION**

Sample name	B.D (in gm/cm <sup>3</sup> )1600	B.D (in gm/cm <sup>3</sup> )1550	B.D (in gm/m <sup>3</sup> )1500	A.P (%) 1600	A.P (%) 1550	A.P (%) 1500	W.A( %) 1600	W.A( %) 1550	W.A( %) 1500
Z	3.487	3.39	3.39	21.43	25.53	25.85	6.133	7.5	7.4
M	3.614	3.47	3.44	17.16	23.05	23.2	4.733	6.62	6.8
F	3.727	3.59	3.535	14.78	21.18	20.3	3.867	5.83	5.8
T	3.605	3.49	3.497	16.8	22.06	22.5	4.600	6.3	6.4
A	3.601	3.46	3.408	15.93	24.30	24.4	5.93	7.02	7.1



a) BULK DENSITY

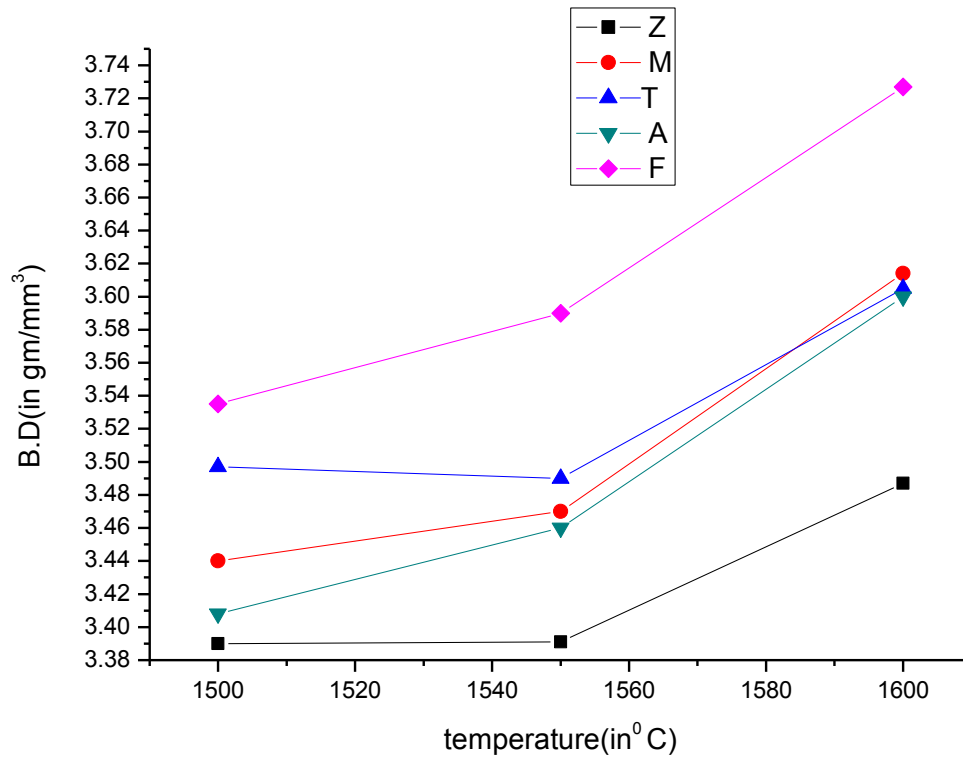


Fig.6 Comparison of bulk density of different samples sintered at different temperature.

Density plot for all the samples showed an increase in density values with increasing temperature due to higher extent of sintering at higher temperatures. Again all the additives were found to have beneficial effect for densification and iron oxide showed the maximum beneficial effect.

(a) Apparent porosity

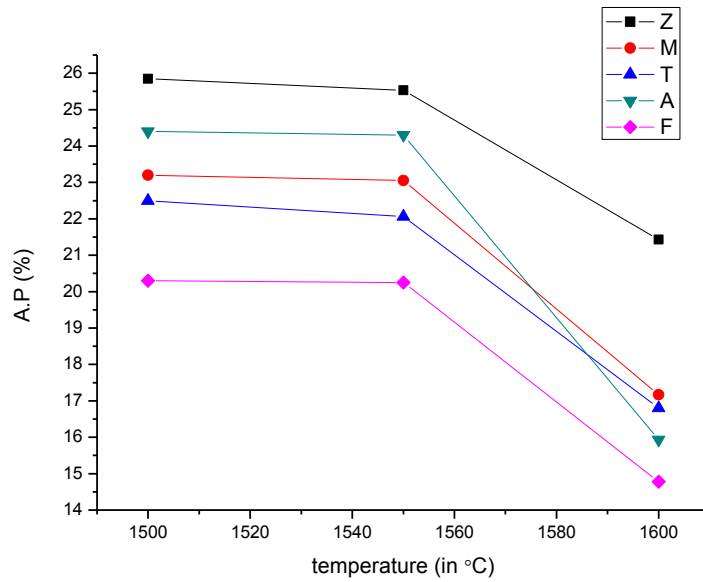


Fig. 7 Comparison of apparent porosity of samples fired at different temperatures.zzz

Apparent porosity plot basically supports the density plot. Increase in temperature reduces the porosity value and the maximum porosity was found for the batch containing zero additives. Iron oxide contains batch showed minimum porosity values for all the temperatures.

(b) Water absorption

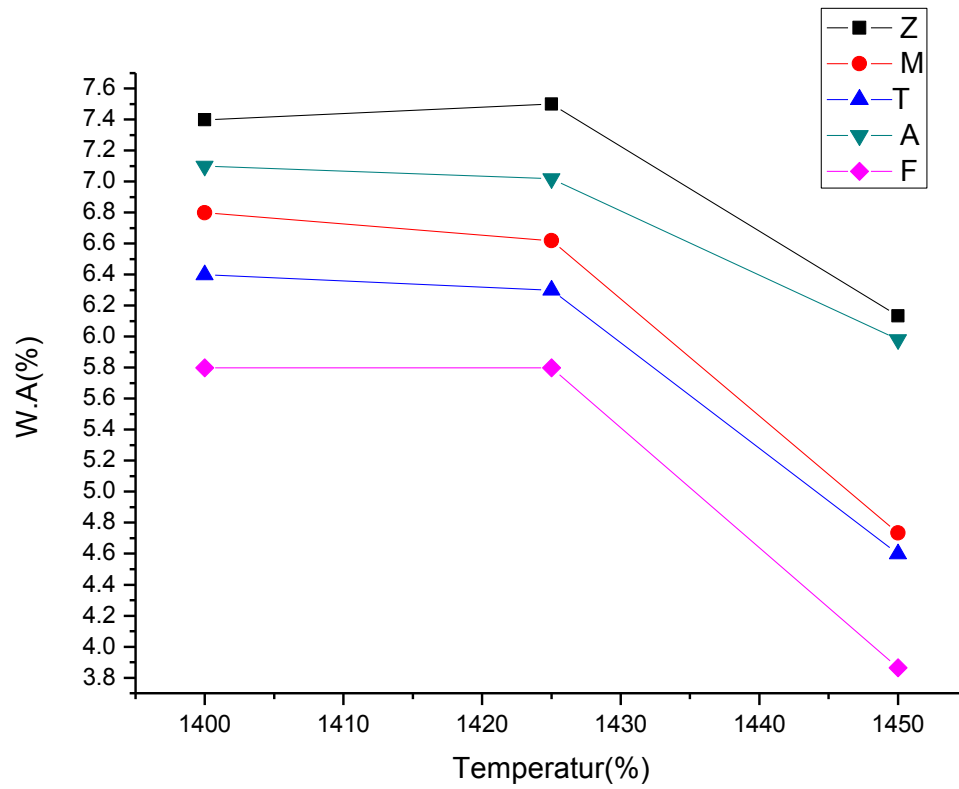


Fig.8 Comparison of water absorption of samples sintered at different temperature.

Water absorption study also shows similar nature as that of the apparent porosity one.

## **Chapter 5 ~ CONCLUSION**

Fired pellet show only zircon and zirconia phases and no free silica phase. Increase in firing temperature was found to increase the dissociation of zircon and zirconia phase intensity of the sintered pellet. The additives showed little beneficial effect on the decomposition behaviour of zircon sand and showed marginally stronger peaks of zirconia phase, especially for the cases of magnesia, titania and iron oxide.

Increase in temperature was also found to increase the sintered density and decrease in the apparent porosity and water absorption values for all the sintered products. Additives were found to have strong effect on these properties but in general additives were found to have beneficial effect on the densification behaviour of the sintered pellets. Iron oxide was found to have the maximum beneficial effect on the sintered properties.

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