"PREPARATION & DENSIFICATION STUDY OF BARIUM ZIRCONATE NANOPOWDER"

A THESIS SUBMITTED IN PARTIAL FULFILLMENT

OF THE REQUIREMENTS FOR THE DEGREE OF

Bachelor of Technology

In the

Department of Ceramic Engineering
By

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Certificate

This is to certify that the thesis entitled, **"Preparation and Densification study of Barium Zirconate ($BaZrO_3$) nanopowders"** submitted by **Mr. Prashant Kumar** in partial fulfilment of the requirements of the award of **Bachelor of Technology** Degree 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.

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12th May, 2011 *Prashant kumar*

Abstract

Barium Zirconate ($BaZrO_3$) is a promising candidate for structural to electronic application. Different industry demands nano scale powder for the technology enhancement and hence, the preparation of $BaZrO_3$ nano-powders and their sintering study through microstructure synchronization are the prime interest of this research. A typical combined wet chemical and calcination technique was employed to synthesis of 100nm $BaZrO_3$ nano-powders. Elongated Barium carbonate ($BaCO_3$) nano rod was prepared through wet chemical method, whereas, near spherical yttria stabilized zirconia nanoparticle was used to prepare this $BaZrO_3$. Transmission electron microscope analysis (TEM), XRD and BET surface area confirmed the purity and morphology of developed nanoparticles. Prior to sintering, dilatometric study was conducted to understand the sintering behaviour this class of nanoparticles. A wide horizon of sintering profile optimized the sintering condition with consideration of relative density and microstructure. The nano powder was near to 98% dense at 1650^oC for 2h. Field Emission Scanning Electron (FESEM) microscope study reveals the grain size is around 250nm. The developed perovskite $BaZrO_3$ nano powders could be successfully used for different sectors.

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Chapter-1

Introduction

1. Introduction:

Perovskite structure like of $BaZrO_3$ possess many significant properties which are responsible for their many technological and scientific applications in the field of sensors, ion conducting, substrate as refractories, electronic component and in solid oxide fuel cells (SOFCs).

1.1. Properties of Barium Zirconate:

- High refractoriness: Due to high melting point (2600^0C), is used for Thermal barrier coatings.
- Less thermal expansion coefficient:($0.87x10^{-5}/^0$C between 25^0C and 1080^0C)[1]. Used as substrate for thin film deposition and superconductors.
- Poor thermal conductivity and thus used as thermal insulation.
- Excellent mechanical strength
- Excellent structural strength
- High corrosion resistant.

1.2. Crystal structure of Barium Zirconate:

Barium zirconate is an ideally perovskite structure having general formula 'ABO_3', where A and B are cation and O is anion. 'A' is divalent and 'B' is tetravalent. A cations are XII fold coordinated by oxygen and B cation lies within oxygen octahedra. The ideal cubic perovskite structure of Barium Zirconate is shown in fig.1.1.

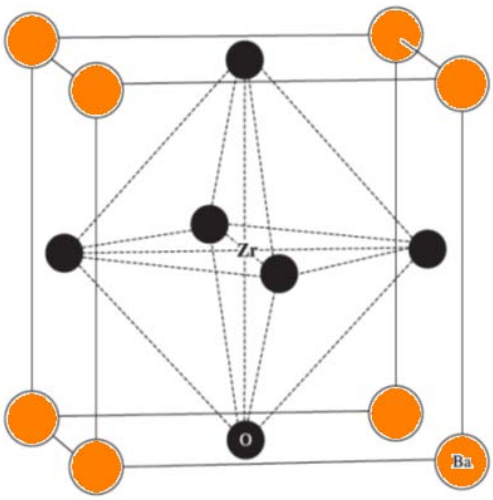

Fig1: Ideal representation of Cubic perovskite structure; ABO_3; where A=Ba, B=Zr and O= Oxygen. [7]

The position of A atoms is at the corner of the cube, the B atoms at the centre and the O atoms at the face centre of the cubic lattice. The space group for the cubic perovskite structure is $Pm\bar{3}m$ [7].

1.3. Applications of $BaZrO_3$:

- Electrochemical devices: Proton conductors in the SOFCS because of its excellent chemical stability in reducing atmosphere.
- Sensors: Humidity sensors, water vapour sensors due to its high thermal and chemical stability.
- Superconductors: Due to its high corrosion resistance.
- Thermal barrier Coatings: Due its high thermal stability, chemical inertness and refractoriness.

1.4. Outline and overview:

The project is actually concerned with the study of preparation and densification of $BaZrO_3$ nano powders at different temperature which has been elaborated in the next few chapters.

The next section is literature review with some similar kind of detailed projects and then the experimental part depicting optimization and outcome of the work and finally the results, discussion and conclusion.

Chapter-2

Literature Review

2. Study of Synthesis routes:

There are different routes discovered for the synthesis of $BaZrO_3$ nano-powders some of them are citrate route method involving citric acid, oxalate route where ammonium oxalate is used, precipitation route in the basic medium like using urea, combustion method using oxalic dihyrazide, sol-gel method and solid state route. However, when the crystallinity is concerned powders of homogeneous and nano range particles are produced from solid state route as this method is apposite to produce powders in the maximum nano range, defect free and pure.[1]

2.1. Densification and study of properties of Barium Zirconate:

D.Y. Gao studied the densification and properties of Barium Zirconate which reveals that with the addition of sintering additive, P_2O_5 the sintering of the Barium Zirconate was greatly achieved and resulting in enhanced mechanical and physical property. With the incorporation of 4 mol% of P_2O_5 and sintered at 1600^oC for 4hrs, a maximum of 94.2% theoretical density was achieved and resulting in increase in hardness and bending strength. [1]

The $BaCO_3$ and ZrO_2 mixed sample was studied profoundly by optimising the reaction kinetics and mechanism of $BaZrO_3$ formation from $BaCO_3$ and ZrO_2 powders et al [2] . The solid state transformation was characterized using DTA-TG curve at constant heating rate of 3^oCmin^{-1} up to 1300^oC.The microstructure evolution and growth of $BaZrO_3$ was optimised using TEM images. The reaction kinetics was calculated which depicts the reaction kinetics and fractions of $BaCO_3$-ZrO_2 mixture in dry air with respect to time.

F. Boschini *et al [3]* studied the synthesis of barium zirconate by precipitation in aqueous basic medium solution below 100^oC. The basic medium is provided by NaOH solution. The

mixed Ba-Zr solution concentration can yield the well-crystallized stoichiometric perovskite phase at low temperature of below 80^{o}C.

M. Bu´cko et al [6] studied the preparation of barium zirconate nanopowders using spray pyrolysis method. The aqueous solution of zirconyl and barium nitrates were produced by dissolving in distilled water to obtain 0.1M solution. This solution was then atomized using ultra sonic spray pyrolysis which conforms the formation of $BaZrO_3$ nanopowders in the range of 25-60nm.

2.2. Objective of the present study:

- To synthesis high crystalline $BaZrO_3$ nanopowders.
- To study the densification and microstructure of $BaZrO_3$ nanoparticles at different sintering condition.
- To achieve maximum relative density at optimum condition.

Chapter-3

Experimental Work

3. Synthesis of Barium Zirconate nanopowder.

3.1. Synthesis of $BaCO_3$ precursor:

$BaCO_3$ was prepared from $BaCl_2.2H_2O$ and $NaHCO_3$ by precipitation route involving the reaction at temperature below 100^oC.

21.114gm of $BaCl_2.2H_2O$ and 17.14gm of $NaHCO_3$ was weighted separately to obtain 20gm of $BaCO_3$ and then diluted in distilled water. The solutions were mixed drop wise in stirring condition. The precipitate obtained was separated from solution by filtering using filter paper, washed and then dried at about 150^oC for 24 hrs.

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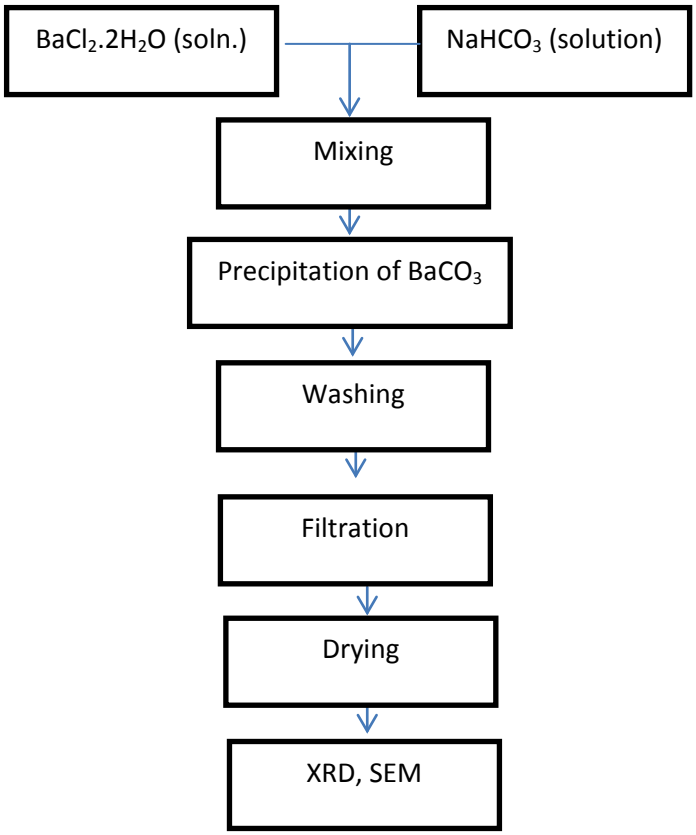

Figure 2. Process flowchart

3.2. . Synthesis of Barium Zirconate powder:

The $BaCO_3$ powder was dry mixed with ZrO_2 for 20min (3 mole% Yittria stabilized Zirconia). The wet mixing initiated with the Vibrating Ball mill in acetone medium (60% volume) and grinded for 90 min using zirconia balls. After grinding the mixture was dried at 75^oC for 24hrs.

The calcined powder was then mixed with 3vol % PVA, an organic binder and mixed for 30 min. The powder was then separately weighted into 5 different compositions and uni-axially pressed (carver press USA) at 3.5 tonne with dwelling time 90 sec. After pressing the green samples were fired at 1250^oC, 1350^oC, 1450^oC, 1550^oC and 1650^oC for 1hr.

Firing was done in electric chamber furnace and initially kept on hold at 650^oC for 1 hour for complete binder burnout and then soaked at firing temperature for 1hr. The heating rate was constant at 3$^oCmin^{-1}$. The fired product was then cooled at room temperature and characterised in terms of bulk density and relative density.

3.3. Different characterization techniques:

a. DSC-TG:

The sample was then thermal analysed in Differential Scanning Calorimetriy and Thermo gravimetriy (NETACH, Germany) at constant heating rate of 10$^oCmin^{-1}$ in the temperature range of 30^oC to 1300^oC and then further calcined at 800^oC for 5hrs and 1100^oC for 1 hr.

b. XRD:

After calcination X-Ray Diffraction pattern was obtained in Philips X-Ray Diffractometer PW 1730 with nickel filtered Cu Kα radiation (λ= 1.5406 A˚) at 40 kV and

30mA was done. The scanning rate was set to 0.04 $^{o}sec^{-1}$ and scanned continuously in the range of 20^{o} to 80^{o}.

c. BET analysis:

The particle surface area was measured using BET analysis (Quantachrome, USA) at temperature of about $300^{o}C$ for 1 hour in liquid N_2 of temperature 77K.

d. Transmission electron microscopy:

The powder of $BaZrO_3$ which was calcined at $1100^{o}C$ for 1 hour was characterized to determine morphology of particles and its microstructure.

e. Dilatometer:

The shrinkage behaviour was obtained by NETZSCH dilatometer model DIL 402 C in which the sample of length 10mm and thickness of 2mm made bar pellet was kept in specimen holder in the centre of the furnace. The heating rate was constant at $10^{o}Cmin^{-1}$ and firing temperature was from room temperature, i.e., $30^{o}C$ to $1450^{o}C$. The atmosphere was N_2 inside the dilatometer.

f. Bulk density and relative density:

Bulk density of the sintered pellets was done by using conventional liquid displacement method using Archimedes Principles in water medium. The dry weight of the pellet (W_d) was determined and then kept in water beaker and then the whole system was put under vacuum for 1 hour. Due to high vacuum pressure air inside the pores comes out. Thereafter, the pellets was soaked in tissue paper and weighted to obtain soaked weight (W_{soa}) and then again the weight of the sample was taken suspending in water to get suspended weight (W_{sus}).

Bulk density formulae :

$$\text{Bulk density, BD} = \frac{W_d * \text{density of liquid}}{(W_{soa} - W_{sus})}$$

$$\text{Relative density, RD} = \frac{\text{Bulk density x 100}}{\text{True density}}$$

g. Scanning electron Microscopy:

The pellets and powder fired at 1250^{o}C, 1350^{o}C, 1450^{o}C, 1550^{o}C and 1650^{o}C were analysed in SEM to get its microstructure details. The pellets were first sputtered by platinum and then scanned in SEM.

h. FESEM and EPMA analysis:

The $BaZrO_3$ pellet sintered at 1650^{o}C was studied under FESEM and EPMA analysis. This work was carried out to study a particular sample at optimum condition.

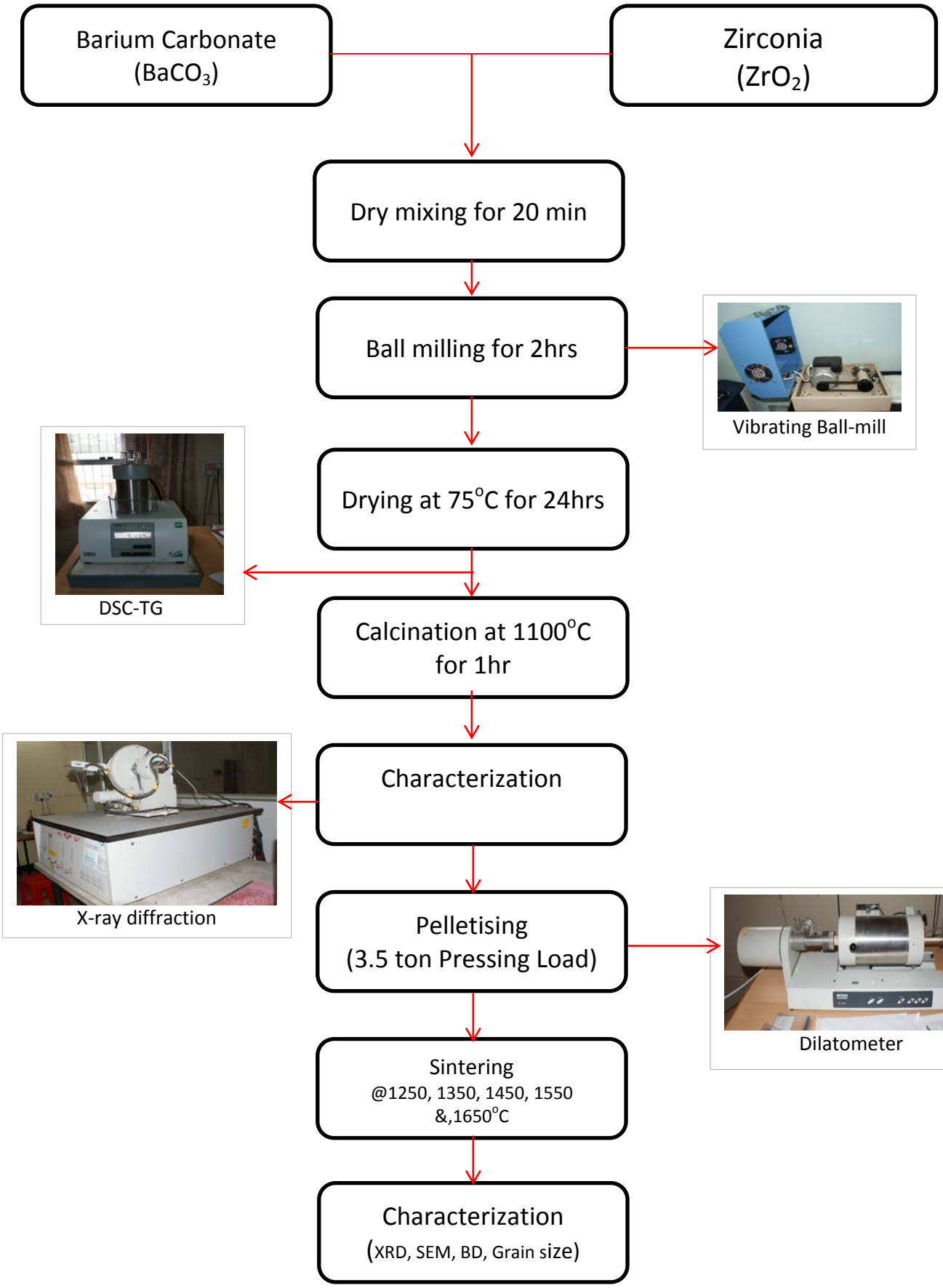

Figure 3. Synthesis and sintering flow sheet of $BaZrO_3$ nanopowders.

Chapter-4

Results and Discussion

4.1. Thermal analysis of precursor ($BaCO_3$ and ZrO_2) in air

The thermal decomposition behaviour was studied and characterized in DSC-TG. The plotted curve showed three endothermic peaks. The peaks at 808^{o}C and 970^{o}C having orthorhombic-hexagonal and hexagonal-cubic phase transformation of $BaCO_3$ in referenced with A. Ubaldini et al [2]. The pure $BaCO_3$ peaks were located at 829^{o}C and 981^{O}C. The TG curve showed weight loss of 1% at temperature 788^{o}C and large weight loss of 8.25% at temperature of 1098^{o}C.

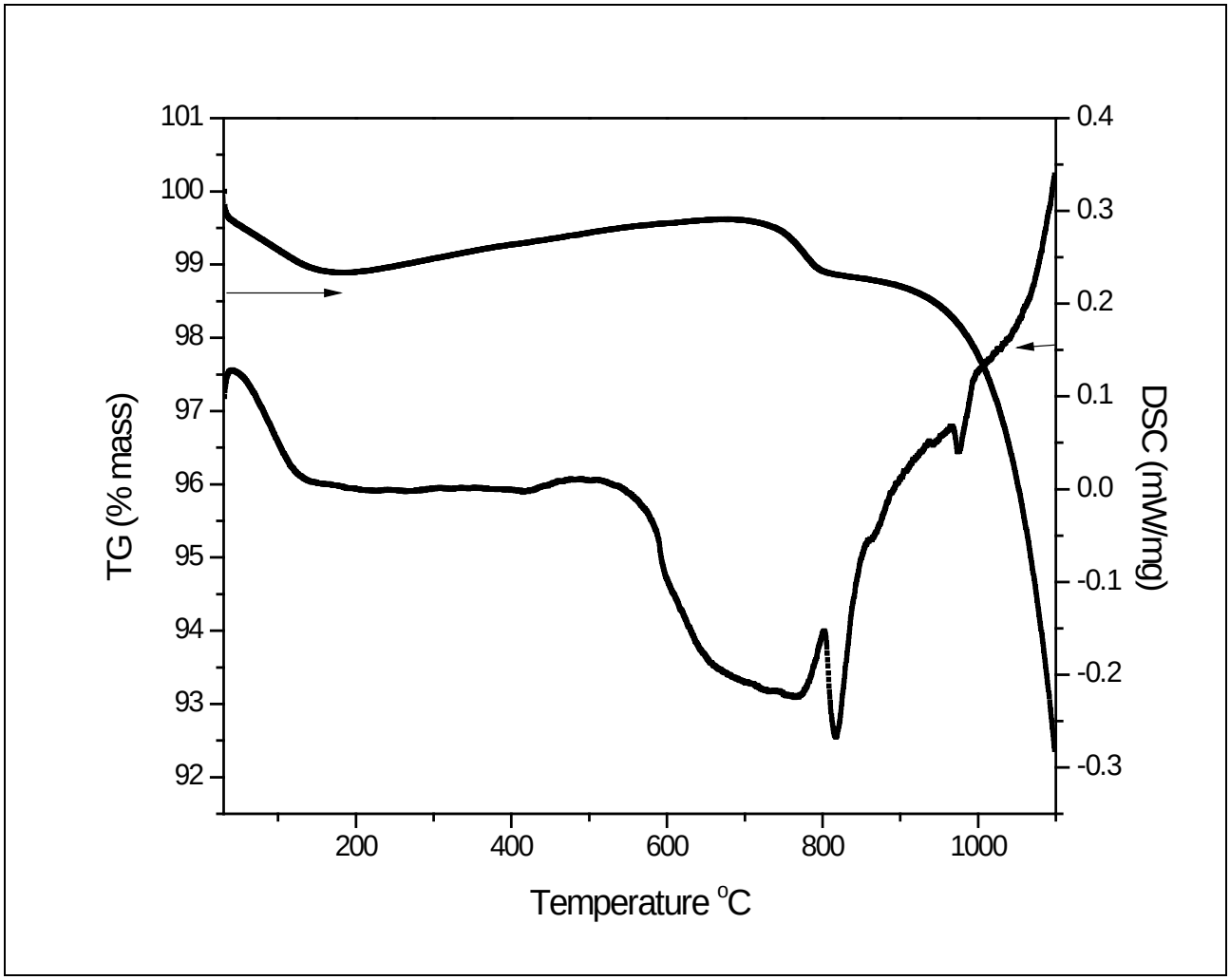

Figure 4: DSC - TG of the precursors

4.2.a. X-Ray diffraction of the calcined powder at 1100^{o}C for 1hr:

The XRD of the calcined powder at 1100^{o}C for 1 hour showed the perovskite structure with the cubic crystal system (JCPDS file no.-06-0399) of $BaZrO_3$.

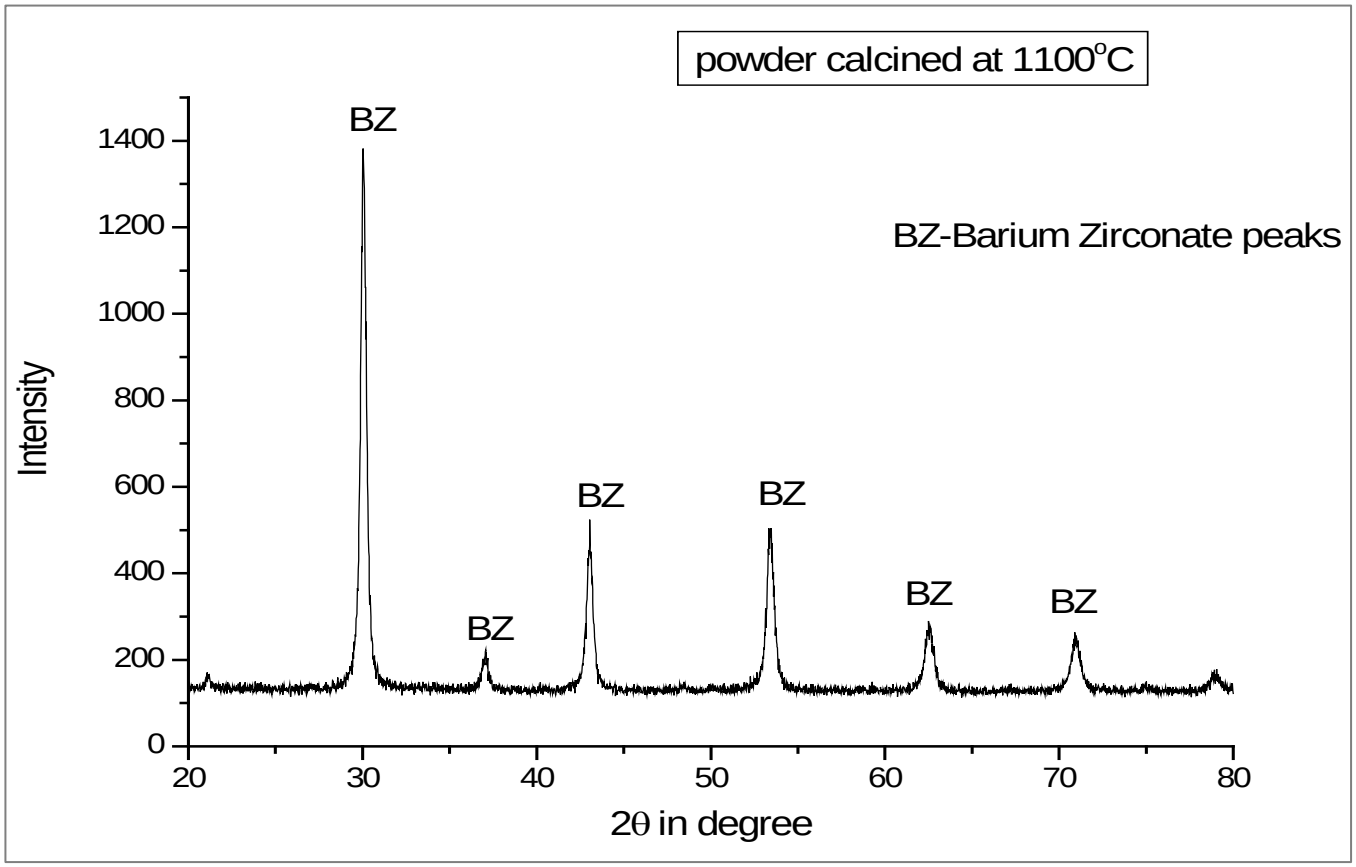

Figure 5: X-Ray diffraction pattern of 1100^{o}C Calcined powder

4.2.b. Composite plot of the XRD of calcined samples (800^{o}C & 1100^{o}C) and un-calcined mixed powder.

The powder which was calcined at 800^{o}C for 5hours revealed that the sample contained major peaks of ZrO_2 and $BaCO_3$ resulting in incomplete phase transformation to $BaZrO_3$. But, when it was compared with the calcined powder at 1100^{o}C it was found that some of the peaks belonging to $BaZrO_3$ and some to $BaCO_3$ phase.

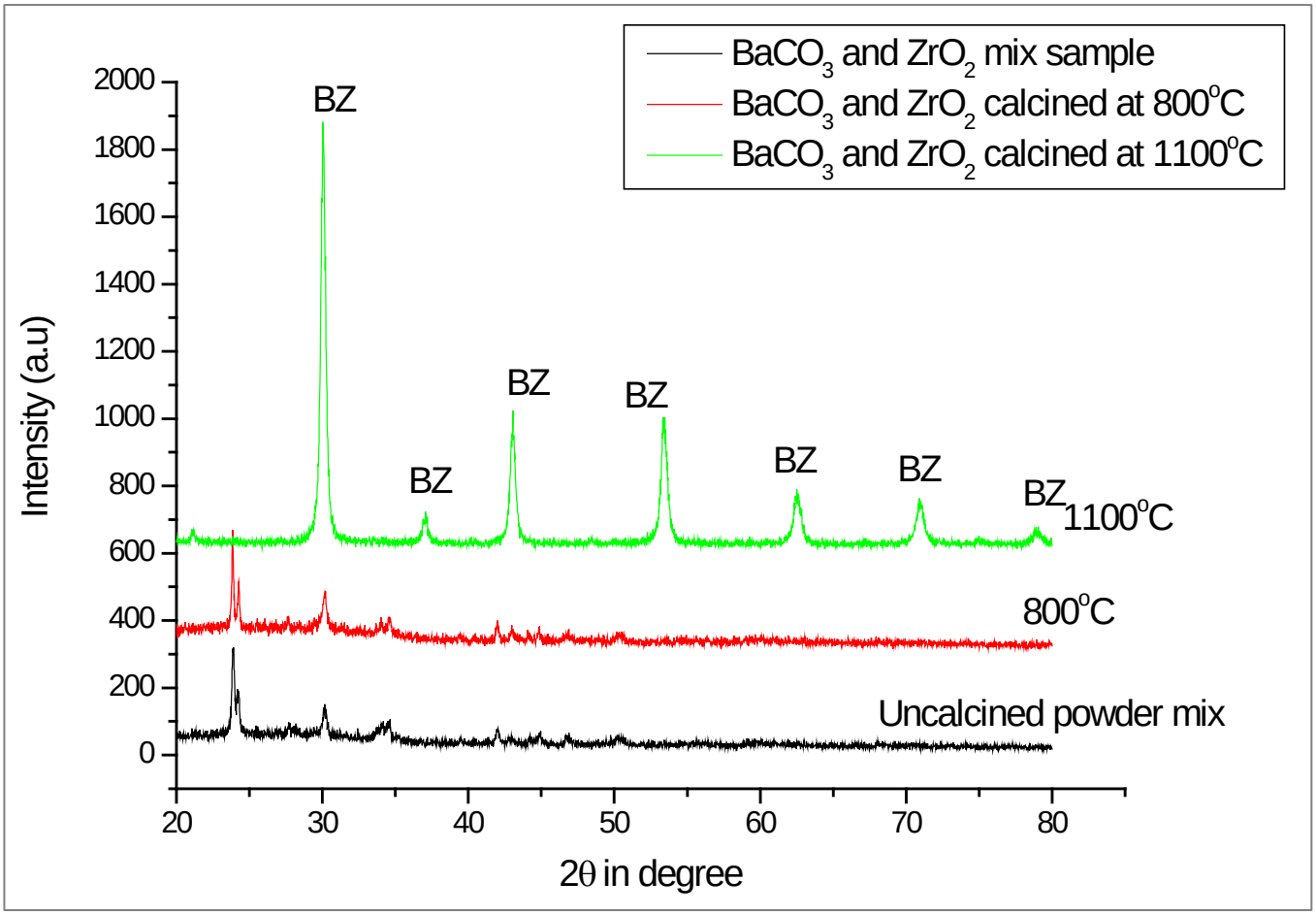

Figure 6: Composite plot of uncalcined and calcined precursors.

4.3. SEM of the precursor ($BaCO_3$) and its distribution on ZrO_2 surface.

The microstructure of the $BaCO_3$ powder obtained after precipitation of $BaCl_2.2H_2O$ and $NaHCO_3$ as shown in figure 8.1 shows the rod elongated shape with crystalline size of B=51.57nm. The elongated particle size ranges from length of 800-900nm and diameter =250-330nm.

The distribution phenomena of $BaCO_3$ and ZrO_2 nanopowders was studied under SEM(figure 8.2*)* and it was found that the rod shaped $BaCO_3$ was covered with nearly spherical shape of Yittria stabilized Zirconia to give maximum surface distribution

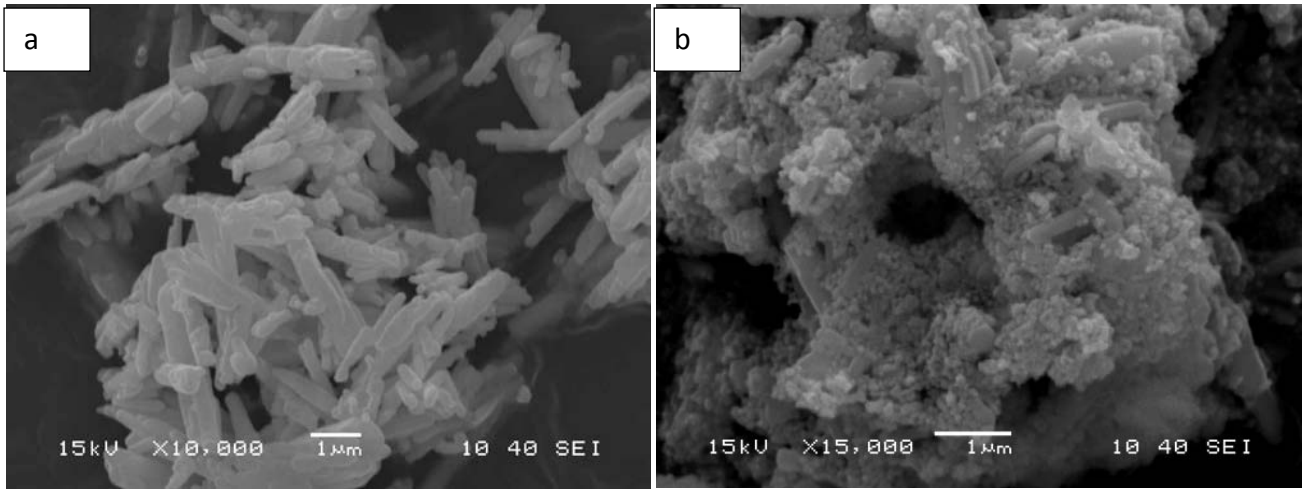

Figure 7: a) SEM of the $BaCO_3$ precursor b) SEM of the mixed $BaCO_3$ and ZrO_2 precursors

4.4. SEM image of Calcined powder at 1100°C for 1 hour

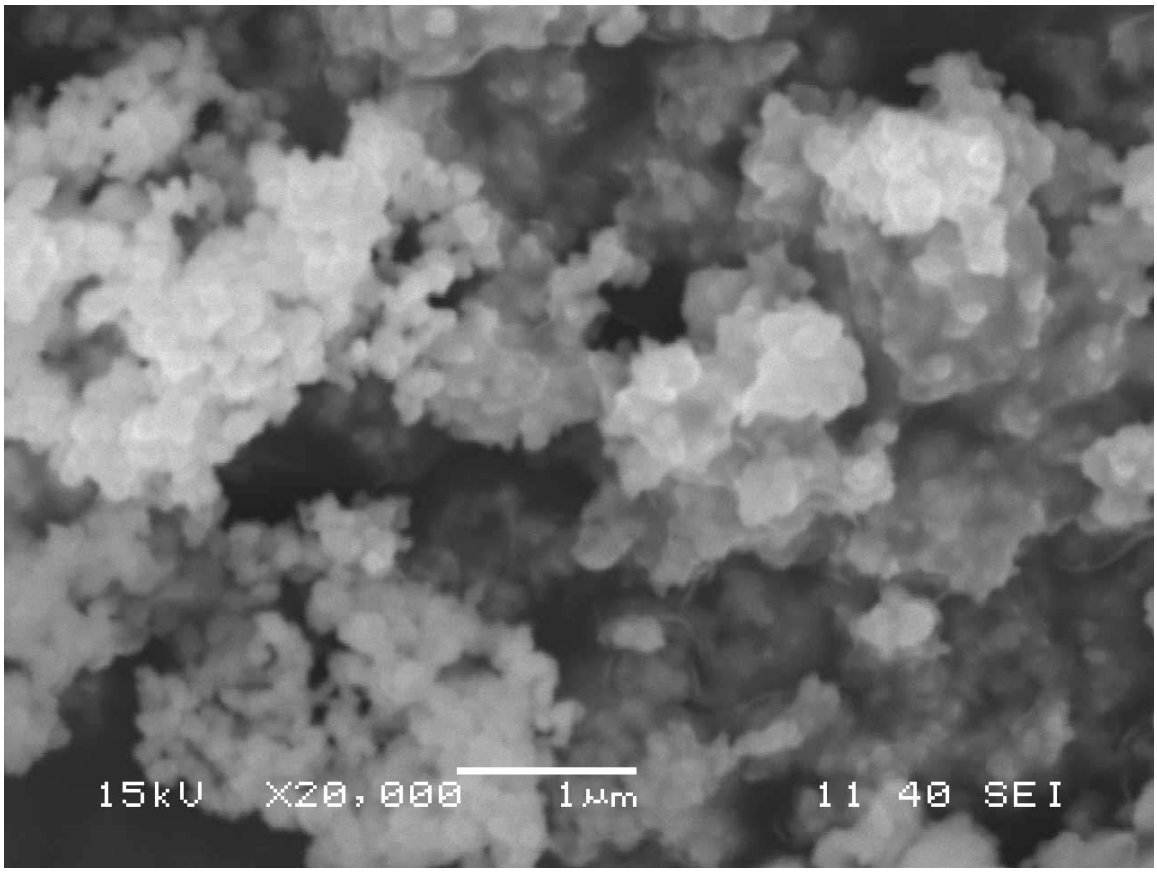

Figure 8: The calcined powder at 1100°C for 1 hour.

SEM microstructure shows that the particles are well formed and the shape is nearly spherical.

4.5. TEM Study of Barium Zirconate powder Calcined at 1100°C for 1 hour.

The particle size of the Calcined powder was found to be 110-130 nm.

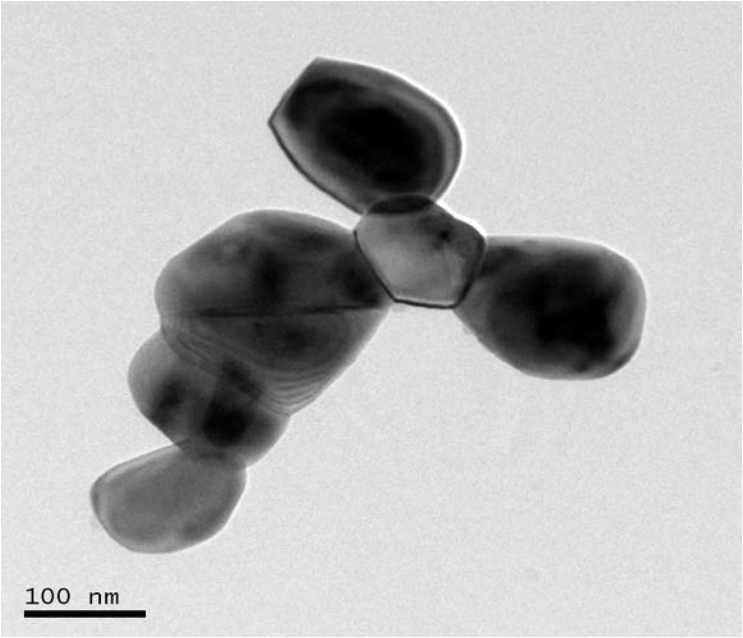

Figure 9: TEM of the 1100°C Calcined sample for 1 hour.

4.6. Surface area:

Brunauer-Emmett-Teller (BET) analysis was done to get the surface area of the powder calcined at 1100°C for 1 hour. The measured surface area was converted to equivalent particle size using the relation as under:

$$D_{BET} = \frac{6000}{\rho \, x \, S_{BET}}$$

Where ,

D_{BET} = Average particle size in nm

S_{BET} = Surface area expressed in $m^{2}.gm^{-1}$.

ρ = theoretical density of the $BaZrO_3$ in $gm.cm^{-3}$

4.6.a. Details of BET Analysis:

Sample weight= 0.1348gm

Outgas temperature=300^{o}C

Analysis time=43.3min

Surface area=8.92m^2gm^{-1}

Theoretical density=6.23gm. cm3

$D_{BET=}$108nm

4.7. Dilatometric study of green specimen prepared from $BaZrO_3$ nanoparticles:

The shrinkage behaviour of $BaZrO_3$ pellet which was shrinked after 1046^{o}C and continued to shrink at temperature 1450^{o}C. The shrinkage initially occurred at 554^{o}C due to decomposition of PVA which burned and formed pores inside the pellet.

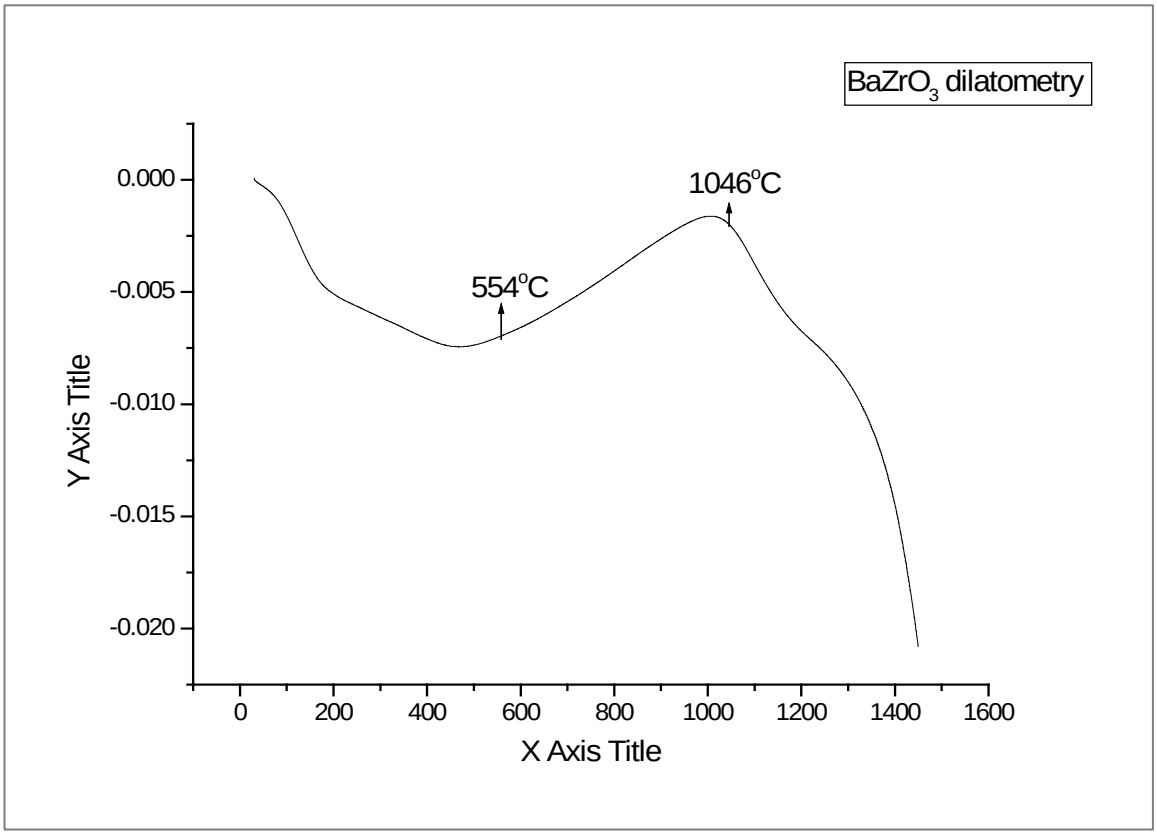

Figure 10. Dilatometry of the mix precursor sample.

4.8. The shrinkage data of different pellets

Table 4.1:Shrinkage value of the pellets:

Pellet No.	Firing Temp (^oC)	Weight in Gm		Diameter in mm		Thickness in mm	
		Before firing	After firing	Before firing	After firing	Before Firing	After Firing
1.	1250	0.8081	0.7698	12	11.9	2.06	2.02
2.	1350	0.8919	.8585	12	11.76	2.28	2.25
3.	1450	0.806	0.7674	12	11.16	2.10	1.93
4.	1550	0.7662	0.7293	12	10.54	1.96	1.78
5.	1650	0.8094	0.7130	12	10.01	2.08	1.58

The bulk density and relative density of the pellets was calculated using Archimedes principle as under:

Table 4.2 Density measurement of different pellets:

SI. No.	Firing Temperature (^oC)	Dry weight (W_{dry})	Suspended weight (W_{sus})	Soaked weight (W_{soa})	Bulk density (g/cm^3)	Relative density (%)
1.	1250	0.7633	0.6373	0.8557	3.50	56.179
2.	1350	0.8585	0.7096	0.9532	3.94	63.402
3.	1450	0.7674	0.6445	0.8271	4.19	67.4
4.	1550	0.7293	0.661	0.7963	5.39	86.67
5.	1650	0.7130	0.6556	0.7730	6.07	97.5

Above data shows that maximum relative density of 97.5% was achieved at firing temperature of 1650^oC for 1 hour.

4.9. XRD of sintered pellets:

The fired pellets at temperature 1250°C, 1350°C, 1450°C, 1550°C and 1650°C were characterized using XRD. As shown in above data, the pellets with increase in temperature became more and more dense resulting in increase in crystallinity as peaks are becoming sharper.

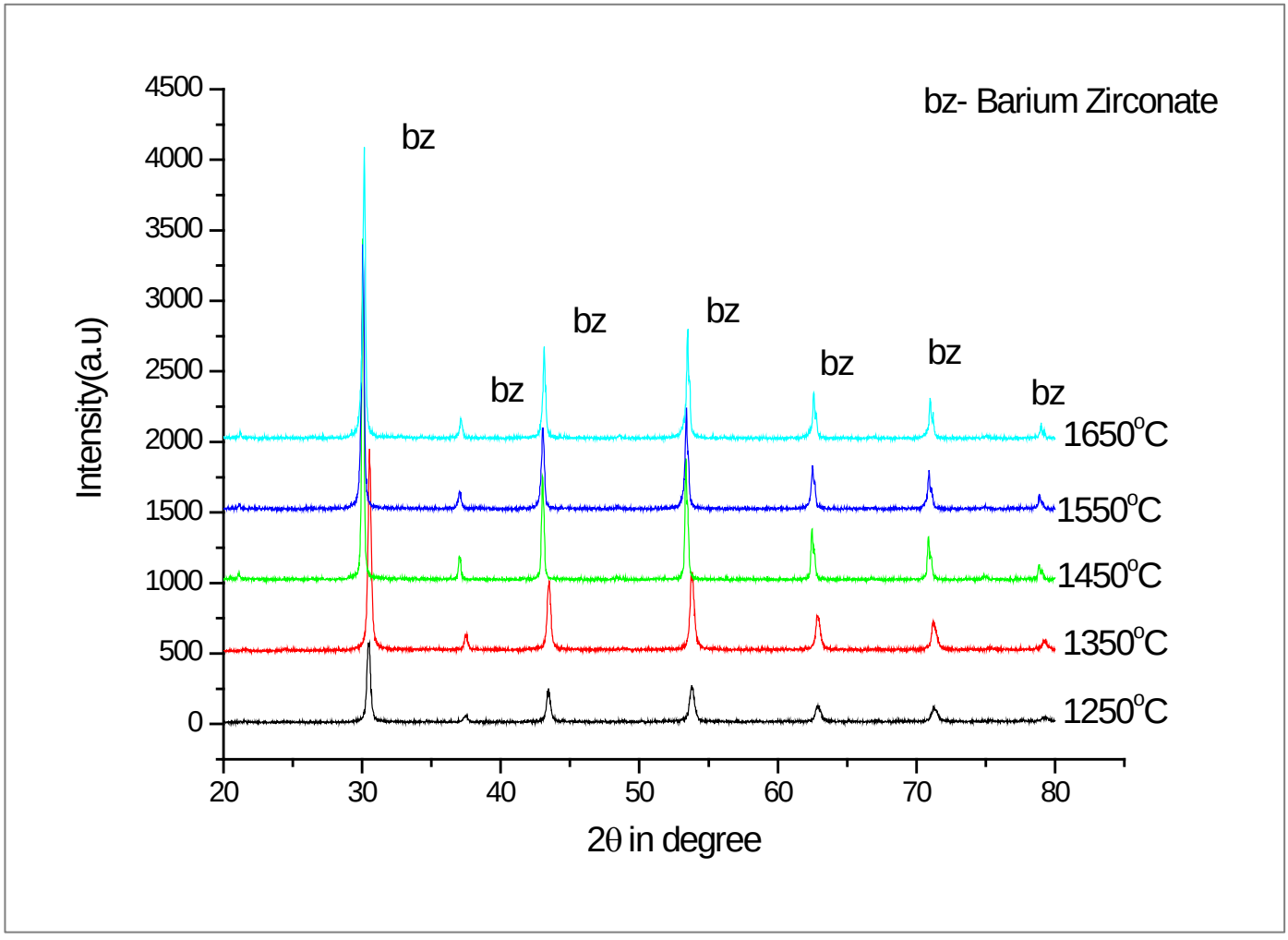

Figure 11: X-Ray diffraction pattern of sintered pellets at different temperature.

4.10. Densification and microstructure:

Listed are the figures after sintering of the green pellets:

a. Pellet sintered at 1250^{o}C for 1 hour.

The SEM microstructure shows that the pores are abundant in 1250^{o}C sintered pellets and the grain size was found to be 71.42nm.

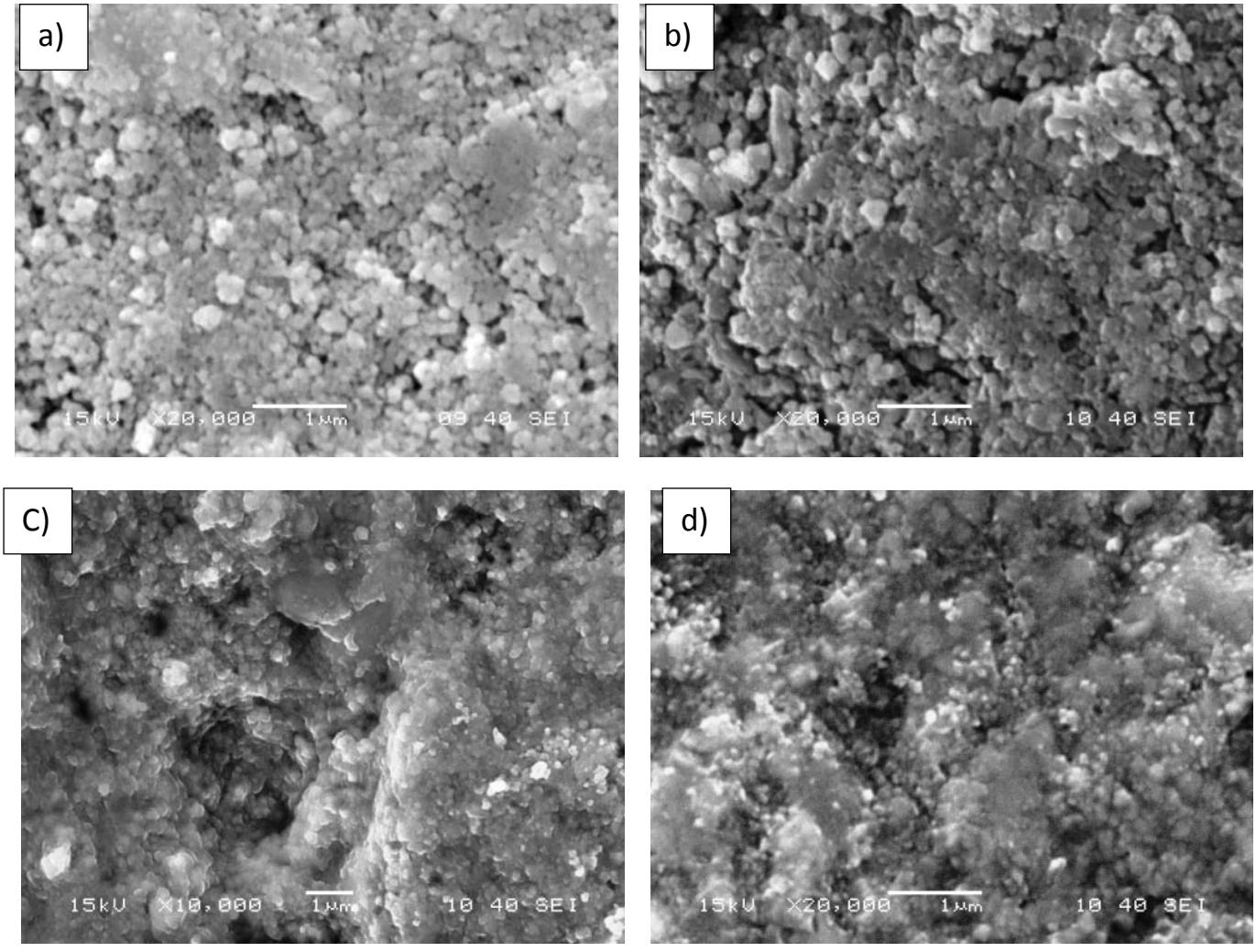

Figure12: SEM microstructure of a) 1250^{o}C sintered pellet b) 1350^{o}C sintered pellets c) 1450^{o}C sintered pellet d) 1550^{o}C sintered pellet

b. Pellet sintered at 1350^{o}C for 1 hour.

The densification is approaching with increase in temperature. The grain size of pellet was found to be 62.5nm.

c. Pellet sintered at 1450^{o}C for 1 hour

The grain size of the pellet was found to be 83.33nm.

d. Pellet sintered at 1550^{o}C for 1 hour

The grain size was found to be 100nm for pellet sintered at 1550^{o}C.

4.11. FESEM and EPMA analysis study at optimum condition.

The grain size was found to be 180-210nm for pellet sintered at 1650^{o}C for 1 hour. EPMA analysis shows that ZrO_2 was yittria stabilised.

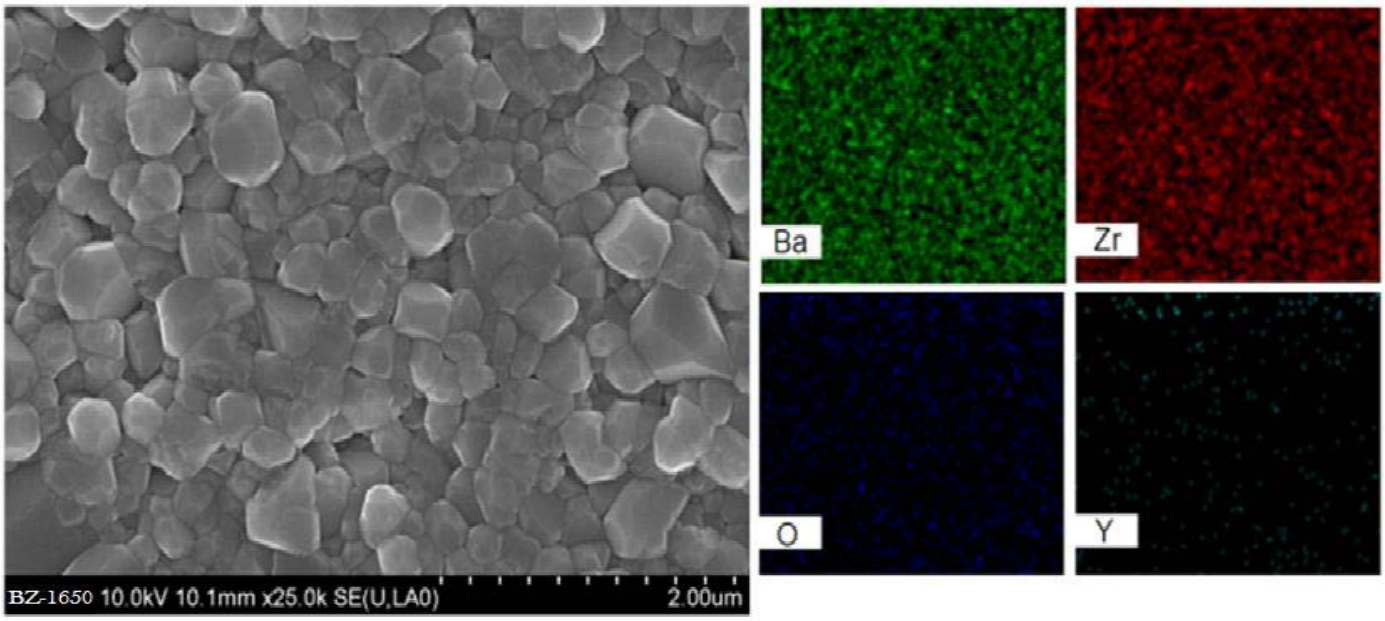

Figure 13: FESEM image of 1650^{o}C sintered pellet and EPMA analysis

4.12. Sintering temperature vs density plot and grain size (from SEM image)

With increase in temperature the grain size increases predominantly and the microstructure study shows that the grain growth increased with increase in temperature. The maximum densification achieved was 97.5% at 1650^{o}; sintered for 1 hour; with a bulk density of 6.07g.cm^{-3}.

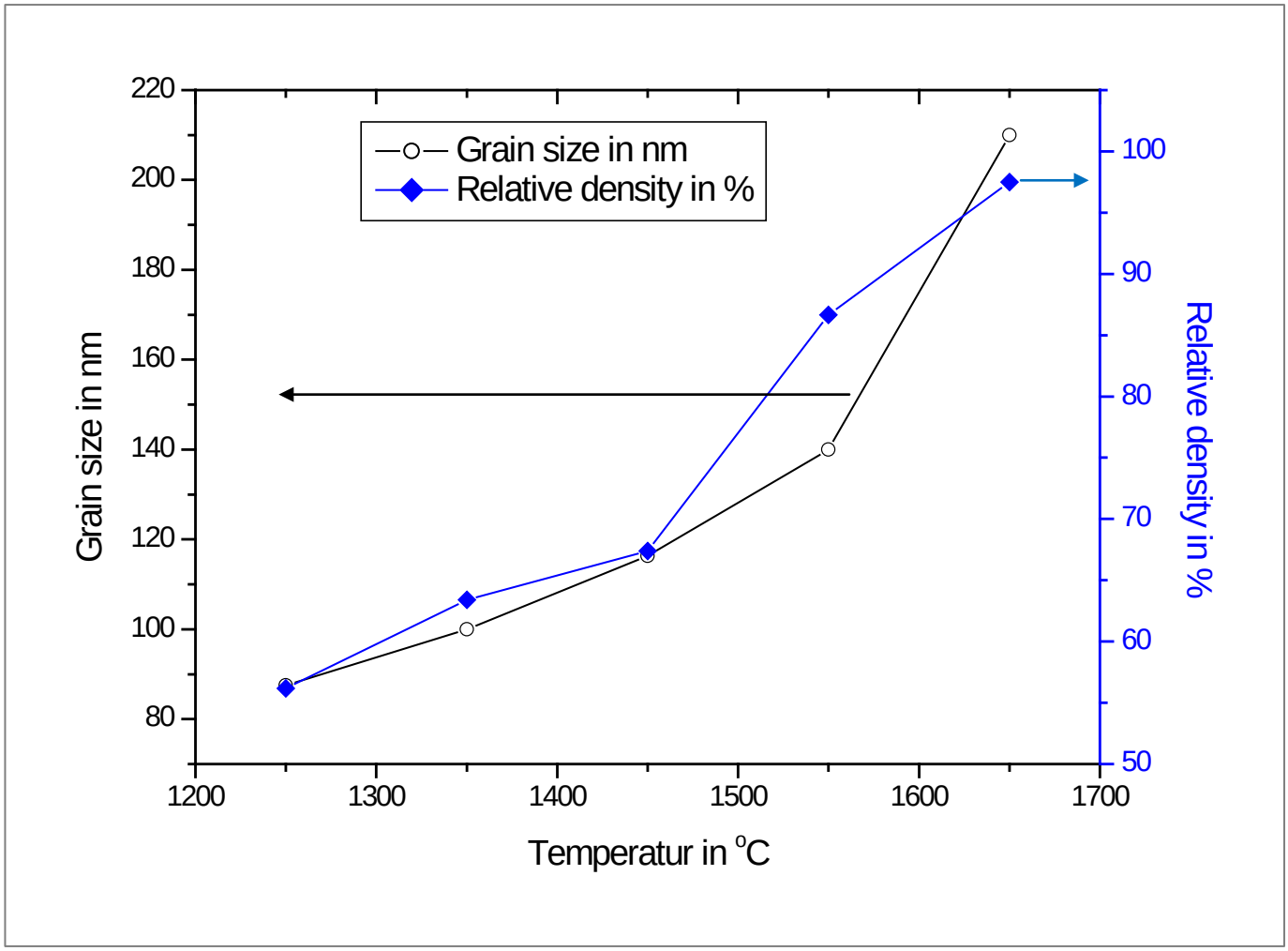

Figure 14: Grain size and relative density analysis with respect to temperature

Chapter-5

Conclusion

5. CONCLUSION:

a. Elongated $BaCO_3$ nanorod was prepared through wet chemical method

b. Yttria stabilized zirconia was act as nucleation site to develop the $BaZrO_3$ nanoparticles

c. The cubic perovskite structure of $BaZrO_3$ was obtained with particle size of 100 nm for calcined powder at 1100^oC for 1 hour.

d. The grain size of the pellets was increasing with increase in temperature due to grain boundary diffusion.

e. Maximum densification of 97.5% was achieved under controlled sintering at 1650^oC for 1 hour with bulk density of $6.05 gm.cm^{-1}$.

f. Densification behaviour of the $BaZrO_3$ pellets approached its maximum value after increasing the temperature of the sintering.

g. Yittria stabilized Zirconia acts as good stabilizing agent toward its phase transformation and formation of $BaZrO_3$.

5.1. Future scope of the work

- Particle size distribution analysis could be carried out to synchronize the grain size of sintered $BaZrO_3$.
- The processing condition can be optimised to carry out the work in order to produce the product in large scale synthesis.
- The shrinkage behaviour can determined with addition of some sintering additives like Fe_2O_3, CaO and MgO.

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