Study of Zirconia-Mullite system: Effect of SrO addition with alumina content variation

A THESIS SUBMITTED IN THE PARTIAL FULFILLMENT

OF THE REQUIREMENTS FOR THE DEGREE OF

BACHELOR OF TECHNOLOGY

By

Kavita Bisoyi

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Under the Guidance of

Prof. Ritwik Sarkar

NATIONAL INSTITUTE OF TECHNOLOGY ROURKELA

CERTIFICATE

This is to certify that the thesis entitled, **"Study of Zirconia-Mullite system: Effect of SrO addition with alumina content variation"** is the bonafide work of Miss **Kavita Bisoyi (Roll no. 108CR035)** in partial fulfilments for the requirements for the award of *Bachelor of Technology* degree in *Ceramic Engineering* at National Institute of Technology, Rourkela is an authentic work carried out by her under my supervision and guidance. Certified further, that to the best of my knowledge the work reported does not form part of any other thesis or dissertation on the basis of which a degree or award was conferred on an earlier occasion on this or any other candidate.

Date: 11 May, 2012

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ABSTRACT

Mullite-zirconia systems have encouraged developing a refractory composite with thermo-mechanical properties, which can be widely used in glass and steel industries. Numerous methods have been employed and researches have been carried out in developing such a composite whose properties can be enhanced with the effect of additives.

In this project work, Strontium oxide has been used an additive and also the alumina content has been varied to study the densification behavior of the zirconia-mullite system. 2, 4, and 6% SrO were added to the stoichiometric and non-stoichiometric batches (with deficient and excess alumina). Then the samples were fired at 1500-1600 $^{\circ}$C and various characterizations were conducted. The bulk density, dimensional density, apparen porosity, and volume shrinkage tests were performed to interpret the nature of the composite with addition of SrO. Also X-ray diffraction analysis was carried out to determine the phases and analyze the phase compositions in various samples.

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1. <u>INTRODUCTION</u>

Extensively composites have been used to enhance the design properties as well as the behavior of materials. Thus they have enormous industrial and technological applications. Considering Zirconia-mullite composites based ceramics, they have been mostly consumed by glass and steel and glass industries. In the glass industries, where high chemical and corrosion stabilities are essential zirconia-mullite has been found to meet up the requirement. Also in steel industries, they find their use in slide gate valves which are the integral part of the continuous casting processes for steel and also for nozzles and stoppers of transfer and holding ladles, where the combined effect of thermal shock and erosion would lead to the rapid failure of other materials.

1.1 Mullite ($3Al_2O_3.2SiO_2$) :

Mullite is an alumino-silicate widely used in traditional refractory applications and one of the most studied crystalline phases in $Al_2O_3.SiO_2$ system. It has been found at the contact of superheated magma intrusions with Al_2O_3-rich sediments, as on the Island of Mull (Scotland), where the name mullite comes from. Due to its high temperature but low pressure formation conditions, mullite occurs very rarely in nature. Still it is one of the most widely encountered and important compounds found in many industrial ceramic products. It has captured a lot of attention in the field of refractories because of its high melting point, excellent high temperature strength along with creep resistance properties. The conventional processing of dense mullite compacts is an energy-intensive procedure which requires high processing temperature due to the slow diffusion kinetics of Si_4^+ and Al_3^+ ions, which makes the starting mullite powder difficult to sinter. Various researchers have worked on only lower the mullatization temperature as the densification has to take place by solid-state reaction at

high temperatures. Moreover, the presence of impurities and mineralizers in those solution-based synthesis techniques can be a major concern related to high-temperature mechanical properties of mullite. So practically it is strenuous to consolidate mullite into fully dense single-phase bodies. To optimize its mechanical properties, some investigations have been attempted using different processing techniques such as hot-pressing, hot-isostatic pressing and sol-gel processing.

1.2 Zirconia Ceramics:

The properties of zirconia (ZrO_2) ceramics suggest that the combination of strength, toughness and chemical resistance should allow application of the materials in harsh environments under severe loading conditions. In conjunction with the development of surface compressively stressed layer many novel applications in wear resistant and cutting devices are envisioned. It is also well known for good hardness, low coefficient of friction, elastic modulus, ionic conductivity, low thermal conductivity, high oxygen ion conductivity and high melting temperature. These properties make it attractive as an engineering material.

1.2.1 Occurrence:

The two main source of Zirconia are baddeleyite (impure monoclinic Zirconia) and Zircon, ($ZrSiO_4$) which occurs as secondary deposits in Kerala, Florida and South Africa. It is frequently mixed in sand with other minerals like rutile and monazite. Baddeleyite is found in smaller deposits and usually contain contaminants such as silica and iron oxide.

1.2.2 Pure zirconia polymorphs:

- Monoclinic (m-ZrO_2, 5.6 g/cm^3); thermodynamically stable from room temperature to approximately 950°C.

- Tetragonal (t-ZrO_2, 6.1 g/cm^3); transforms from monoclinic upon heating at approximately 1150°C (transition start temperature) or back to monoclinic upon cooling at approx. 950°C (transition finish temperature) . This is a martensitic transformation with large hysteresis and relative volume change approx. 5 %.

- Cubic (c-ZrO_2, 6.1 g/cm^3); transformation t ↔ c occurs at approximately 2300°C (hysteresis maximally 30°C); c-ZrO_2 melts at approx. 2700°C.

All engineering ceramic applications of zirconia require full or partial stabilization of the structure. Primarily the tetragonal to monoclinic phase transformation and the associated volume change preclude the use of unstabilised zirconia in bulk form. So use of zirconia in a fairly divided dispersed form to enhance the thermal shock resistance of other ceramic materials is recommended. The superior of zirconia ceramics are thought to be due to microcracks generated in the vicinity of zirconia particles, which help to arrest any cracks propagating as a result of thermal stresses. The discovery and utilization of the transformation-toughening effects of zirconia particles in brittle matrix have resulted in improved mechanical properties of ceramics. Transformation toughening occurs as the result of a dilation and shear strain which occurs in zirconia particles during tetragonal-to-monoclinic phase transformation.

1.3 Zirconia-mullite composite:

Zirconia-mullite composite has been developed in order to achieve high thermo-mechanical properties where simply use of mullite ceramics was inadequate. Applications of mullite were limited because of its poor properties at ambient temperature. As a result, it is usually reinforced with particles or fibres (whiskers) of zirconia to produce composites with superior properties. Different mechanisms are involved in the toughening of mullite composite

with zirconia additions are stress-induced transformation, microcracking, crack bowing and crack deflection. Thus a refractory, although not of great strength, would have a superior crack stopping ability and would find applications where integrity of the structure is all important. Although, mullite and zirconia are the major constituents in the composite, the physical characteristics, microstructure and properties of the resulting ceramic may be different.

1.4 Methods of preparation of Mullite-Zirconia composite:

Mullite–ZrO_2 composites have been prepared though multifarious routes including sintering of mixed mullite and ZrO_2 powders, reaction sintering of mixtures of ZrO_2 and mullite precursors, plasma spray using plasma arc of mullite-zirconia mixture, reaction sintering of zircon ($ZrSiO_4$) and Al_2O_3, and crystallization of rapidly quenched melts in the system Al_2O_3–ZrO_2–SiO_2 with subsequent sintering. However, the reaction sintering method remained the most commonly used because of its low cost. However, it requires relatively high temperatures 1400–1650∘C for several hours. Particularly in refractories, mullite and zirconia are both phases resulting from the use of zircon in high alumina content compositions.

1.4.1 Reaction sintering of alumina and Zircon sand:

Zircon sand is used in refractories, ceramics and chemical industries. Technology is available to extract zirconia from this sand. Stabilized zirconia has emerged as a structural and refractories material. Chemically, it is $ZrSiO_4$ with small amounts of impurities like Al_2O_3, TiO_2 and CaO. Zircon sand is available in the market in two forms.

The zircon sand, and the zircon flour. Latter is a fine powder obtained by vibrogrinding zircon sand in Al_2O_3-1ined jet mill. Heating the zircon sand to 1700 °C dissociation occurs into zirconia and silica. It is represented by a reaction:

$$ZrSiO_4 \rightarrow ZrO_2 + SiO_2$$
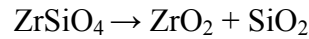
On addition of alumina, the liberated SiO_2 reacts with Al_2O_3 to form mullite ($3Al_2O_3.2SiO_2$), releasing ZrO_2. Zircon ($ZrSiO_4$) with alumina acts as a bonding phase and its thermal decomposition adds zirconia and silica by reaction sintering of zircon and alumina in the temperature range 1400-1600°C. The reaction is represented as:

$$2ZrSiO_4 + 3Al_2O_3 \rightarrow 3Al_2O_3.2SiO_2 + 2ZrO_2$$
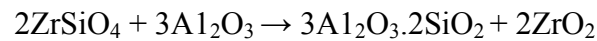
Thus, the mullite-zirconia composites can be developed. A literature shows various properties of a reaction sintered zirconia mullite composite, which has been shown in the table 1.

Properties	value
Green density (g/cc)	2.6
Fired density (g/cc)	3.7
Apparent porosity (%)	<0.5
Water absorption (%)	<0.5
E_o experimental (GPa)	189
E_o calculated (GPa)	219

Table 1. Various physical properties of zirconia-mullite composite prepared from reaction sintering route

A typical zirconia-mullite composite consists of 42 - 55% Al_2O_3, 16 − 20% SiO_2, and 25-36% ZrO_2 (+HfO_2). Major mineral phases are mullite and zirconia.

1.4.2 Stabilization of zirconia:

As we know tetragonal to monoclinic transformation is critical in zirconia. So it is highly essential to stabilize the zirconia may be fully or partially. But obtaining fully stabilized zirconia has not been proved economical. Its structure is a cubic solid solution which doesn't form any liquid phase till 2710°C. So the high temperature requirement for FSZ has restricted its application. Thus we need to work upon partially stabilized zirconia. A smaller addition of stabilizers like CaO, MgO, Y_2O_3, CeO_2, and TiO_2 into zirconia will bring its structure into a tetragonal phase at a temperature higher than 1100 °C, and a mixture of cubic phase and monoclinic or tetragonal phase at a lower temperature.

In this project work Strontium oxide has been selected as a stabilizing agent. Also there is an attempt to observe the changes in the properties varying the strontium percentage as well as stoichiometry of the composite (related to alumina percentage).

2. <u>LITERATURE REVIEW</u>

Hamidouche, N. et al. (J. Am. Ceram. Soc. (1996) page.441-445) have shown that the addition zirconia to mullite system improves its mechanical properties such as fracture toughness at high temperatures. The mechanical properties of mullite-zirconia composite have been determined from room temperature up to 1400 °C. It has been observed that the thermo-mechanical behavior is sensitive to the phase transformation of zirconia.

Rendtorff et al. (Ceramics International 34(2008)2017-2024) have prepared the composite using two different processing routes such as reaction sintering (RS) of alumina and zircon and direct sintering of mullite - zirconia grains. The two processing routes conducted to similar phase composition but differences in microstructure were analyzed. These differences include shape and size of intergranular zirconia, t-ZrO_2 content, and the mullite crystal morphology. The best performance of the reaction sintered composite has been explained by these factors. Also the thermal shock resistance test showed improved results when zircon was used as bonding phase.

Bodhak et al. (J. Am. Ceram. Soc., 94 [1] 32–41 (2011) prepared zirconia-mullite composite via microwave heating and explained some typical behavior of the same at high temperatures. They explained the pinning effect of ZrO_2, which controlled the mullite grain growth and enhanced the microstructural homogenization, and better packing of mullite grains of the mullite–zirconia composites. It is believed that the good microwave energy absorbance ability of ZrO_2 particles leads to volumetric heating and helps in rapid neck growth between mullite particles by enhancing grain boundary and bulk diffusion kinetics. So, they explained that this

improvement in sintering kinetics results in significant enhancement of mechanical strength with a minimal increase in density for 10% zirconia reinforced mullite composite at 1500° C.

Castro (Ceramics International 35 (2009) 921–924) has developed zirconia-mullite composites from aluminium dross and zircon. A detailed microstructural study of the same was performed by XRD, SEM and EDS analysis. With increase in temperature and time porosity coalescence and rearrangement of zirconia particles in the mullite matrix was observed. Samples sintered at 1500 ^{o}C for 6 h showed a continuous mullite matrix with dispersed zirconia particles. At the same time residual alumina and zircon indicated incomplete reaction.

Rendtorff et al. (Ceramics International 35 (2009) 779–786) studied the properties and thermal shock resistance of mullite-zirconia-zircon composites. The composites studied were sintered at 1600°C. On cooling the monoclinic phase transformation took place in those grains having a size higher than the critical one, as was seen by XRD. During the TS test, when thermal cycles of $\Delta T = 1000$ and 1200°C were applied, the monoclinic to tetragonal phase transition occurred during quenching. For $\Delta T = 1200$ °C, the transformation was completed, while it partially proceed for $\Delta T = 1000$ °C and no phase transition occurred for lower ΔT. The flexural strength showed a gradual increase with the amount of zircon in the original composition, which was found to be little lower than original mullite composition. The difference was explained by the concept of residual porosity and the formation of microcracks due zirconia transformation during cooling

2.1 Role of magnesia additives:

Haldar (Ceramics International 29 (2003) 573–581) has presented a detailed study on the addition of 4-8% MgO on zirconia-mullite composite. The bulk density of the samples was

found to decrease with increase in temperature with varying amounts of magnesia. He says with higher percentage of magnesia mullite formation is enhanced and there is a transient liquid phase formation. This large volume of liquid phase has helped in particle rearrangement and effecting packing leading to high shrinkage or density. The relative tetragonal zirconia percentage was found to maximum with 6% MgO content. Also the fracture toughness of the sintered samples was higher than the pure mullite. A decreasing trend of modulus of elasticity was noticed with increasing sintering temperature (1500-1600 °C).

2.2 Role of MgO and Cr_2O_3 additive:

Maitra et al. (Ceramics International 28 (2002) 819–826) has argued that MgO, as a stabilizer of zirconia caused precipitation of tetragonal zirconia from ZrO_2–MgO solid solution, and also some periclase, which probably promoted the formation of mullite providing nucleation sites in the microstructure. The combined effect of the additives affected the sintering process that is evidenced from the enhanced volume shrinkage. Composites with MgO and Cr_2O_3 showed a progressive increase in specific gravity value with the increase in the sintering temperature. Though Cr_2O_3 can form Cr-substituted expanded mullite lattice, its role on the formation of the crystalline phases further from the amorphous phases is limited. So the significant change in specific gravity was not observed only with Cr_2O_3 addition. The presence of magnesia based phases hinders the grain boundary movement at high temperature which probably resulted in better interlocking of Cr^{+3} containing expanded mullite crystals and reinforcement of mullite matrix by zirconia grains. Flexural strength and fracture toughnes were found to be increased for MgO and MgO- Cr_2O_3 addtives. But in case of MgO addition the result of flexural strength was more prominent due to low glassy phase formation and the fracture toughness was also

comparatively higher e due to a larger amount of transformable t-ZrO_2 and by a micro-crack nucleation at transformed m-ZrO_2 particles.

2.3 Role of titania addition:

Ebadzadeh et al. (Ceramics International 28 (2002) 447–450) worked upon the Mullite–Zirconia composite materials, prepared by reaction sintering of a-alumina and aluminium nitrate as alumina sources, and zircon powder. Then an effect of TiO_2 addition was studied. Results showed the enhanced reaction between alumina and zirconia as well as the improved dissociation of zircon with formation of zirconia and mullite upon introduction of titania. Addition of 3.5 weight% of titania was found responsible for the sharp change of t-ZrO_2 concentration at low sintering temperature (1400 °C). It was noticed that the concentration of t-ZrO_2 decreases with temperature. It was concluded that the addition of titania leads to change of reaction sintering, densification and microstructure which can alternatively affect the formation temperature and the retention of t-ZrO_2 phase in the composite.

2.4 Role of yittria addition:

Das et al. (Journal of the European Ceramic Society 18 (1998) 1771-1777) prepared mullite-zirconia composites containing 0-7 mol% yittria by the reaction sintering process from Indian coastal zircon flour and calcined alumina. Addition of yittria ensured a dense composite material at comparatively low sintering temperature. At 1600 °C, the presence of higher amount of yittria led to agglomeration of zirconia particles resulting in a heterogeneous microstructure. Though the composite containing 7% yittria was witnessed to possess highest percentage of t- ZrO_2 it was associated with low density with porous structure. It was explained that the increment of mullite in the composite is responsible for the down fall of density. The addition of yittria

reduced the martensitic transformation temperature (M_s). Also it facilitated the forward reaction by forming solid solution with zirconia and mullite. Addition of titania is more effective because it does not form any detrimental low melting phase. The thermal expansion co-efficient was found minimum for the highest amount of yittria added composite. Withal the thermo-mechanical properties were improved.

2.5 Role of disprosia addition:

Das et al. (Journal of the European Ceramic Society 20 (2000) 153-157) has studied the mechanical properties of effect of zirconia-mullite composite with 0-4.5 mol% dysprosium oxide, which was prepared from reaction sintering of Indian zircon flour and calcined alumina. Significant densification was achieved after addition of dysprosia. The thermal expansion co-efficient were found to be reduced in presence of additive. It was observed that dysprosia formed solid solution with mullite. It was assumed that the dysprosium ion occupied the AlO_6 octahedral chains by replacing the Al^{3+} ion. Lattice spacing was increased due to this replacement which causes low thermal expansion co-efficient. It was envisaged that the dysprosia helps in densification by liquid phase formation as well as by stabilization in tetragonal zirconia state. The martensitic transformation temperature reduction was observed to a lower extent because the maximum disprosia is utilized in the formation of glassy phase. The presence of dysprosia increased the room temperature flexural strength, hardness and fracture toughness. The sample with 2.5 mol% dysprosia showed the best mechanical property.

2.6 Role of lanthanum oxide addition:

Sarkar and othes (*Central Glass and Ceramic Research Institute, Kolkata, India)* studied the effect of lanthanum oxide on reaction sintering of zirconia-mullite composites. The densification

study showed addition of of La_2O_3 strongly decreases apparent porosityand total porosity, but increases closed porosity. Again densification increases the presence of additive but the extent of increase decreases with >6 mol% addition. HMOR tests showed high strength for 3% La_2O_3. However further addition decreased the property because of greater degree of liquid formation at high concentration of lanthanum oxide. It is evident that the higher amount of lanthanum oxide helps in better retention of the tetragonal phase.

2.7 Role of SrO additive:

Kmlko lu (Journal of the European Ceramic Society 14 (1994) 45-51) observed the effect of SrO additive on the densification and mechanical properties of the composite. He reported the enhanced densification with 1.25mol% SrO addition. The additive free samples were observed to have an increment of 6% in the density with increase in the dwell time(1-4h) at temperature 1500 °C, where as the 1.25% SrO added samples were found with 14% enhanced density with 1 hour soaking time at 1500 °C. The study related to the mechanical properties showed maximum strength and toughness values for 0.50 wt % SrO addition. It was explained that the reason SrO was not effective at smaller contents might be due to the titanium oxide impurity of the zircon raw material that reacted with strontium oxide prior to silica at the initial stage of sintering. Probably $SrTiO_3$ exerted a poisoning effect at the grain boundaries, causing a decrease in the fracture strength. After all the TiO_2 was used up, the remaining SrO became effective in improving the mechanical strength. With larger amounts of SrO, $SrTiO_3$ could be swept to the surface by the glass phase. The removal of glass phase from the grain boundaries increased the bending strength and fracture toughness values considerably.

3. <u>EXPERIMENTAL PROCEDURE</u>

3.1 WORK PLAN:

- Study of the effect of SrO additive as well as Al_2O_3 percentage in the zircon flour in the zirconia-mullite composite.

- Addition of 2%, 4% and 6 % of SrO to the stoichiometric and non-stoichiometric (excess alumina and deficient alumina) batches.

- Sintering of the prepared pellets at varying temperatures such as 1500°C, 1550°C, and 1600°C.

- Densification study of the prepared pellets such as bulk density, apparent porosity, volume shrinkage, phase analysis using X-ray diffraction study

3.2 RAW MATERIALS:

In this project work zircon flour (Indian Rare Earth Limited, Chatrapur) and calcined alumina were taken as raw materials and as a source of SrO, $SrCO_3$ was taken. The raw materials were characterized for the detection of oxides and impurity contents using chemical analysis, specific surface area using the BET technique (nitrogen gas at liquid-nitrogen temperature) and phase study was performed by X-ray diffraction analysis.

3.3 BATCH CALCULATION:

Batches with stoichiometric and non-stoichiometric amount of zirconia, alumina has to be prepared. So, one batch for stoichiometric composition and two other batches for non-stoichiometric composition (one with deficient alumina, another with excessive alumina) are

required. Now to each mother batches varying amount of strontium oxide has to be added. The strontium variation has been chosen to be 2%, 4%, 6% by weight of the total batch. As there are again three sintering temperatures (1500°, 1550°, 1600°C), so total number of variation of composition is 36 (3×4×3). For each composition preparation of three pellets has been planned.

For the complete mullatization and zirconia dissociation from the reaction sintering of zircon and alumina the reaction is shown below.

$$2ZrSiO_4 + 3Al_2O_3 \rightarrow 3Al_2O_3.2SiO_2 + 2ZrO_2$$
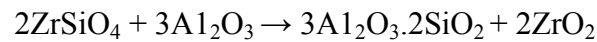
The table 2 shows the chemical analysis of zircon flour. From there the required amount of zircon and alumina can be calculated.

Chemical properties	Weight in 100 g
ZrO_2 (+HfO_2)	64.45
SiO_2	34.35
Fe_2O_3	0.16
TiO_2	0.44
Al_2O_3	0.63

Table 2. The chemical analysis of zircon fines showing various oxides.

For mullite formation:

✓ SiO_2 requires 3 Al_2O_3. That means, 120.172 g of SiO_2 requires 305.892 g of alumina.

✓ 100g Zircon flour has 34.35 g silica and 0.63g alumina.

✓ So 34.35g silica requires 87.436g alumina.

✓ The extra requirement of alumina is (87.436-0.63) = 86.806 g

✓ Stoichimetric batch contains 86.806g alumina if there is 100 g of zircon flour.

✓ Similarly deficient alumina batch must contain 76.806 (10g deficient) alumina

✓ Excessive alumina batch should contain 96.806 g alumina.

To prepare mother batches of total 120 g each the required zirconia and alumina weights are shown below in table 3.

Type of mother batch	Wt of Zircon flour (g)	Wt of alumina (g)
Stochiometric batch (O)	64.24	55.76
Non stoichiometric batch (A-)	67.87	52.13
Non stoichiometric batch (A+)	60.97	59.03

Table 3. The varying weight of zircon and alumina in the mother batches O, A- and A+

Now for 2, 4, and 6 wt% of SrO addition require amount of $SrCO_3$ has been calculated and shown in table 4.

Type of batch	Wt of mother batch(g)	Wt of $SrCO_3$ (g)
Pure batch	30	-
2 wt% addition of SrO	30	0.855
4 wt% addition of SrO	30	1.71
6 wt% addition of SrO	30	2.564

Table 4. The varying weight of $SrCO_3$ in 30 g of the mother batch with 0, 2, 4, and 6 wt% of SrO addition

For the identification of the samples naming the samples is very important. So the samples have been named according to the mother batches and percentage of SrO addition in them. The sample nomenclature has been given in the table 5.

Mother batch	SrO added batch	Temperature (°C)
O (stoichiometric)	**O** (0 % addition)	1500
	O2S (2% addition)	1550
	O4S (4% addition)	1600
	O6S (6% addition)	
A- (deficient alumina)	**A-** (0 % addition)	1500
	A-2S (2 % addition)	1550
	A-4S (4 % addition)	1600
	A-6S (6 % addition)	
A+ (excess alumina)	**A+** (0 % addition)	1500
	A+2S (2 % addition)	1550
	A+4S (4 % addition)	1600
	A+6S (6 % addition)	

Table 5. Nomenclature of samples prepared

3.4 PELLET PREPARTION:

The weighed batches were attrition-milled in a pot mill with alumina grinding media in an iso-propyl alcohol medium for 20 minutes. Milled wet batches were then dried at 100°-120°C for 24 h. The pellets were then pressed each of around 0.85g with an addition of 5 wt% of PVA (4 % polyvinyl alcohol solution-binder). The pressure applied was 1.5 ton in a CARVER PRESS and the dwell time was set to be 30 sec. Now with proper care the green pellets were kept for drying for 24 h at around 100-120 °C.

3.5 FIRING OF SAMPLES:

Firings of the pellets were done at the required temperatures 1500°, 1550°, and 1600°C in a furnace. Here program was set for 1 h soaking time at 650°C for binder removal and then 3 h soaking time at the specified sintering temperature. After taking out the samples from the furnace carefully, they were named and kept separately to differentiate.

3.6 CHARACTERIZATION:

3.6.1 Bulk Density:

A useful property for refractories is bulk density, which defines the material present in a given volume.

The bulk densities 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:

B.D. = Weight in air / (soaked weight – suspended weight) x Liquid density

Dimensional density calculation:

Density of each pellet formed was measured using the formula: D = M/V

Where, D= density, M= mass

$$V = \pi d^2 h/4 \text{ (Volume)}$$

The diameter (d) and height/thickness (h) were calculated using digital *VERNIER CALLIPER*

and mass (M) was measured by weighing machine.

3.6.2 Apparent Porosity:

The apparent porosity is a measure of the volume of the volume of the open pores into which a

liquid can penetrate, as a percentage of the total volume. This is an important property in cases

where the refractory is in contact with molten charge and slag. A low apparent porosity is

desirable since it would prevent easy penetration. A large number of small pores have an

important influence on the refractory behavior. However, a measure of the true porosity, which

also takes into account the volume of closed pores, gives a reasonable idea of the texture of the

material as well as sintering characteristics. In fact, porosity, bulk density and apparent solid

density have been termed as "Vital Statistics" of refractory shapes.

It measured from the soaked weight, suspended weight determined as explained earlier. It can be

expressed as:

A.P. (%) = [(Soaked weight – Weight in air) / (soaked weight – suspended weight)]×100

3.6.3 Volume shrinkage:

It measured by calculating the difference between the green body volume and volume after firing

of the pellets. The diameter and thickness of the pellets were measured by a Vernier caliper.

$$V = \pi d^2 h/4 \text{ (Volume)}$$

Shrinkage (%) = [(V$_{\text{before firing}}$ −V$_{\text{after firing}}$)/V$_{\text{before firing}}$] ×100

3.6.4 X-ray diffraction:

It is a versatile, non-destructive technique that reveals detailed information about the chemical composition and crystallographic structure of natural and manufactured materials. XRD is a powerful tool used to detect the presence of phases in the material.The main principle behind XRD is Bragg's law which states

$$n\lambda = 2d\sin\theta$$

where, d = spacing between diffracting planes,

θ = incident angle,

n = any integer

λ = wavelength of the beam

As study of the various phases and their analysis is the main objective of this project work XRD analysis was performed. This was done by Philips' X-ray diffractometer with Nickel filtered Cu Kα radiation (1.5406A°). The diffraction was done at angle 15°-60° with scanning speed 2°/min. Then from the XRD plot various peaks corresponding to the various phases were analyzed and also the composition of important phases like mullite, tetragonal zirconia, monoclinic zirconia etc was studied.

4. <u>RESULTS AND DISCUSSION</u>

4.1 Raw material Characterization:

Zircon: The chemical analysis of zircon flour has already been shown in table 2. The particle size was analyzed from the sieve testing method to be 96% finer than 45 μm. loose bulk density was measured by tap density calculation method and the value has been found to be 1.84 g/cc. The XRD plot of the zircon powder has been shown in figure 1.
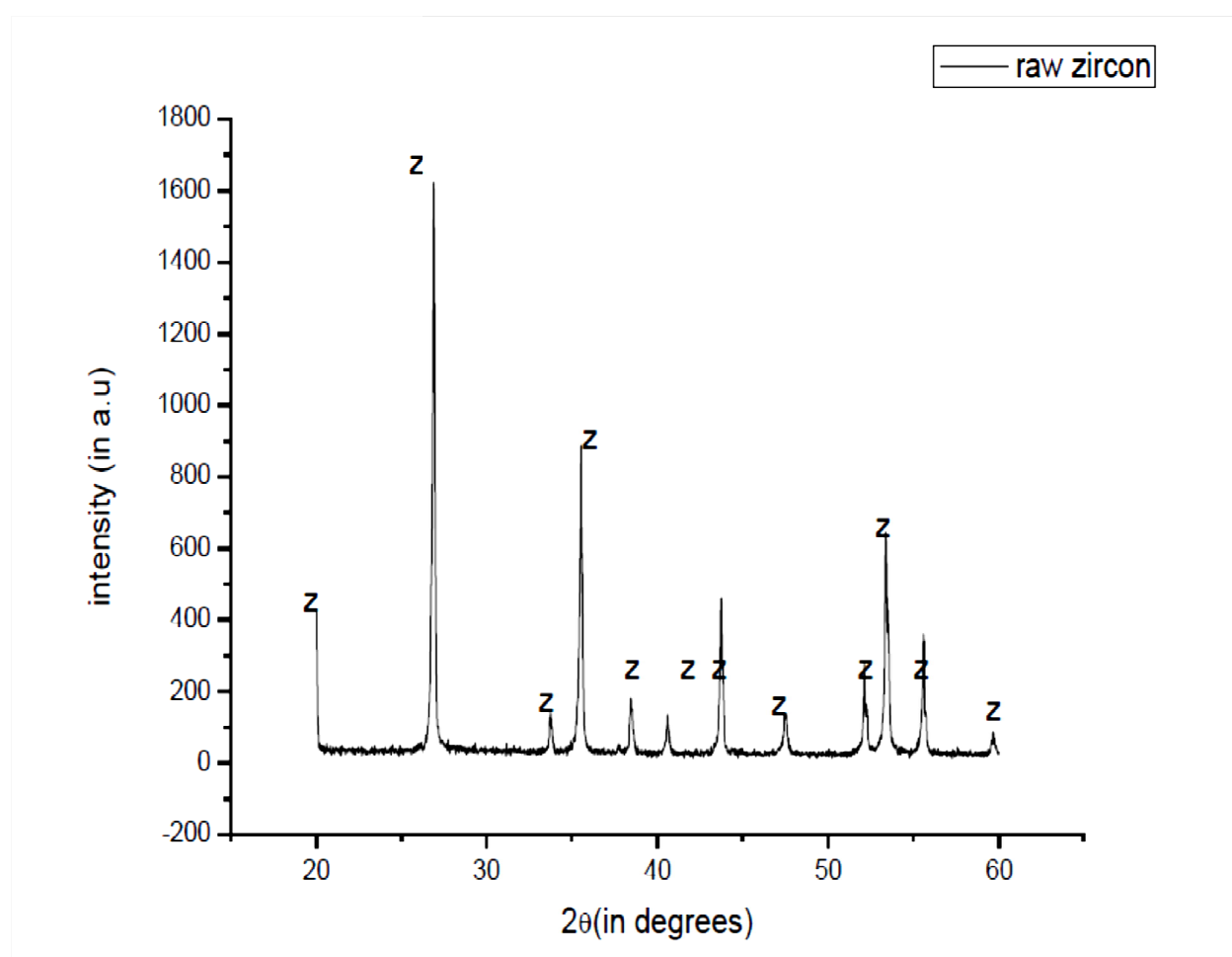

Fig. 1 XRD plot of raw unfired zircon sample

Alumina: The chemical analysis of reactive alumina (CL 370) is shown in table 6.

Oxides	Weight percentage
Al_2O_3	99.7
Na_2O	0.10
CaO	0.02
SiO_2	0.03
MgO	0.01
Fe_2O_3	0.02

Table 6. The chemical analysis of reactive alumina and the weight % of various oxides

The physical property experiments upon reactive alumina sample revealed the BET surface area to be 3.0 m^2/g. D50 Cilas was found to be 2.6 μm. Figure 2 shows the fineness chart of the alumina sample.
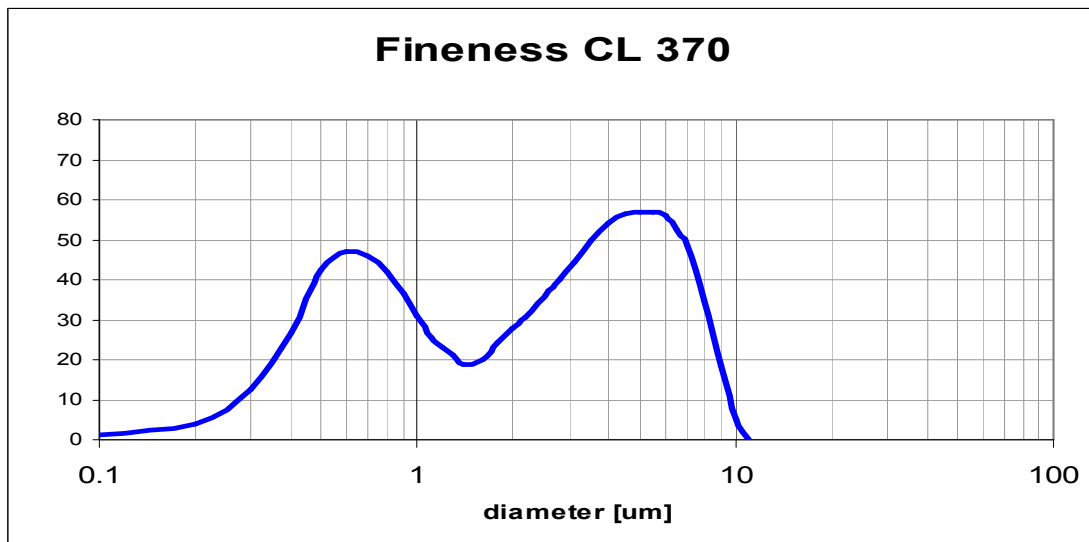
Fig.2 fineness of alumina sample

4.2 Bulk density:

The measured bulk density of pellets has been shown in table 7, 8, and 9. The bulk densities of the samples were found to be ~3.19 g/cc for the stoichiometric batch, increasing to around 3.65 g/cc for 6% SrO addition. Similarly for A- batch the density has increased from around 3.1 g/cc to 3.6 g/cc. In case of A+ batch the density value has increased from 3.2 g/cc to 3.57 g/cc. It was observed that for O and A- batch 4 % SrO addition has maximum density value. But in case of A- batch maximum density has been achieved by 6% SrO added batch. But the difference is not much significant.

Name of sample (1500°C)	Bulk density (g/cc)	dimensional density (g/cc)	Apparent porosity (%)
O	3.19	3.06	21.7
O2S	3.42	3.22	4.75
O4S	3.57	3.44	1.98
O6S	3.65	3.55	1.88
A-	3.19	2.96	23.04
A-2S	3.45	3.28	4.61
A-4S	3.43	3.39	2.49
A-6S	3.57	3.51	3.12
A+	3.25	3.06	21.23
A+2S	3.37	3.27	7.49
A+4S	3.59	3.43	3.15
A+6S	3.57	3.54	3.14

Table 7. Bulk density, dimensional density and apparent porosity of samples fired at 1500°C

Name of sample (1550°C)	Bulk density (g/cc)	Dimensional density (g/cc)	Apparent porosity (%)
O	3.18	3.10	20
O2S	3.49	3.38	0.94
O4S	3.63	3.56	1.91
O6S	3.52	3.45	2.45
A-	3.22	3.19	19.86
A-2S	3.37	3.33	2.68
A-4S	3.49	3.36	3.28
A-6S	3.51	3.57	3.83
A+	3.07	3.02	22.6
A+2S	3.32	3.26	5.04
A+4S	3.55	3.27	3.94
A+6S	3.55	3.53	3.32

Table 8. Bulk density, dimensional density and apparent porosity of samples fired at 1550°C

From the table 7-9, it can be written off that bulk and dimensional densities that almost comparable. Also the bulk density values with SrO variation has been well presented through the figures 3-5.

Name of sample (1600°C)	Bulk density (g/cc)	Dimensional density (g/cc)	Apparent porosity (%)
O	3.1	3.08	23.58
O2S	3.43	3.39	2.74
O4S	3.67	3.44	2.74
O6S	3.51	3.50	2.51
A-	3.06	3.16	23.43
A-2S	3.33	3.33	5.57
A-4S	3.55	3.42	3.94
A-6S	3.63	3.54	2.5
A+	3.18	3.05	18.47
A+2S	3.37	3.25	7.42
A+4S	3.57	3.43	3.96
A+6S	3.54	3.53	2.99

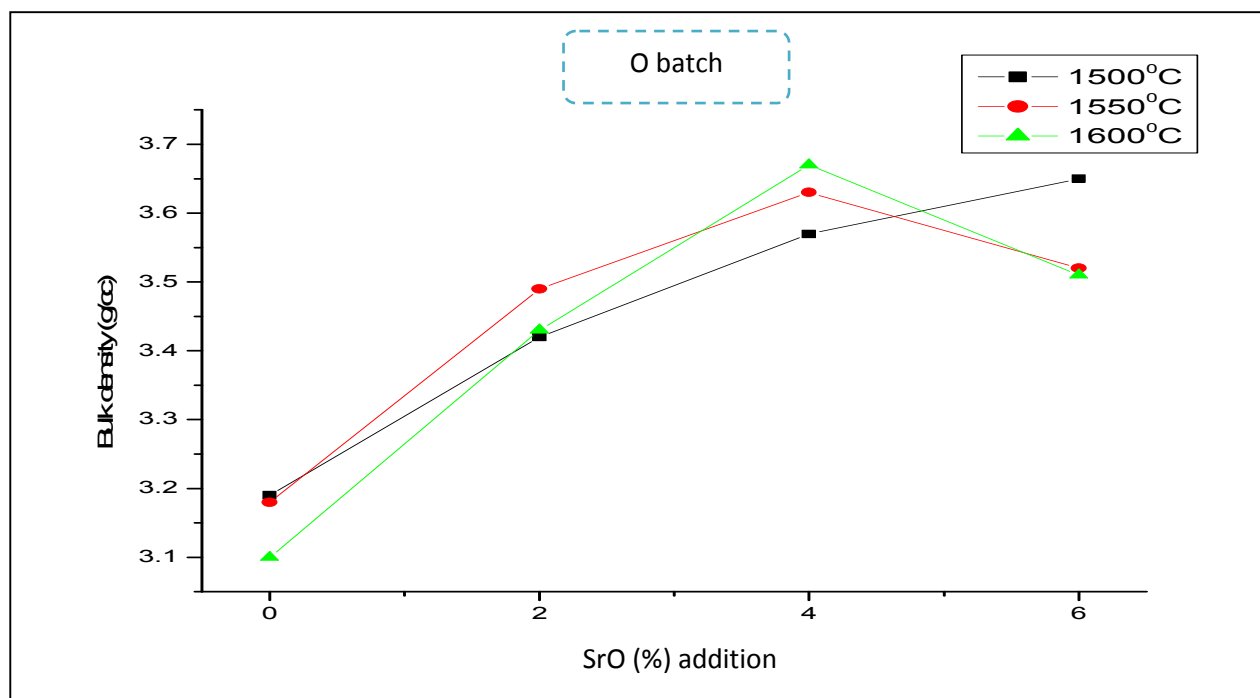Table 9. Bulk density, dimensional density and apparent porosity of samples fired at 1600°C

Fig. 3 Bulk density of (stoichiometric) O batch with varying SrO percentage
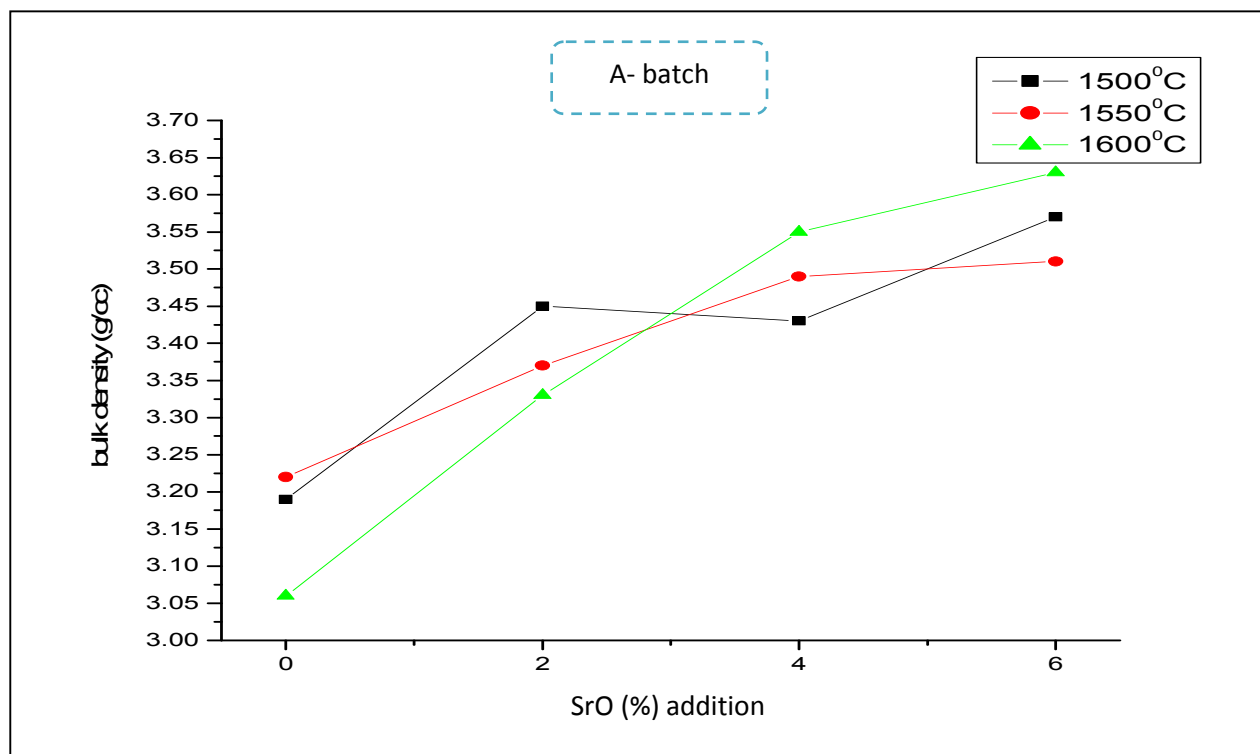

Fig. 4 Bulk density of (non-stoichiometric) A- batch with varying SrO percentage
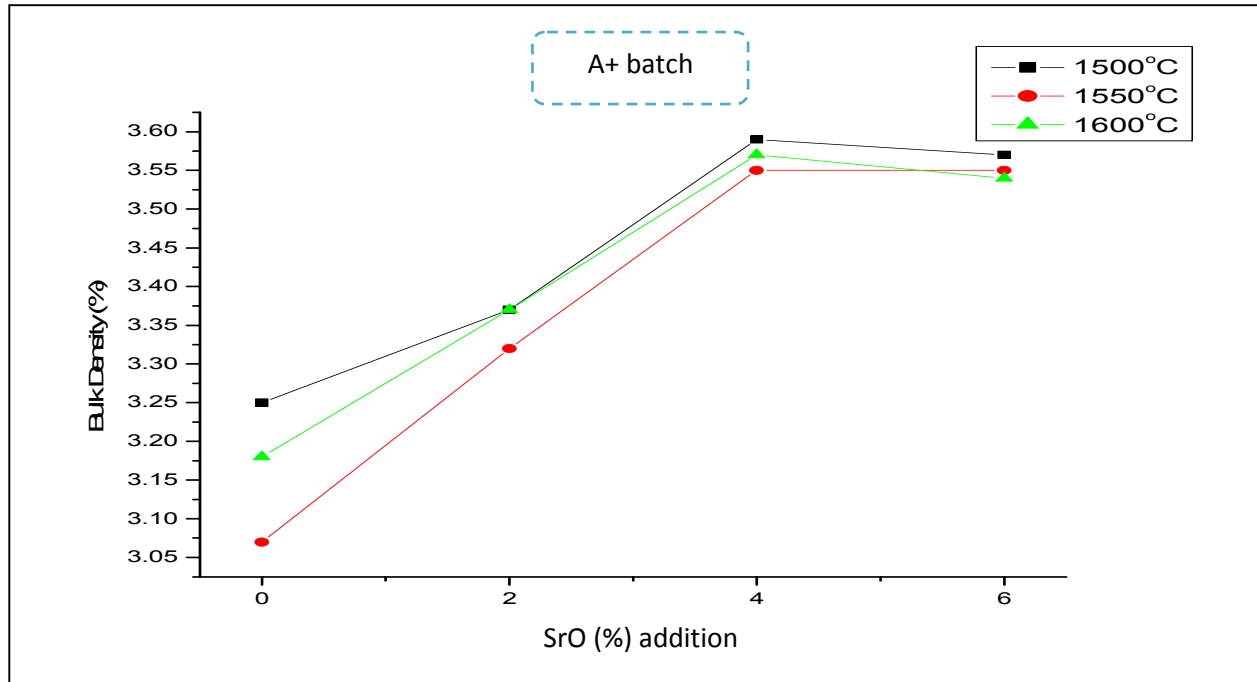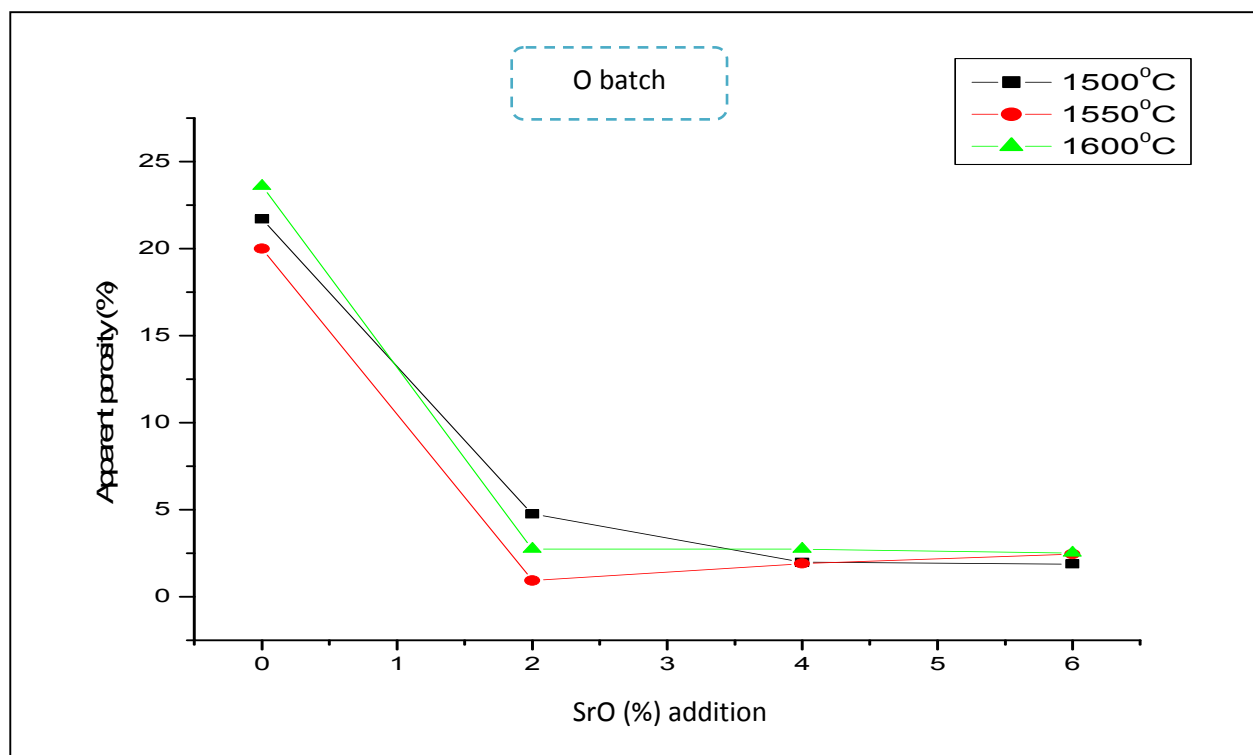
Fig. 5 Bulk density of (non-stoichiometric) A+ batch with varying SrO percentage

It is clear from the figures that with addition of SrO helps in densification of the composite, which is definitely beneficial for the zirconia-mullite composite. Now the bulk density vs SrO % additions figures support this theory.

4.3 Apparent porosity:

The apparent porosity values have been noted down in table- 7, 8, and 9. Also they have been expressed graphically in figure 6, 7, and 8. As we have already seen that the density increases with increase in SrO content. It is also evident that apparent porosity decreases to a greater extent. The porosity measurements have revealed that the values for mother batches (O, A-, A+) is around 20-22%, which decreases to around 2.5-3.0%.

Fig. 6 Apparent porosity of (stoichiometric) O batch with varying SrO percentage
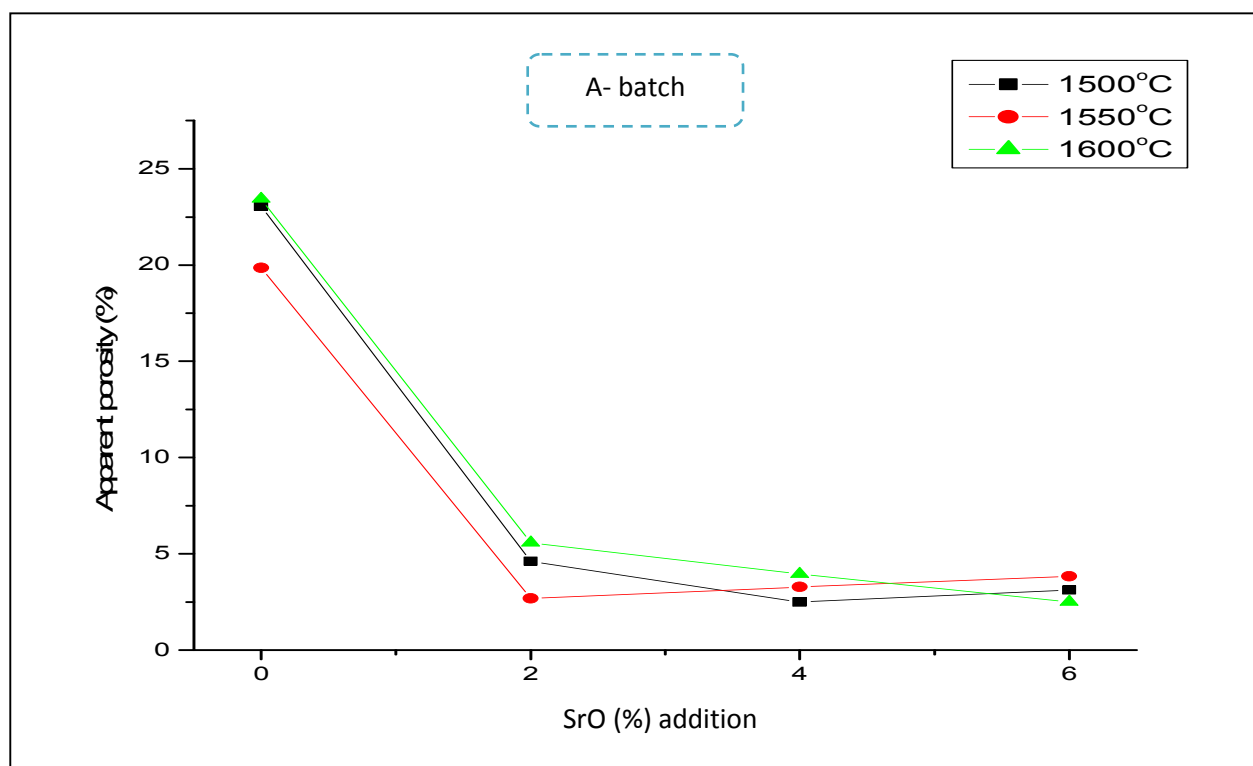

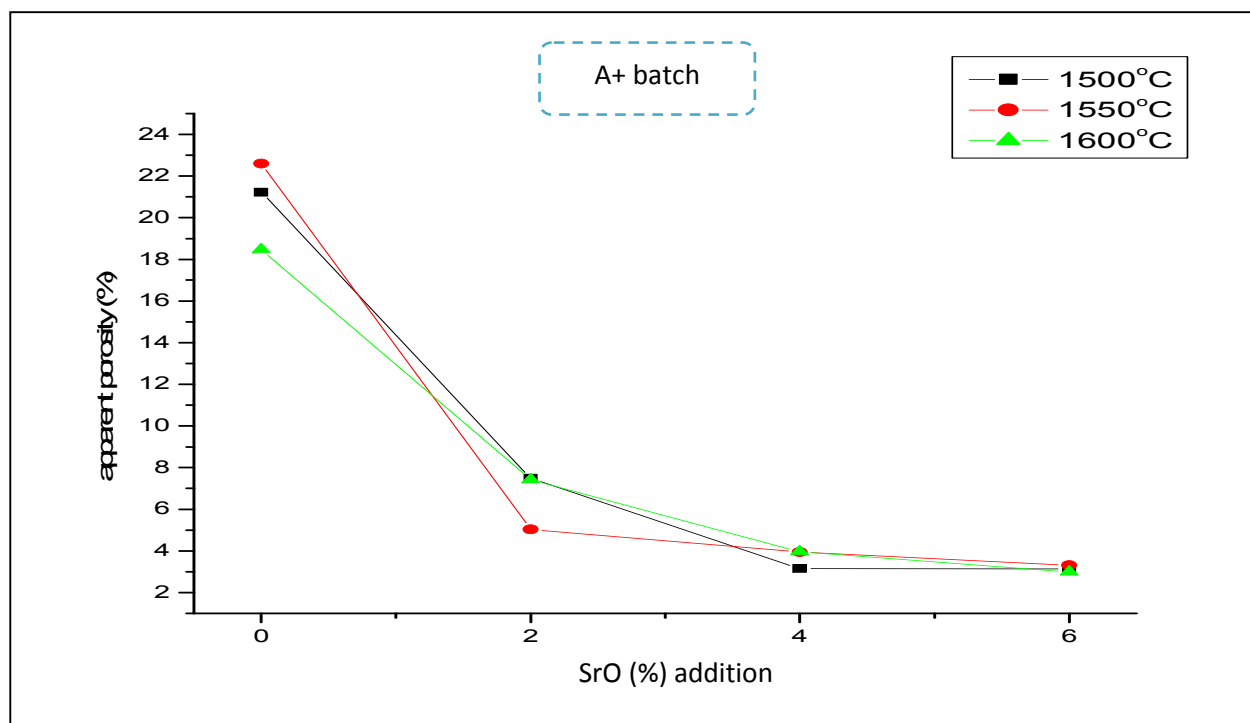Fig. 7 Apparent porosity of (non-stoichiometric) A- batch with varying SrO percentage

Fig. 8 Apparent porosity of (non-stoichiometric) A+ batch with varying SrO percentage

4.4 volume shrinkage:

The volume shrinkages of samples have been sighted in table 10. Also the graphical representation of the same has been shown in figures 9,10.

Name of sample	Shrinkage at 1500°C (%)	Shrinkage at 1550°C (%)	Shrinkage at 1600°C (%)
O	15.20	15.8	14.34
O2S	19.14	22.47	21.78
O4S	25.29	22.90	24.34
O6S	27.04	24.68	24.82
A-	16.33	17.13	13.8
A-2S	19.67	21.36	23.95
A-4S	22.06	22.59	23.64
A-6S	25.28	26.67	26.68
A+	12.96	13.48	13.93
A+2S	28.89	21.82	18.98
A+4S	25.07	22.54	25.72
A+6S	28.57	29.39	26.35

Table 10. Volume shrinkage values of various batches with temperature of sintering variation

Supporting the density appraisal and apparent porosity decrement the volume shrinkage of samples has again displayed the beneficial effect of SrO addition.
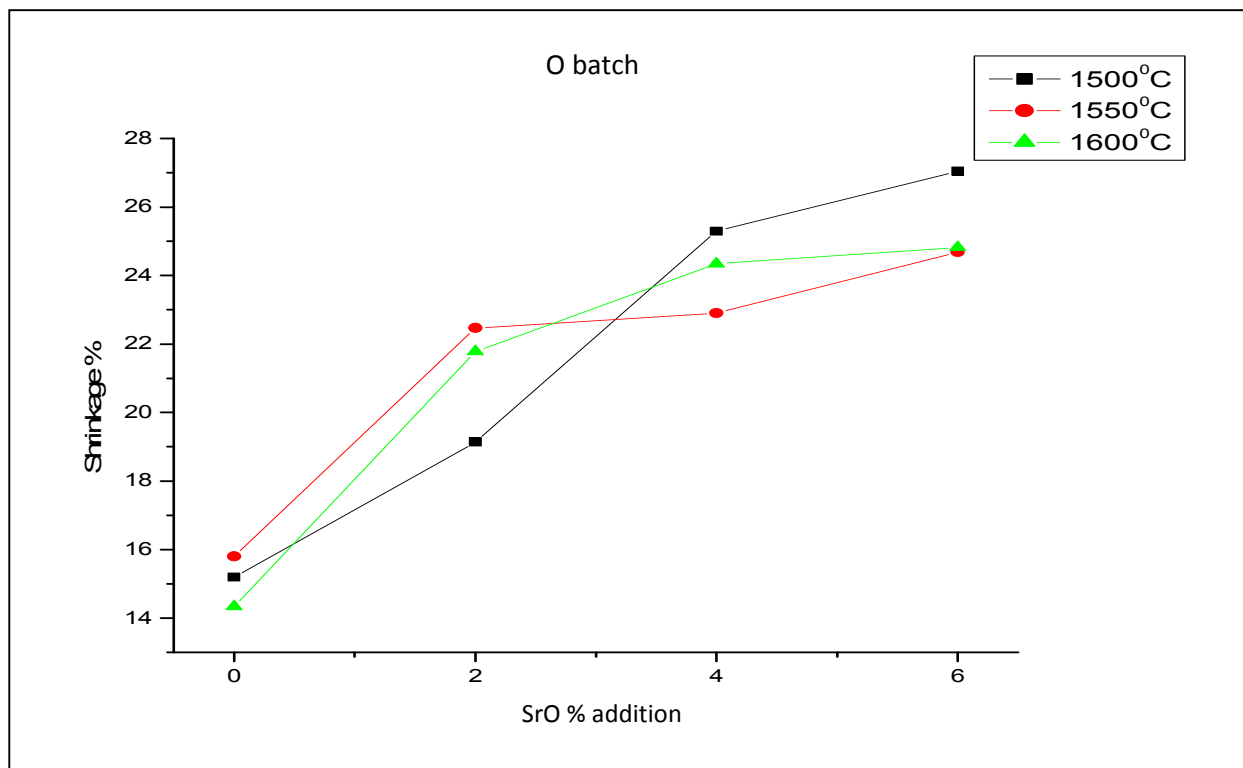
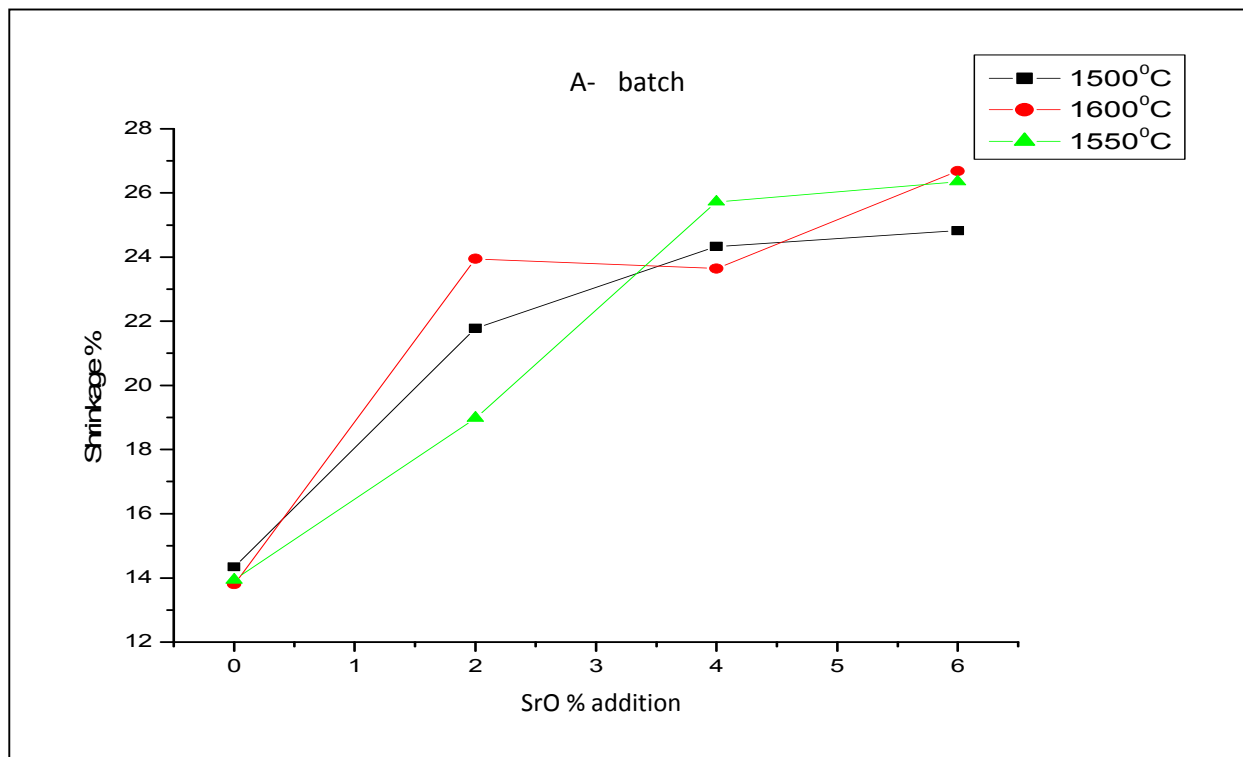Fig. 9 Shrinkage of O batch at various temperatures with SrO (%) variation

Fig. 10 Shrinkage of A- batch at various temperatures with SrO (%) variation
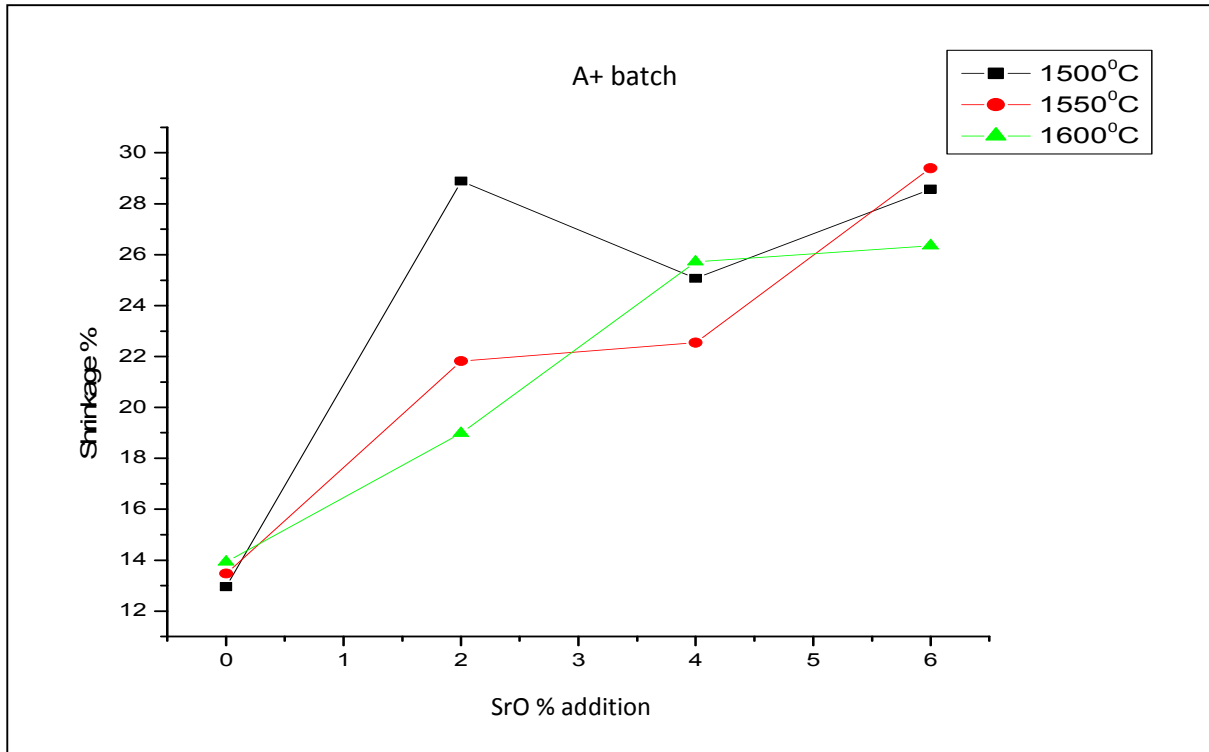
Fig. 11 Shrinkage of A+ batch at various temperatures with SrO (%) variation
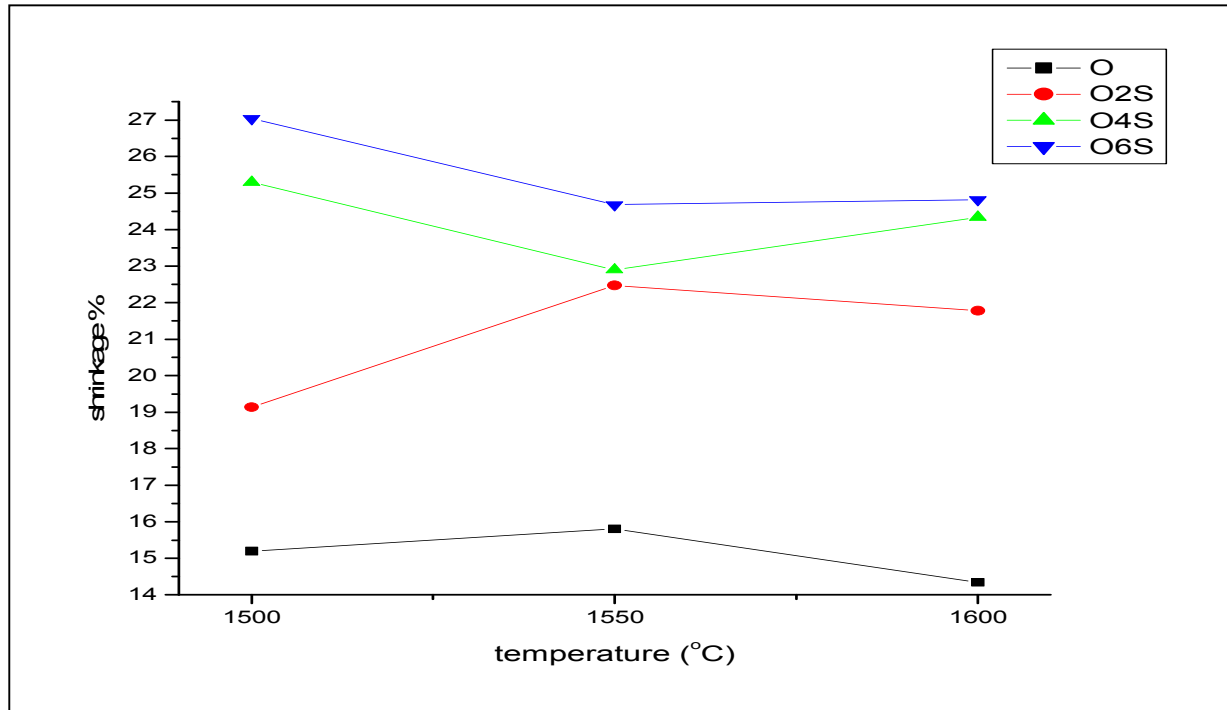

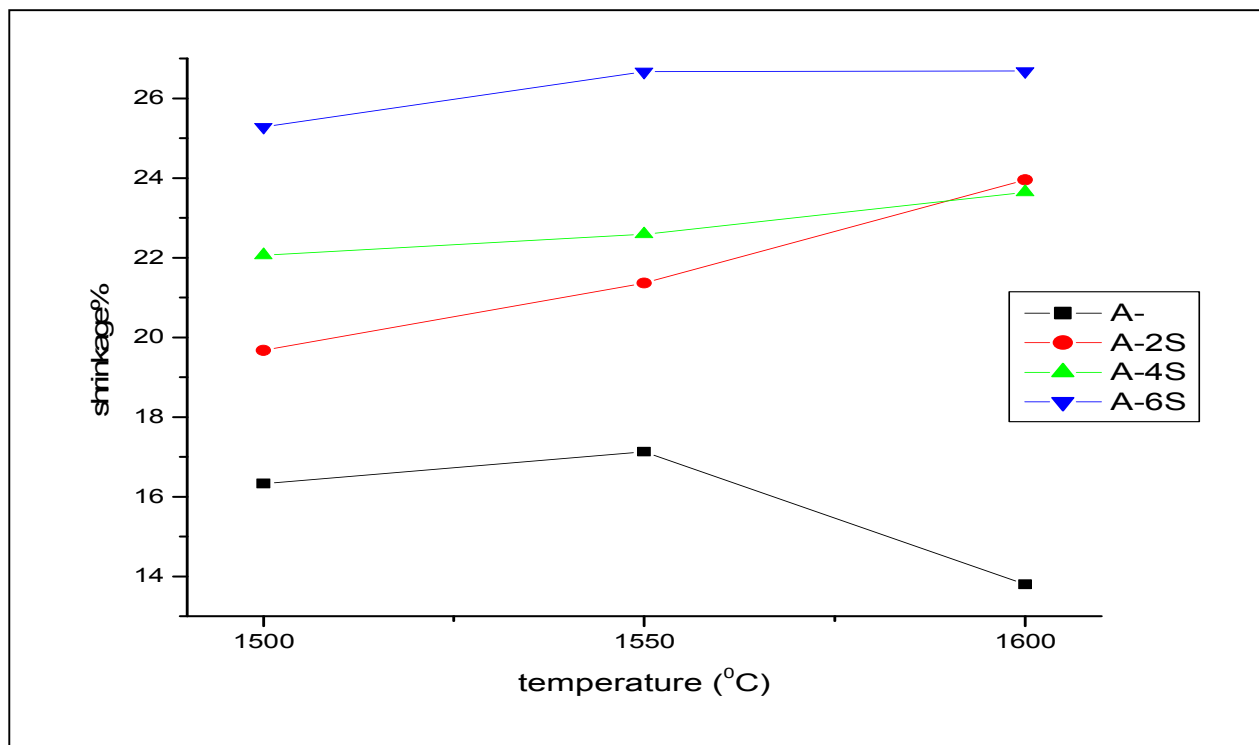Fig. 12 shrinkage vs temperatures graphs for O batch

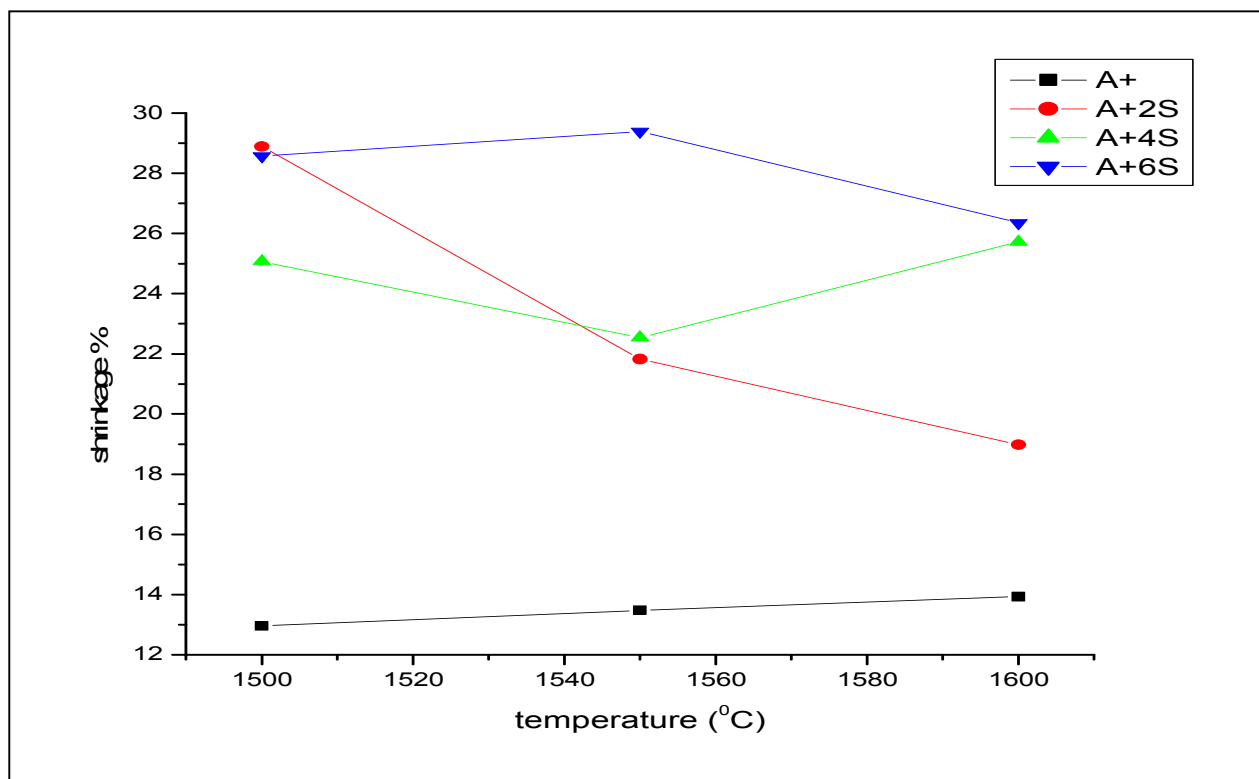Fig. 13 shrinkage vs temperatures graphs for A- batch

Fig. 14 shrinkage vs temperatures graphs for A+ batch

4.5 X-ray diffraction:

XRD analysis of the samples revealed the presence of various major phases such as: zirconia (monoclinic and tetragonal), mullite, corundum, and zircon.
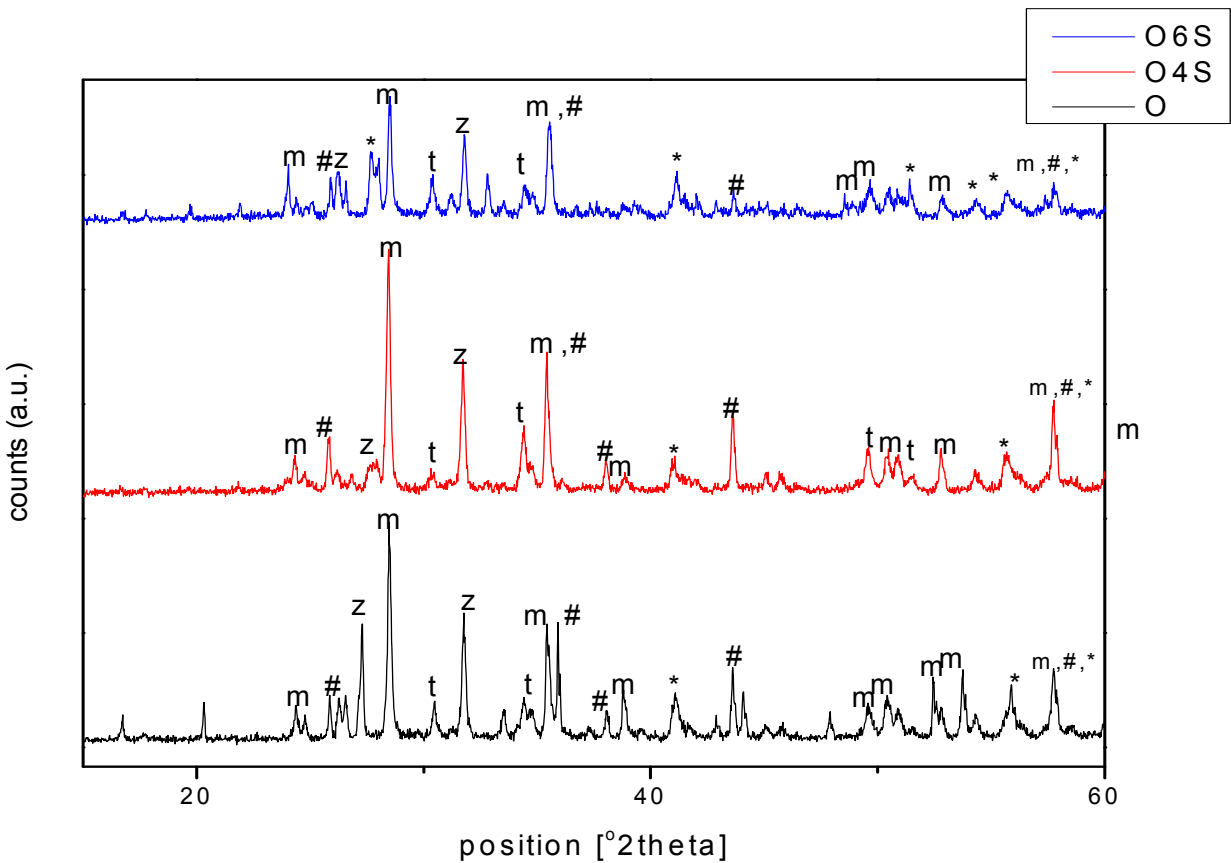

Fig. 15 XRD pattern of stoichiometric batch(O,O4S, and O6S) fired at 1500°C

m= monoclinic zirconia

t= tetragonal zirconia
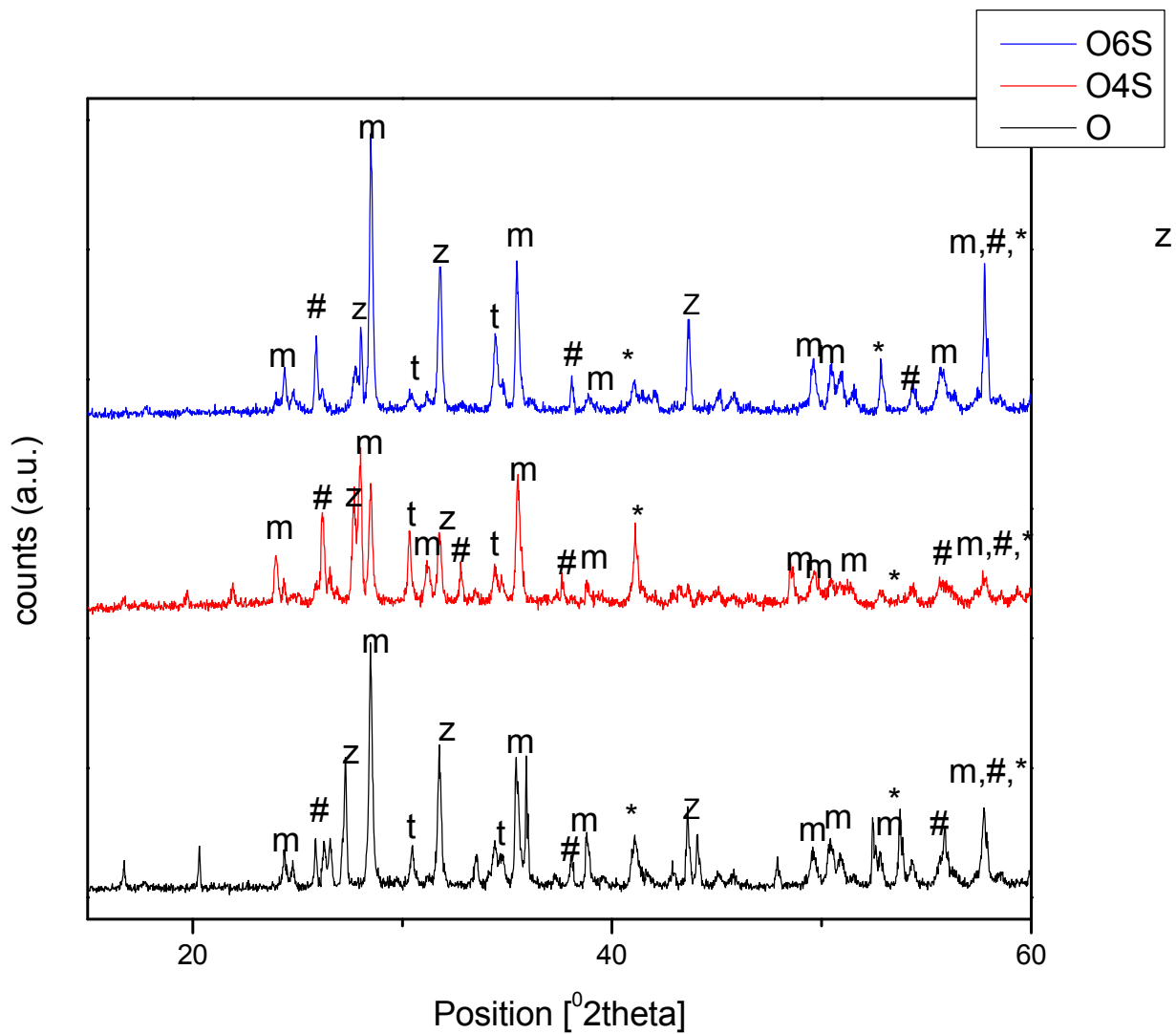
*= mullite

#= corrundum

z= zircon

Fig. 16 XRD pattern of stoichiometric batch(O,O4S, and O6S) fired at 1550°C

m= monoclinic zirconia

t= tetragonal zirconia

*= mullite
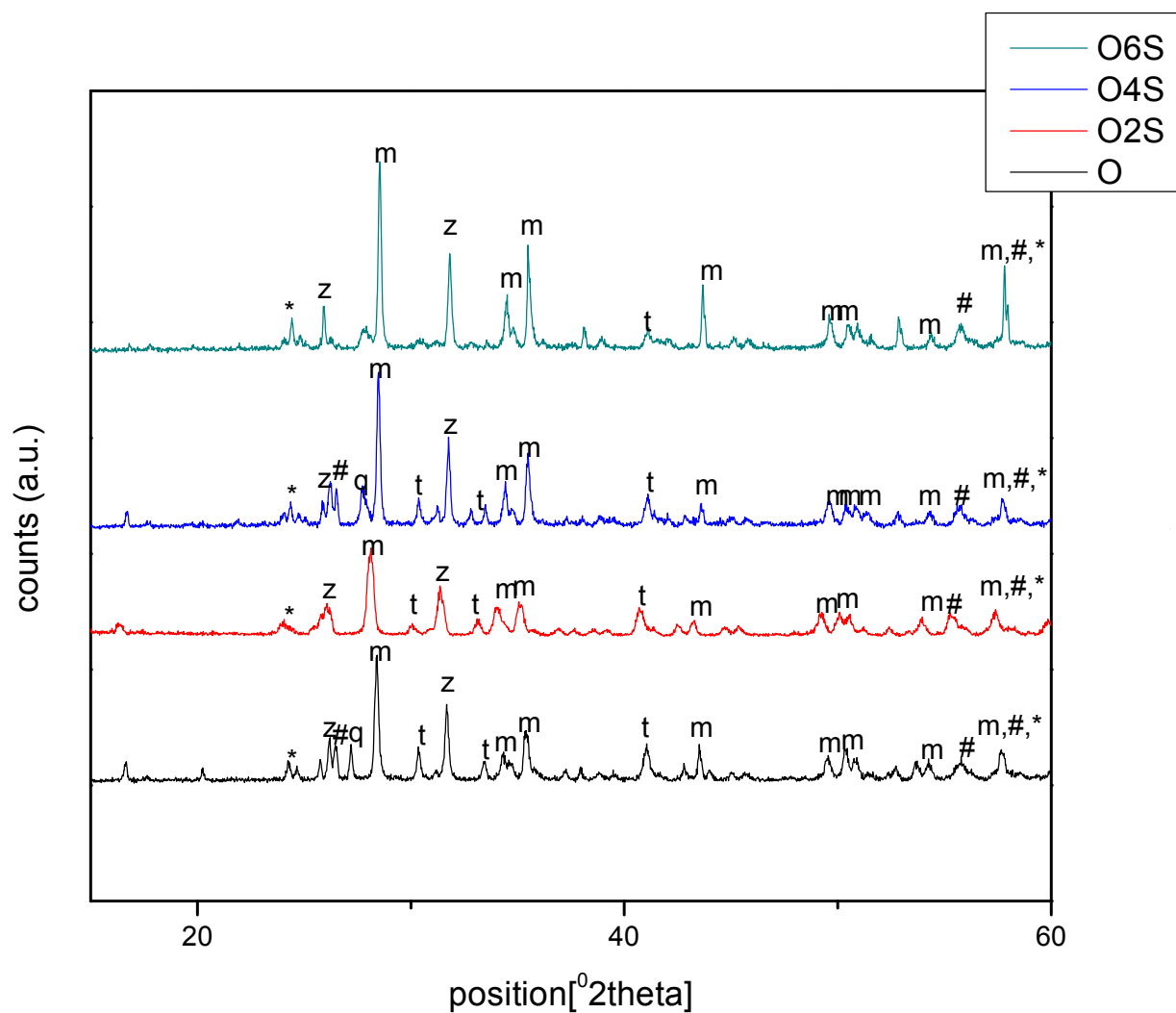
#= corrundum

z= zircon

q= quartz

Fig. 17 XRD pattern of stoichiometric batch (O, O2S, O4S, and O6S) fired at 1600°C

m= monoclinic zirconia

t= tetragonal zirconia

*= mullite

#= corrundum

z= zircon

q= quartz

Sample	t-ZrO$_2$ at 1500°C (%)	t-ZrO$_2$ at 1550°C (%)	t-ZrO$_2$ at 1600°C (%)
O	17	19	20
O4S	36	31	31
O6S	28	16	22

Table11. Retention of tetragonal zirconia percentage in the O batches (O, O4S, and O6S)

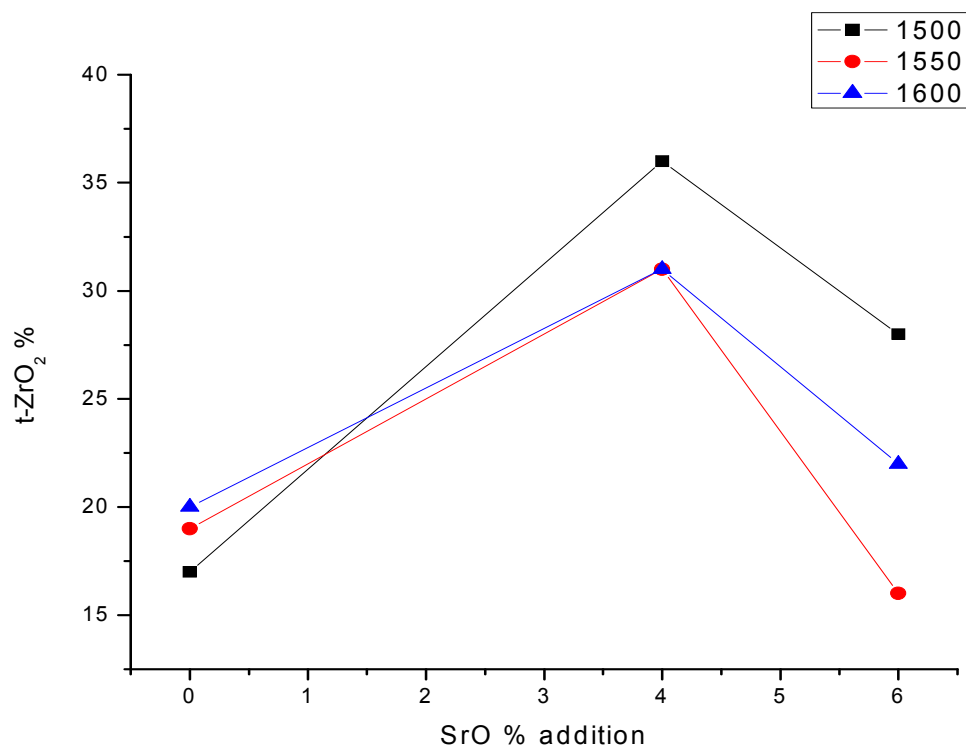

Fig.18 Tetragonal zirconia percentage retention versus SrO percentage in O batch

From the table 11 and fig. 18 it is clear that for the 4% SrO added stoichiometric batch shows higher tetragonal zirconia percentage retention within the total zirconia content. This way O4S batch may be useful in terms of mechanical properties because of the transformation toughening of the tetragonal zirconia.
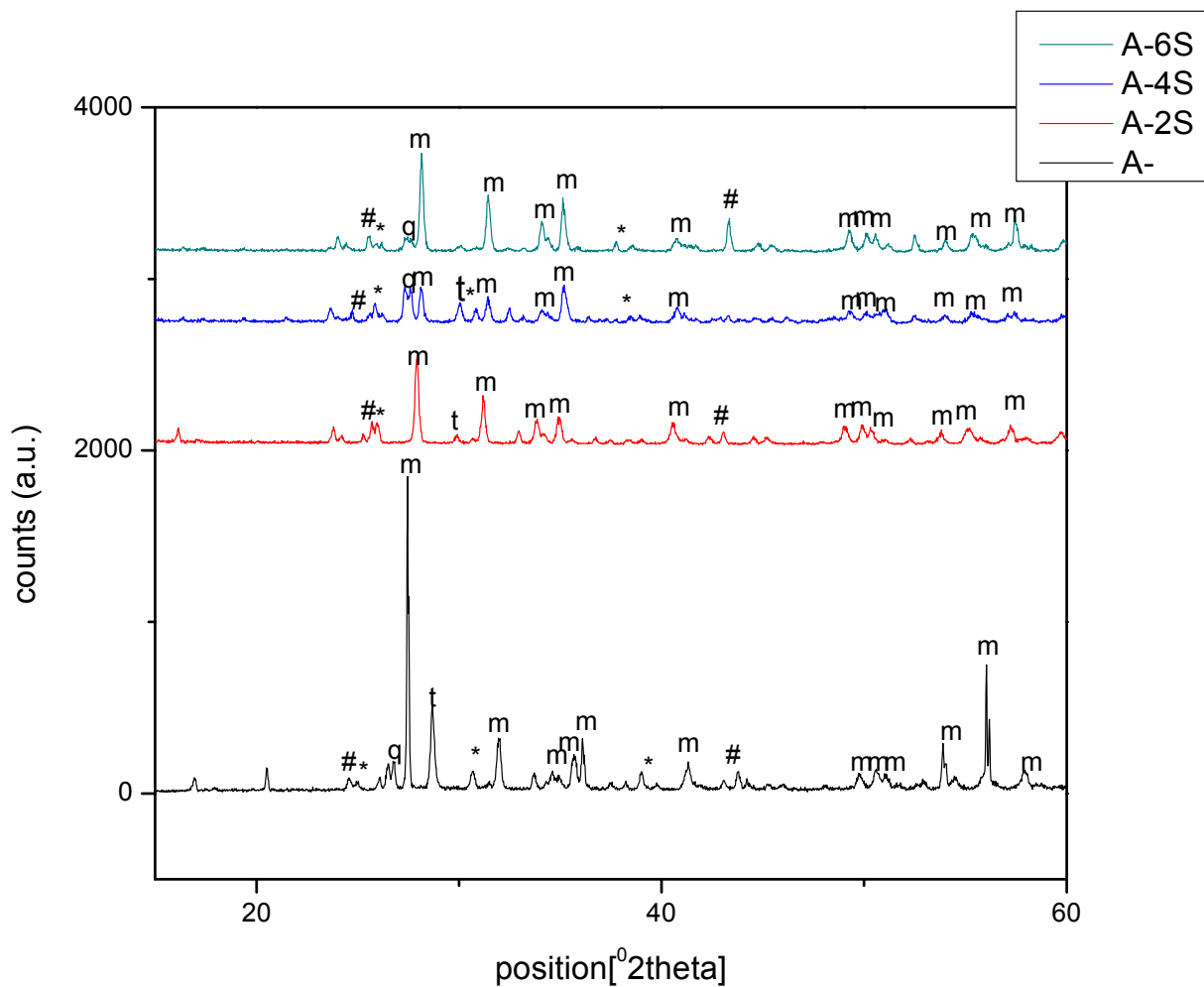
Fig. 19 XRD pattern of non-stoichiometric batch (A-, A-2S, A-4S, and A-6S) fired at 1600°C

m= monoclinic zirconia

t= tetragonal zirconia

*= mullite

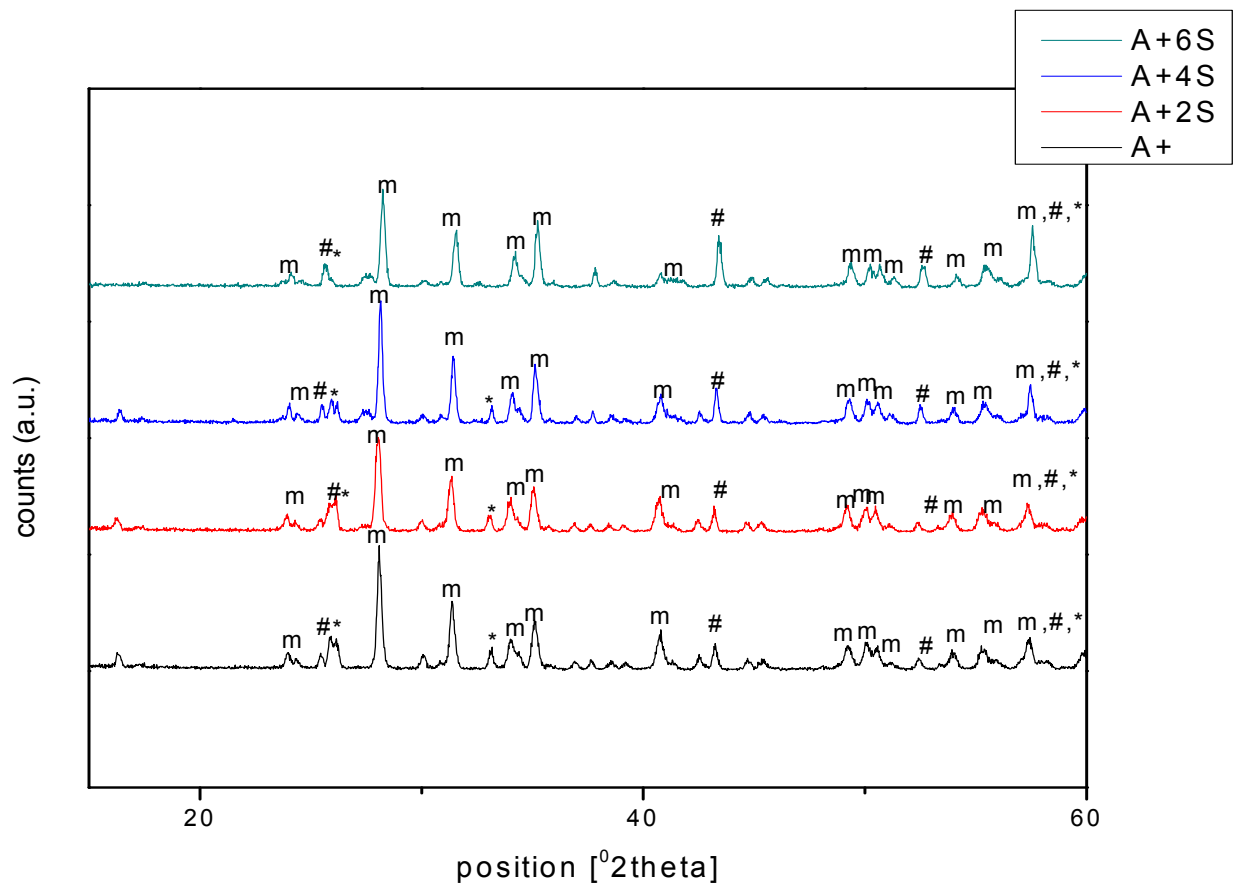#= corrundum

z= zircon

q= quartz

Fig. 20. XRD pattern of non-stoichiometric batch (A+, A+2S, A+4S, and A+6S) fired at 1600°C

m= monoclinic zirconia

t= tetragonal zirconia

*= mullite

#= corrundum

z= zircon

q= quartz

PHASE ANALYSIS:

Table 12 shows the phase composition of various batches fired at 1600°C.

Sample	m-ZrO2(%)	t-ZrO2(%)	Mullite(%)	Corundum(%)	Zircon (%)	others
A+	35	4	53	5	3	-
A+2S	27	1	50	19	3	-
A+4S	21	2	34	41	2	-
A+6S	15	1	22	60	2	-
A-	22	4	47	14	3	10
A-2S	14	6	38	28	1	13
A-4S	16	1	35	32	2	14
A-6S	25	1	24	48	2	-
O	19	5	29	35	5	6
O2S	22	1	57	21	-	-
O4S	13	6	47	23	8	3
O6S	7	2	30	41	20	-

Table12. Various phase compositions of batches fired at 1600°C

From the phase analysis as shown in Table 12 percentages of various mineral phases can be interpreted. It seems the volume % of mullite is decreasing with increase in SrO content. Withal the improvement of corundum and zirconia percentage it can be said that somehow SrO is hindering the reaction sintering of zirconia-mullite system. The reaction of zirconia alumina being a reversible process SrO at high temperature promotes the backward reaction by releasing zirconia and alumina from the system. The reason for high density, low porosity and shrinkage can be explained through the fact that, strontium oxide generally reacts with the impurities and the residual silica to form glassy phase. This accounts for the lowering of desnsities.

5. <u>CONCLUSION</u>

1. Addition of SrO helps in densification of zirconia-mullite system.

2. Maximum density achieved was around 3.65 g/cc with additive and without additive it was around 3.1 g/cc for O batch. Similarly the density values varied between 3.06-3.63 g/cc for alumina deficient (A-) batch. Upper limit of alumina excess batch (A+) density was 3.57g/cc and the lower limit was 3.07g/cc.

3. Density values increase with increase in SrO percentage from 0-6% for all the batches

4. Apparent porosity reduces to a greater extent with the additive effect of SrO.

5. Without additive, porosities for O,A-, and A+ batches were maximum 23.58% , 23.43% , 22.6% respectively and with additive it lowered to around 1.88%, 2.5% and 2.99%.

6. Supporting the density appraisal and apparent porosity decrement the volume shrinkages of samples have again displayed the beneficial effect of SrO addition.

7. Shrinkage for O batch (without additive) was around 15.20%, which increased to 27.04% with additives. Considering the non-stoichiometric batches, shrinkage value for A- batch raised from 13.8% to 23.64% and for A+ batch the addition of SrO upgraded the shrinkage from12.96% to 28.57%.

8. From XRD analysis major phases found were monoclinic zirconia, tetragonal zirconia, zircon, mullite, corrondum and traces of other phases like quartz.

9. It was observed that tetragonal zirconia retention was relatively higher in stoichiometric batch with 4% SrO addition compared to other percentage addition of the same (O) batch.

10. Irrespective of slight variation of t-zirconia in total zirconia amount, the overall t-zirconia percentage retained was very low to call for the strengthening of the composite.

11. The phase composition analysis proclaimed that the percentage of mullite is subsequently decreasing with addition of SrO, where as corrundum and zircon phases were upgarded.

12. It means the addition of SrO impeded the formation of Zirconia-mullite composite.

13. Study of effect of SrO additive has affirmed the inhibitory effect of the same for the formation of Zirconia-mullite composite.

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