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**AN INVESTIGATION OF SUBMICRON PARTICLES
OF OXIDIC MATERIALS PREPARED BY
NEBULIZED SPRAY PYROLYSIS AND BY THE
SONOCHEMICAL METHOD**

**A THESIS
SUBMITTED IN PARTIAL FULFILLMENT OF THE
REQUIREMENT FOR THE DEGREE OF
MASTER OF SCIENCE
AS A PART OF INTEGRATED Ph.D. PROGRAMME**

**By
M. Kalaiselvam**

**TO
MANIPAL ACADEMY OF HIGHER EDUCATION
MANIPAL**

THROUGH



**JAWAHARLAL NEHRU CENTRE FOR
ADVANCED SCIENTIFIC RESEARCH
BANGALORE**

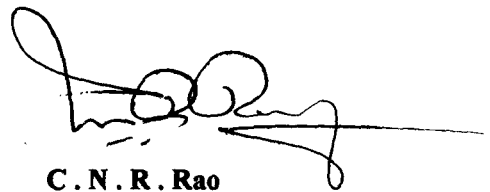
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STATEMENT

This is to certify that the work reported here has been carried out in the Nanomaterials laboratory at the Jawaharlal Nehru Centre for Advanced Scientific Research under my supervision.

A handwritten signature in black ink, consisting of several loops and a long horizontal stroke extending to the right.

C . N . R . Rao

**President
Jawaharlal Nehru Centre for
Advanced Scientific Research.**

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PREFACE

Ceramics have been with man since the beginning of civilization and at present it has found application in almost all places where solid materials can be used ranging from automobile engine parts to gas sensors. The composition of the ceramic may vary from simple metal oxide (Al_2O_3) to complex multicomponent metal oxides [$\text{Pb}_{0.92}\text{La}_{0.08}(\text{Zr}_{0.6}\text{Ti}_{0.4})\text{O}_3$] offering a wide range of properties ranging from mechanical hardness to ferroelectric memory. It is known that these properties vary with the size of the particles that constitute the bulk and it is also established that most useful properties are enhanced if size of the constituent particles is reduced. Hence engineering of sizes is about the same as engineering of properties. Hence we decided to synthesize metal oxides by nebulized spray pyrolysis and by sonochemical synthesis and study the effect on their properties.

The thesis comprises of two parts. In the first part of the thesis synthesis of ceramic powders of submicron sizes by the method of nebulized spray pyrolysis is discussed. The systems addressed are Al_2O_3 , ZrO_2 , $\text{Al}_6\text{Si}_2\text{O}_{13}$, $\text{PbZr}_{0.5}\text{Ti}_{0.5}\text{O}_3$. In the second part of the thesis sonochemical route to prepare nanoparticles of TiO_2 and ZrO_2 is discussed.

ACKNOWLEDGMENTS

I express my gratitude to Prof. C.N.R. Rao, FRS for suggesting the problems and for the inspiring guidance. I am grateful to him for his encouragement and his tolerance.

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I am grateful to Mr. Nagaraja Rao for the keen interest he has shown in my education. I also thank all the staff in the office for all the help they have rendered with the warmest of smiles. I should also thank Ms. E. Nandakumari and Mr. Basavaraj for helping me with all the warmth in all possible and almost impossible ways.

I am indebted to my friends who have been with me in good and bad times alike. I cannot mention every one of them but I should profess the contribution of Mr. I.V.R. Sivakumar, Mr. Saji Varghese, Mr. Srinivasa Gopalan, Ms. Gargi Raina, Ms. Sadika Sultana and Ms. S.T. Aruna.

The part played by my mother, father, brother and sister are the ones which only they could have. I shall ever be indebted to them.

PART I

SUBMICRON PARTICLES BY NEBULIZED SPRAY PYROLYSIS

I.1. INTRODUCTION

Solids composed of particles of size less than 100 nm are called nanostructured materials. These particles have a large surface area to mass ratio that results in a large fraction of atoms on the surface of the solid, where the environment (acting forces, coordination, etc.) is different from that of the bulk. Many properties of materials depend on the concentration of defects (unsaturated bonds) and as the number of surface defects increase with the surface area (the surface planes contain more defects than the other planes in the bulk) the properties are modified accordingly. Properties that are modified vary from sintering temperature¹ to electrical² and magnetic properties (superparamagnetism in Fe)³. Optical absorptions show the presence of discrete levels as the particles are composed of small number of atoms (typically of the order of 1000A)⁴. As the properties of the materials vary with the particle size, materials can be tailored to meet specific requirements .

There are various methods of preparing nanoparticles and these can be broadly divided into two categories Physical methods and Chemical methods. As these names imply, those processes in which only physical processes like drying, evaporation, milling etc. are involved are called physical methods and those in which a chemical reaction is involved are called chemical methods. The physical methods include laser ablation⁵, laser

Pyrolysis of sprays is a well established technique for depositing films and for making fine powders. Atomization of solutions can be done by a number of methods including pneumatic, electrostatic and ultrasonic methods. These atomizers differ in droplet size, rate of atomization and droplet velocity. The velocity of the droplet when it leaves the atomizer is important because it can determine the heating rate and the residence time of the droplet during the pyrolysis. The nozzle atomizers are very efficient in producing large quantities of powders but the ultrasonic nebulizers produce droplets of controlled size (as the droplet size varies inversely with the frequency of the transducer) which is very important for advanced applications. A variety of oxide films were prepared using this technique by Joubert et al.⁷, Wold et al.⁸, Messing et al.⁹ and Raju et al.¹⁰ This method is a simple and gentle chemical route to prepare nanostructured materials and was therefore chosen to prepare fine powders. The process of nebulized spray pyrolysis consists of three major process which are a) nebulization, b) transportation by carrier gas and c) pyrolysis of the spray in a furnace.

Unlike other spray pyrolysis methods, nebulized spray pyrolysis has a great amount of control over the characteristics of the droplets and hence that of the particles. Thus particles can be produced with a wide variety of sizes which can be used for a wide variety of applications¹¹. The parameters that control the morphology are atomization, the residence time in the furnace and furnace temperature. These are discussed below.

a) Atomization parameters : The amplitude and hence the capillary wavelength affect the diameter of the droplets produced.

The relationship being

$$D = \alpha \lambda_c \quad (1)$$

where D is the droplet diameter, α is a proportionality constant and λ_c is the capillary wavelength. From Kelvin's equation λ_c can be written as

$$\lambda_c = (8\pi\sigma / \rho f^2)^{1/3} \quad (2)$$

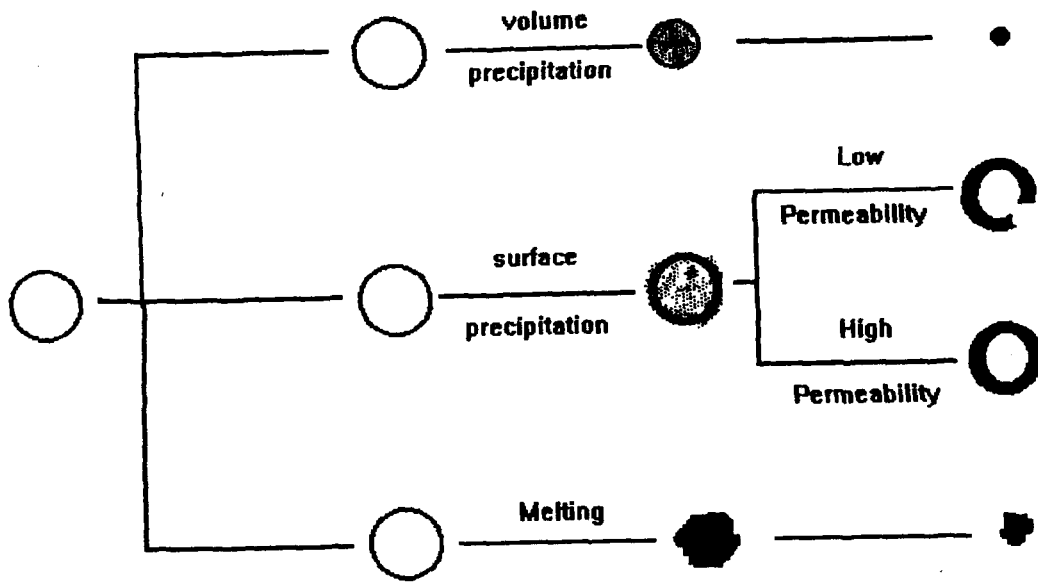
where σ represents the surface tension of the liquid, ρ its density and f the ultrasonic excitation frequency. Hence the droplet size varies as two-thirds power of the frequency.

b) Height of the liquid column : Langlet and Joubert have shown that the rate of atomization increases until it reaches a maximum and then it decreases peaking at an optimum value.

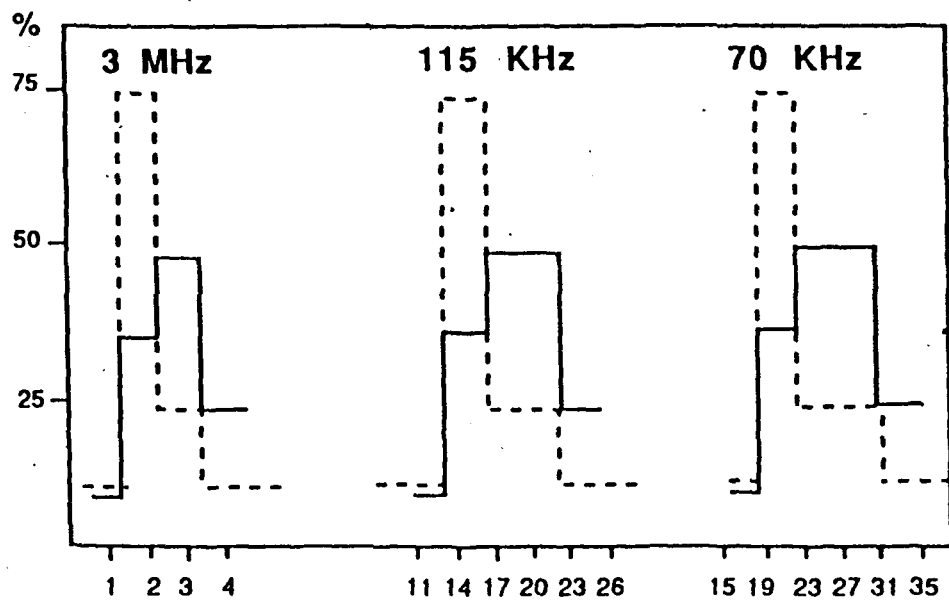
c) Rate of heating : If the rate of heating is high then there is a high tendency for surface precipitation of the droplets leading to the formation of hollow spherical particles. If the rate of heating is high and the precipitate is not permeable to the solvent then the solvent has to escape making a pore in the hollow and at times multiple pores are also formed.

d) Transport column : The transport column should not be very long and should not have sharp bends before reaching the furnace because these would increase the chances of coagulation of droplets and hence produce particles with more than one size.

e) Frequency : The relation between the frequency and the droplet diameter is according to relation(2). The amount of the liquid atomized depends on the frequency too and the dependence is plotted in fig.1.1b.



(a)



(b)

Fig.1.1. a) Effect of precipitation conditions on particle morphology and b) Quantity (----) and volume (—) distribution of water droplets obtained by ultrasonic atomization.

I.a.SCOPE OF THE PRESENT STUDY

Alumina is a very important ceramic. Its physical properties are in extremes. It has a very high value of mechanical hardness and melting point (>1800 and it depends on its purity). It has very low values of thermal and electrical conductivities. Alumina is hence used as abrasives, insulating fillers in high voltage junctions, dielectric in capacitors (breakdown voltage is 20 kVmm^{-1}) and synthetic ruby as laser source etc. Due to its high melting point and high insulating ability it is used as substrates for circuits and as packing for semiconductor microcircuits. As a support for catalysts alumina has established itself (common examples are $\text{Rh/Al}_2\text{O}_3$, $\text{Pd/Al}_2\text{O}_3$ etc.). It is also used for making high temperature laboratory wares.

Mullite properties similar to alumina and has a few more superior features like the ability to sustain thermal shocks. It is also a potential refractory material and is less brittle compared to alumina.

Zirconia is also a hard and refractory material. It has low thermal conductivity at low temperatures but at high temperatures it becomes conducting ($1200\text{-}2500 \text{ }^\circ\text{C}$) and it is therefore used as a heating element in oxidizing atmospheres. It undergoes phase transformation monoclinic \rightarrow tetragonal \rightarrow cubic before melting and is therefore stabilized by adding CaO , MgO , Y_2O_3 etc. Zirconia is also used in preparing piezoelectric ceramics like PZT and PLZT.

PZT is a piezoelectric material and hence it has application in various fields from pickups of gramophones to nebulizers for medical and industrial purposes.

Our aim is to prepare these materials of submicron sizes as the first step towards the study size effects.

I.2. EXPERIMENTAL

I.2.1. Apparatus

The schematic diagram of the apparatus locally fabricated for ultrasonically nebulized spray pyrolysis is shown in fig 1.2. It consists of two zones (a) the atomization chamber and (b) the pyrolysis reactor. The source liquid is kept in the atomization chamber which is designed such that the bottom of the chamber is having a cylindrical opening to fit the PZT transducer which oscillates at a frequency of 1.72 MHz. The special feature of this design is that the upper electrode of the PZT transducer is in direct contact with the source liquid. This gives the highest energy transfer to the liquid when compared to the non-contact method, which is used when there is a possibility of the electrode material to react with the solution. A minor disadvantage is that the liquid pH has to be maintained around 7. The liquid level in the atomization chamber is maintained by using a constant level burette which also allows the measurement of the volume of the liquid nebulized.

When a high frequency ultrasonic beam is directed at the liquid gas interface through the PZT transducer, a geyser forms at the surface of the liquid and the height of the geyser is proportional to the acoustic intensity and the physical properties of the liquid (vapor pressure, viscosity, density and surface tension). When the amplitude of the acoustic exceeds a threshold value, a continuous and regular mist (nebulized spray) is generated. The nebulized spray produced in the first chamber is transported by a carrier gas, which was dry air in all our experiments, introduced through a side port.

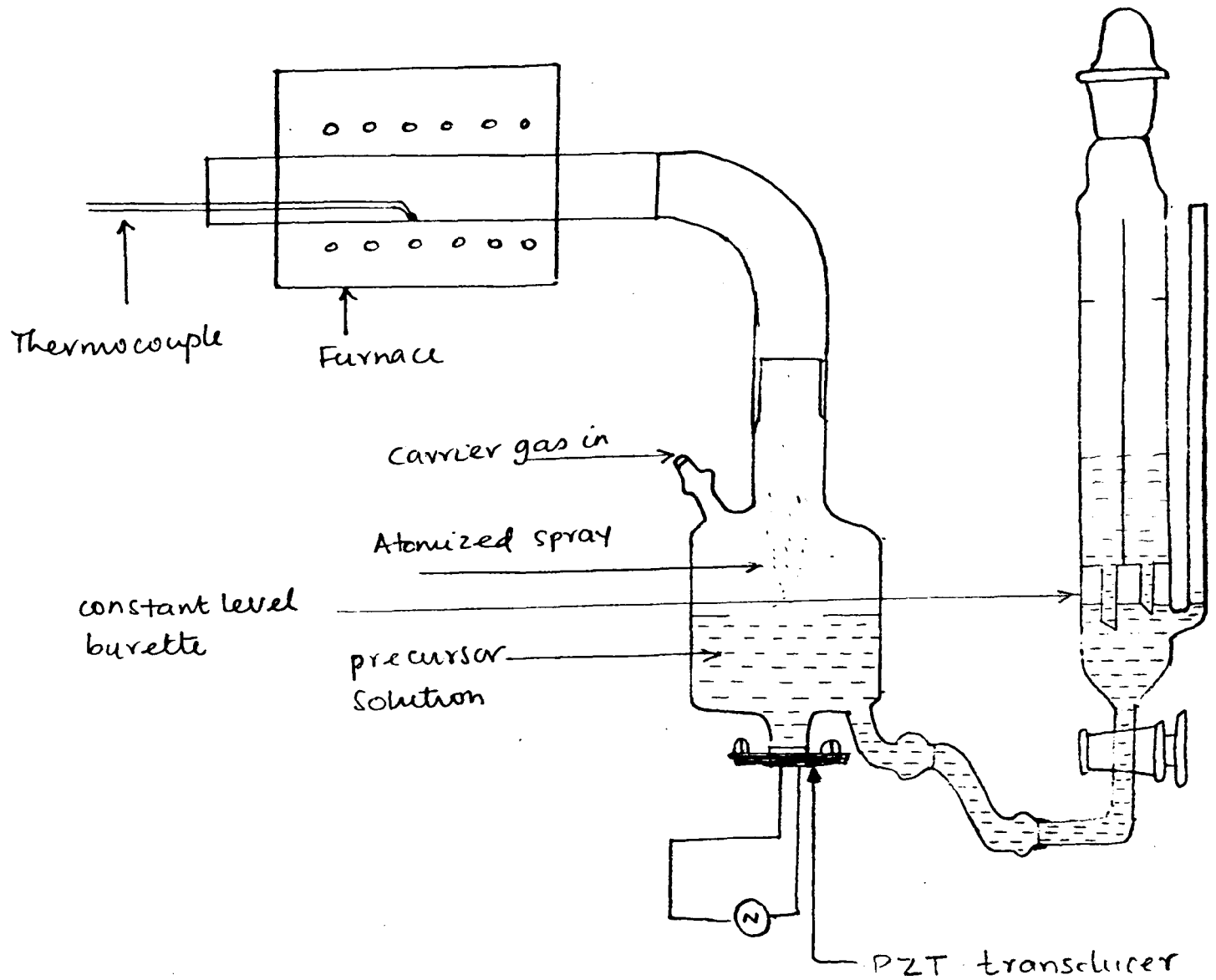


Fig.1.2. Schematic diagram of the nebulized spray pyrolysis apparatus used for the preparation of spherical oxide particles.

The second zone is a long quartz tube which is kept in a furnace at a preset temperature. The process of drying and thermolysis takes place in this zone and sintering is done in a separate furnace. The reason for having a single zone for drying and thermolysis is the following. If precipitation occurs slowly, there is a tendency for different components with different solubility in the droplet to precipitate at different times which would lead to inhomogeneity in composition. The product consisting of fine powder is collected in a collector fixed at the other end of the quartz tube.

1.2.2. Preparation

The precursors used for the synthesis of these oxides are listed in table 1.1. The solvent used for dilution was methanol for the whole of the study which was distilled over magnesium before use.

The glass and quartz components of the setup were thoroughly cleaned. The setup was assembled and the furnace was allowed to reach a preset temperature and the carrier gas flow was switched on. The 0.1 M of the precursor solution was loaded and the height adjusted such that there is a maximum spray density. After the nebulization starts the flow is adjusted such that the mist is dilute which is at about 6-8 lit/min. This dilution of mist is to reduce the probability of coalition of droplets. The experiment is carried out for 8 - 10 hours and the powder collected in a cotton based collector.

SYSTEM	PRECURSOR	TEMPERATURE (°C)
ZrO ₂	Zirconium propoxide	450
Al ₂ O ₃	Aluminum nitrate	400
Al ₆ Si ₂ O ₁₃ (mullite)	Aluminum nitrate & Silicon ethoxide	400
Pb(Zr _{0.5} Ti _{0.5})O ₃	Lead acetate, Titanium isopropoxide & Zirconium propoxide	400

Table 1.1. The precursors and the temperatures of the experiments.

I.2.3. Characterization

For scanning electron microscopy a Leica S440i was used and for EDX analysis Oxford Si(Li) detector was used. Image analysis was done employing a Leica Quantimet Q500MC. For X-ray diffraction studies a Seifert XRD 3000 was used. For TEM studies a JEOL 3010 was used.

I.3. RESULTS AND DISCUSSION

The particles formed are spherical in shape and have gaussian distribution. Some experimental runs show coagulation of droplets which result in the distribution curve peaking at two values or more values. As deposited particles are amorphous and in general are hollow and have pores on their surfaces.

The particle itself is composed of smaller particles which is seen in the calcined powders of the materials and this is only logical to expect. A surface, say (100) plane of silicon, if polished so that the plane produced is not exactly parallel to the plane but is inclined one degree with respect to the plane then, it develops steps and terraces to lower its energy. A similar phenomenon in 3-D would be the reduction of the material of the shell to form particles of smaller dimensions so that all the planes which enclose the mass are low index or reasonably higher index ones. The presence of pores on the surface indicates that surface precipitation predominates and the rate of diffusion of the solute is relatively less fig 1.1a. When the concentration of the solute is reduced, to say 0.001M, shells of very thin walls are formed and the escaping of the solvent molecules make larger pores leaving

nearly hemispherical solid behind. This is seen in fig 1.3 which is a TEM micrograph of ,
such particles of PZT.

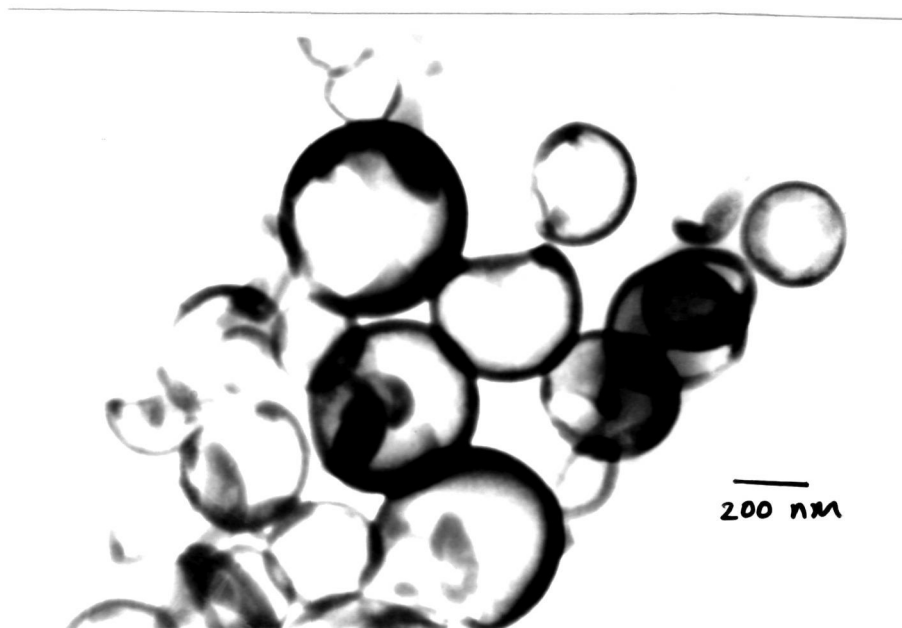


Figure 1.3. Nearly hemispherical shells of PZT formed by the decomposition of very dilute precursor solutions.

I.3.1. ZrO₂

The SEM image of particles obtained by nebulized spray pyrolysis of 0.1 M solution of zirconium propoxide in methanol at 723 K is shown in fig 1.4a. These particles are spherical and the size distribution of these particles is shown in fig 1.5. The distribution shows the particles to be in the range of 0.5 - 1.8 μm . The first peak at 0.5 micron is the true size of the particles and the other two are the particles produced by the agglomeration of two or more droplets. The particles are hollow shells and have pores on their surfaces that results from the predominance of surface precipitation and low permeability of the shell to the solvent. The as prepared particles are amorphous. The TEM image of as prepared amorphous particles is shown in fig 1.4b. and this image also confirms the spherical nature of these particles. However, after heating these powders at 823 K for 12 hours, they transformed to a tetragonal phase ($a = 3.64 \text{ \AA}$, $b = 5.27 \text{ \AA}$)[figs 1.6a and 1.6b]. These images establish that the particles remain spherical even after heat treatment and further indicate that the spherical particles in turn are composed of tinier particles. Further heating of the powder at 1023 K for 12 hours resulted in monoclinic phase($\underline{a} = 5.14 \text{ \AA}$, $\underline{b} = 5.21 \text{ \AA}$, $\underline{c} = 5.31 \text{ \AA}$ and $\beta = 99.21^\circ$) as confirmed by the X-ray diffraction pattern shown in fig 1.6c. The SEM and TEM micrographs of the powders calcined at 1023 K is shown in fig.1.7a and 1.7b respectively. The TEM micrograph shows the particle to be hollow and an aggregate of particles of much smaller size. The size of these individual particles which constitute these shells are, from Scherrer's equation, calculated to be 37 nm. The breadth of the diffraction lines in fig 1.6b and 1.6c imply the fineness of these particles.

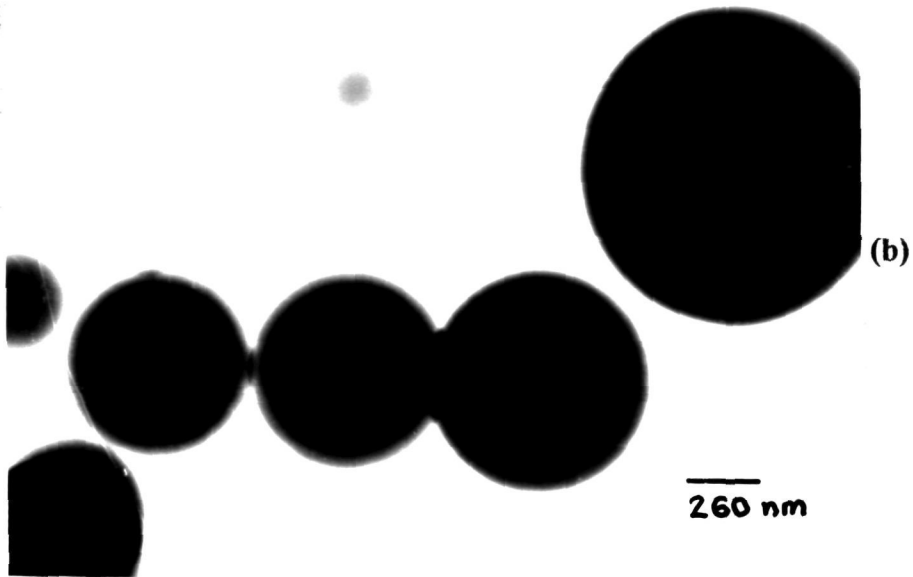
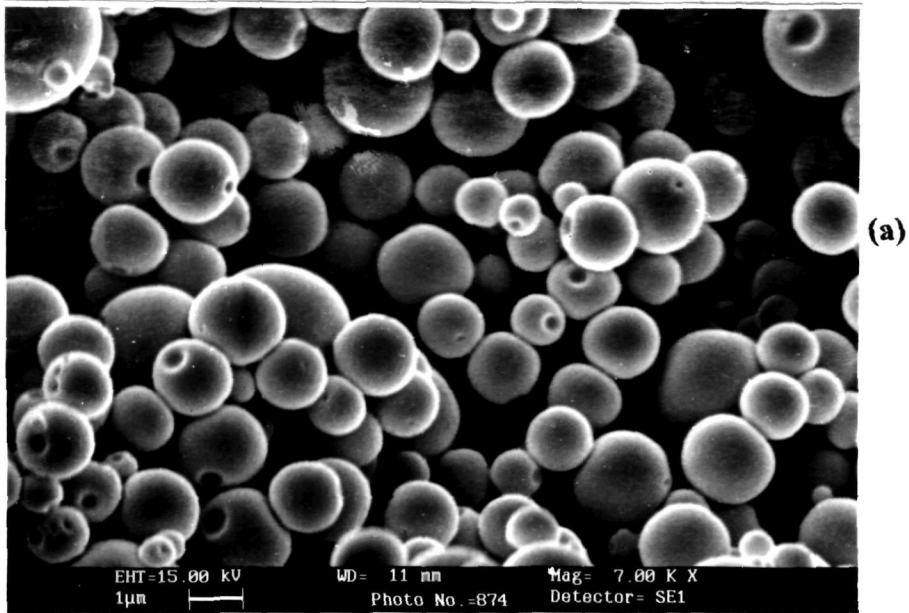


Fig 1.4. a) SEM micrograph and b) TEM micrograph of the as prepared powders of zirconia

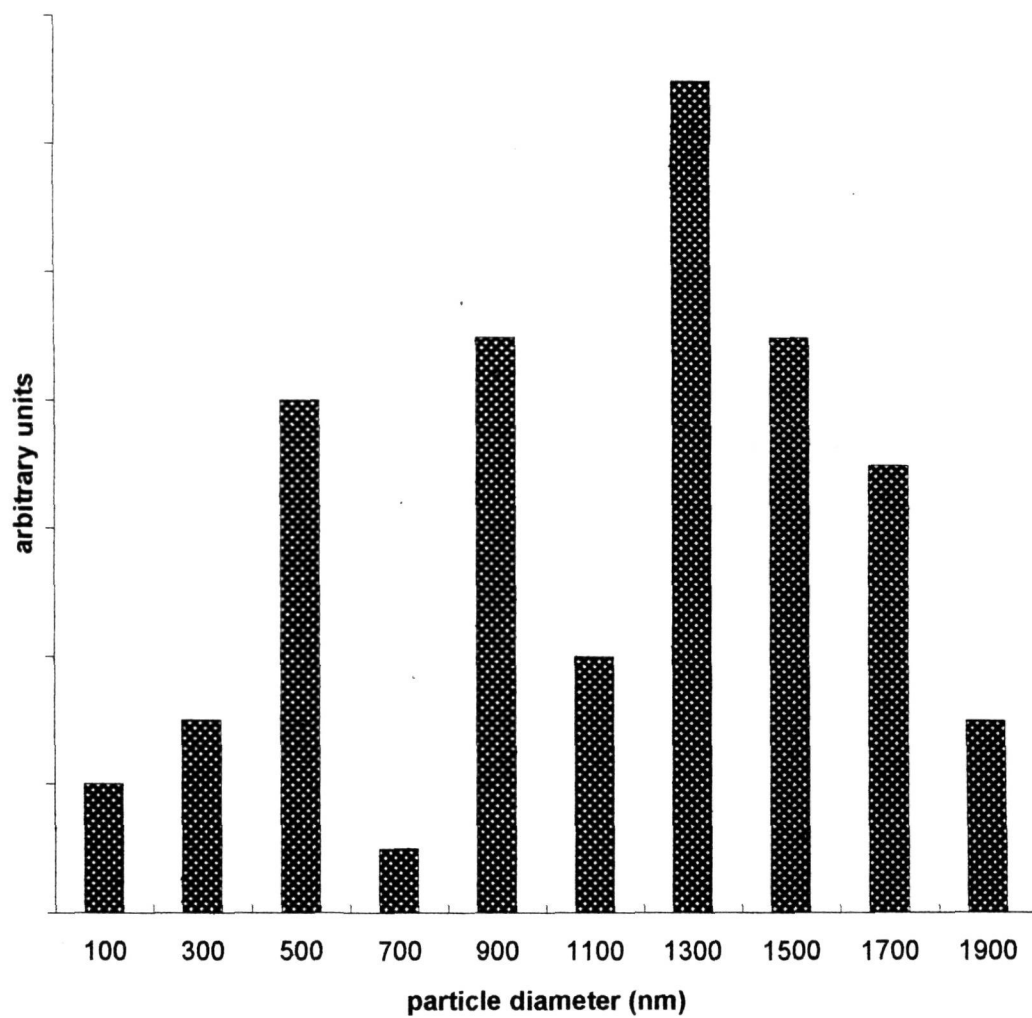


Fig.1.5. Particle size distribution of zirconia particles.

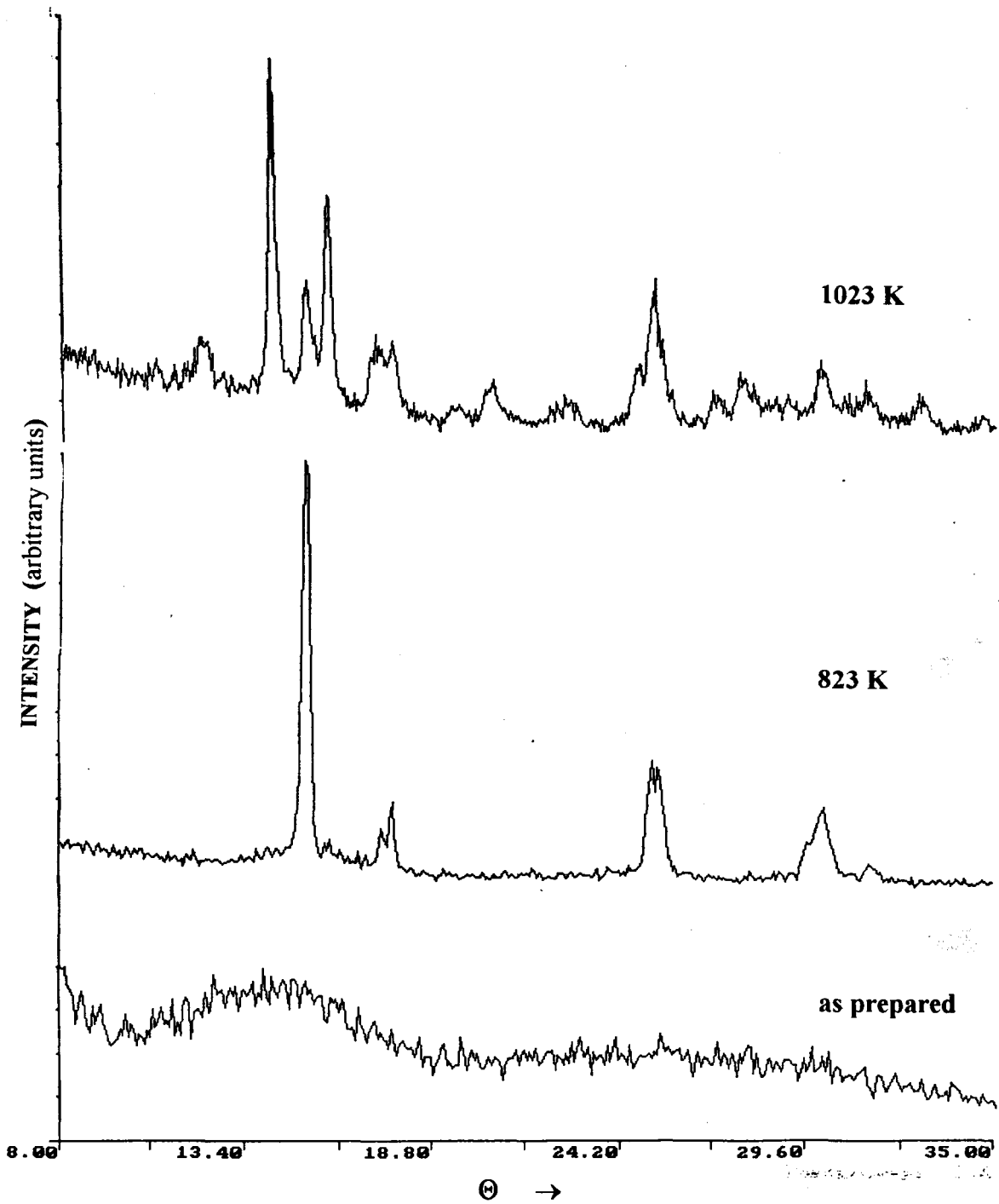


Fig.1.6. X-ray diffraction patterns of zirconia powders.

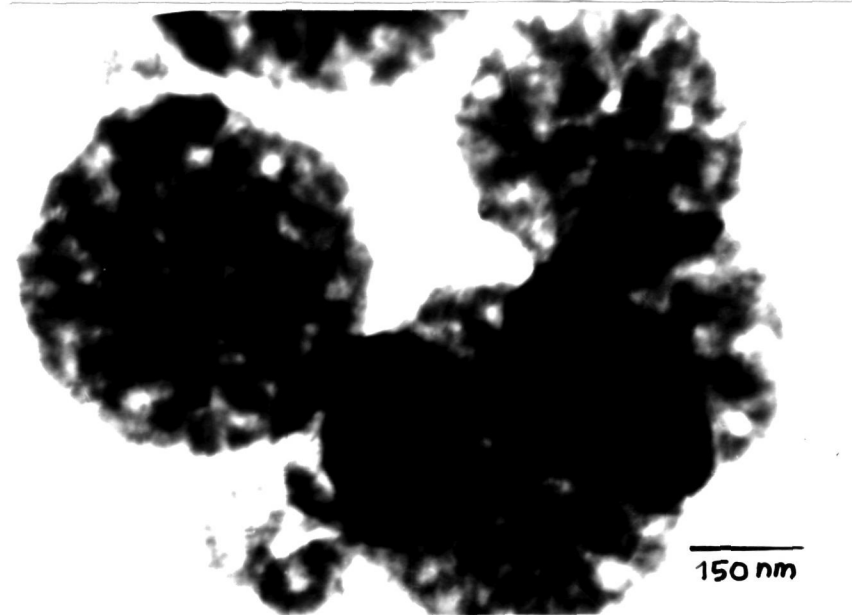
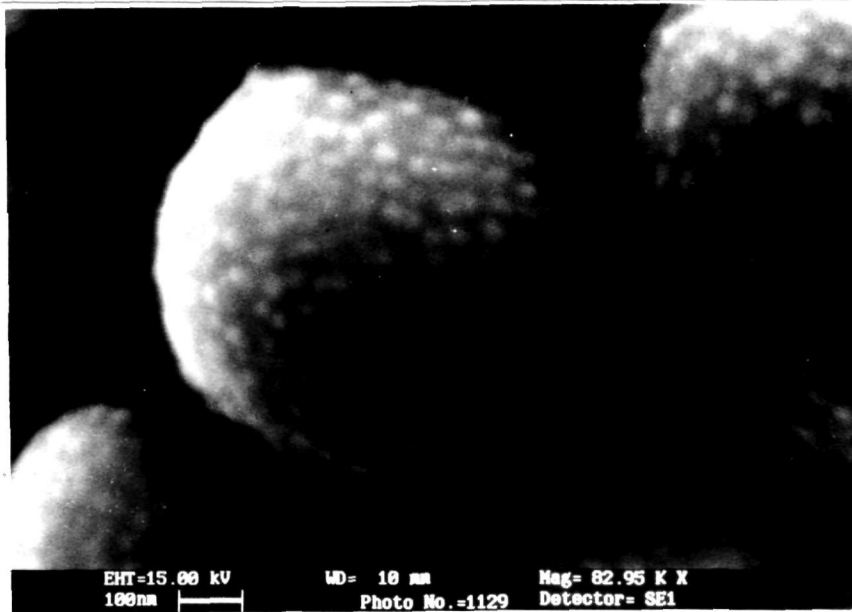


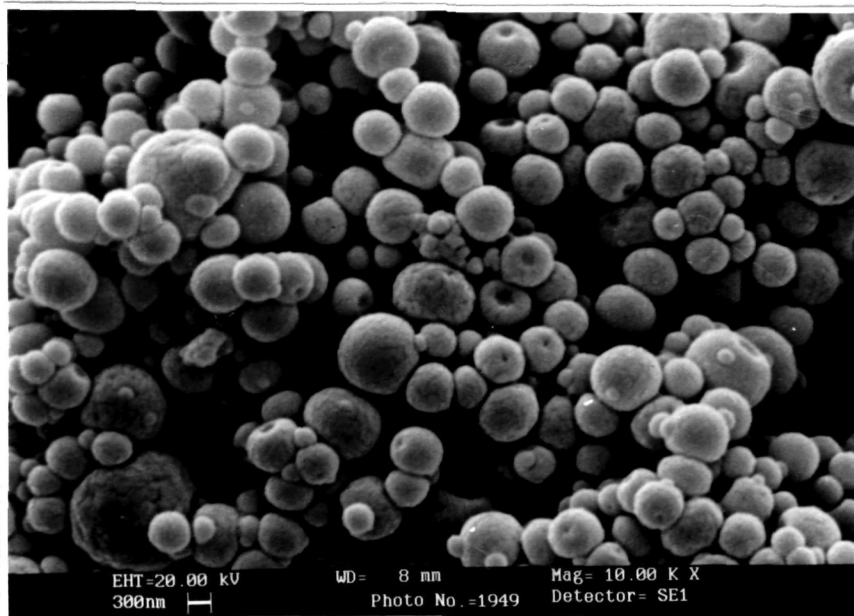
Fig. 1.7. a) SEM and b) TEM micrographs of zirconia particles calcined at 1023 K for 12 hours.

1.3.2. Al₂O₃

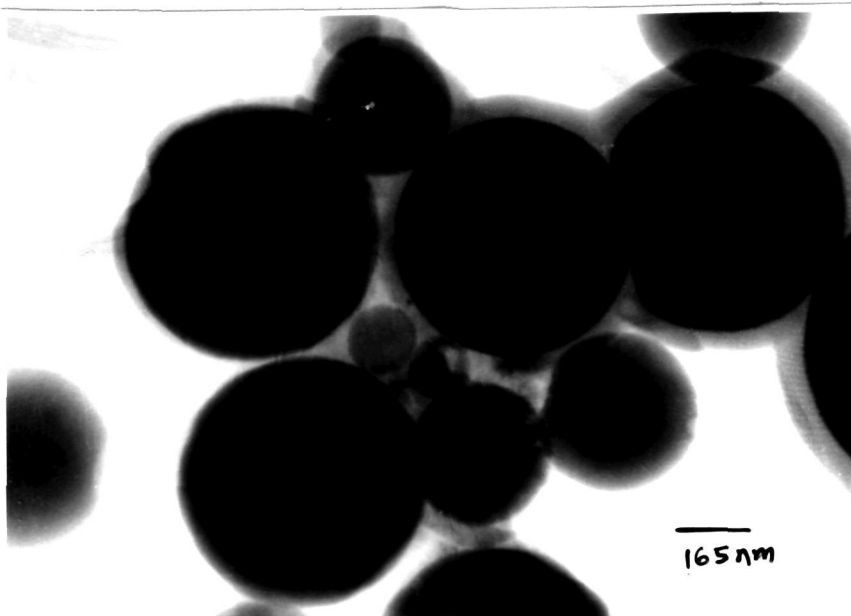
The SEM micrographs of the particles of alumina prepared by the nebulized spray pyrolysis of Al(NO₃)₃ is shown in fig 1.8a. and the corresponding TEM micrograph in fig 1.8b. These particles are hollow shells but unlike in the case of zirconia powders these particles seem to have a greater permeability to the solvent. This can be inferred from the lack of pores in all the particles(fig.1.8a). The particles are nearly spherical and the sizes are distributed with a mean diameter of about 400 nm (fig 1.9). The as prepared powders were amorphous (fig 1.10a) and they didn't crystallize even after heating at 1073 K for 12 hours (fig 1.10b). After heating at 1473 K for 24 hours they transformed to the α -phase (a = 4.755 Å, c = 12.984 Å)[fig 1.10c]. The SEM micrograph of the samples heat treated at 1073 K for 12 hours is shown in fig1.11a and the morphology of the particles are seen not to change upon heating. The powder heated at 1073 K showed broad lined indicating the fineness of these particles and the value of particle size estimated by Scherrer's equation is 10.2 nm. The SEM and TEM micrographs of the powders are shown in figs1.10a and 1.10b respectively and the annealed particles are confirmed to be hollow with pores. It is also clearly seen in fig 1.11b that every single particle is composed of a large number of smaller particles of size less than 50 nm.

1.3.3. Al₆Si₂O₁₃ (Mullite)

The particles prepared by nebulized spray pyrolysis of the precursor mixture (table1.1) were spherical and their SEM micrograph is shown in fig1.12a.



(a)



(b)

Fig.1.8. a) SEM and b) TEM micrographs of as prepared alumina particles.

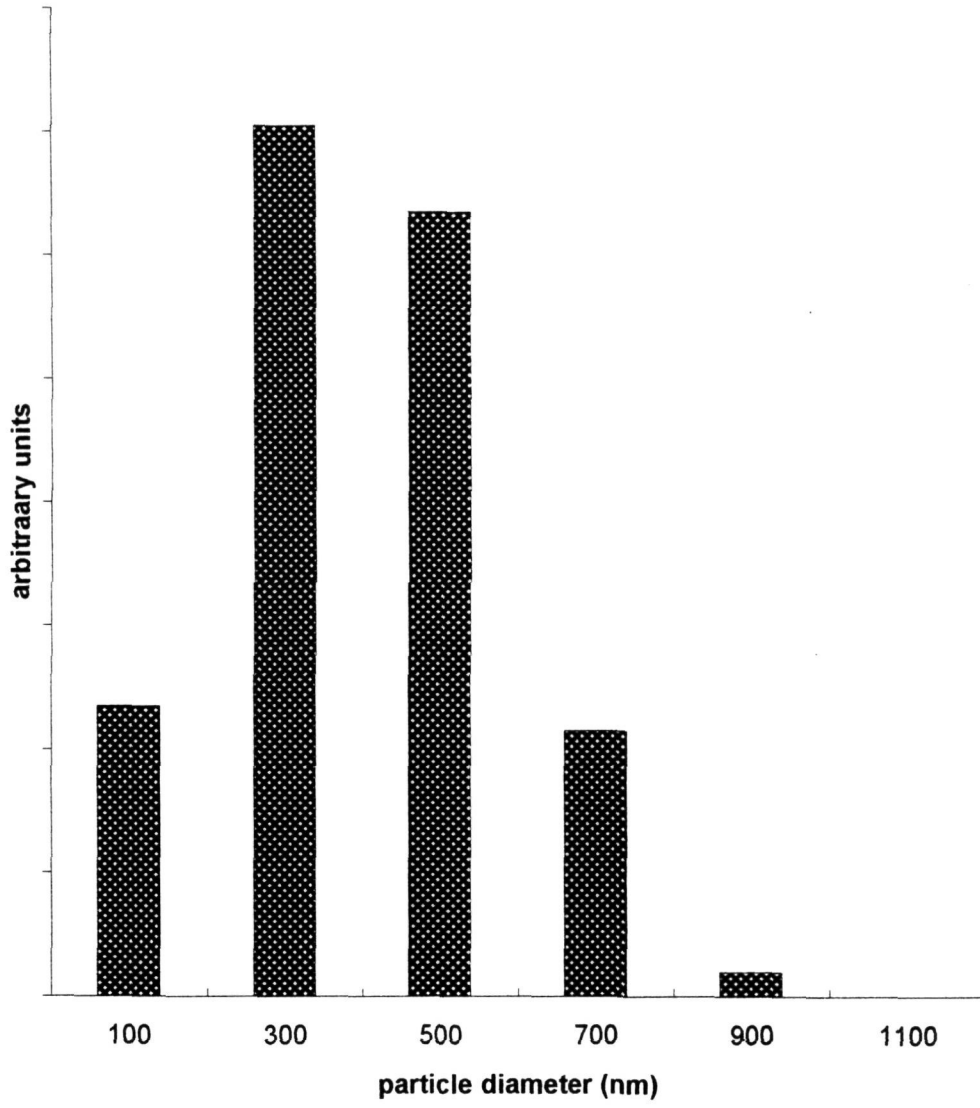


Fig.1.9. Particle size distribution of alumina particles.

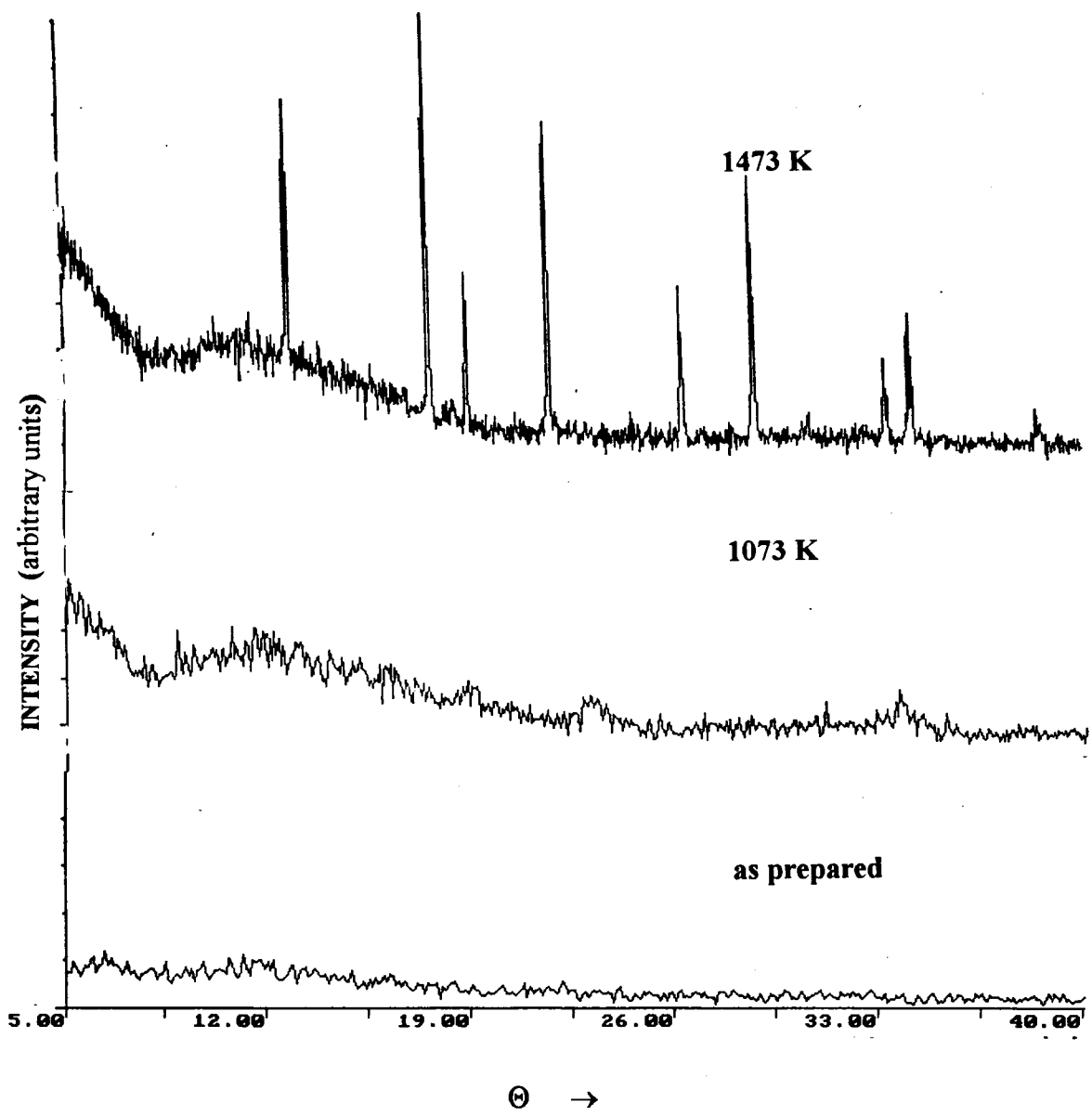
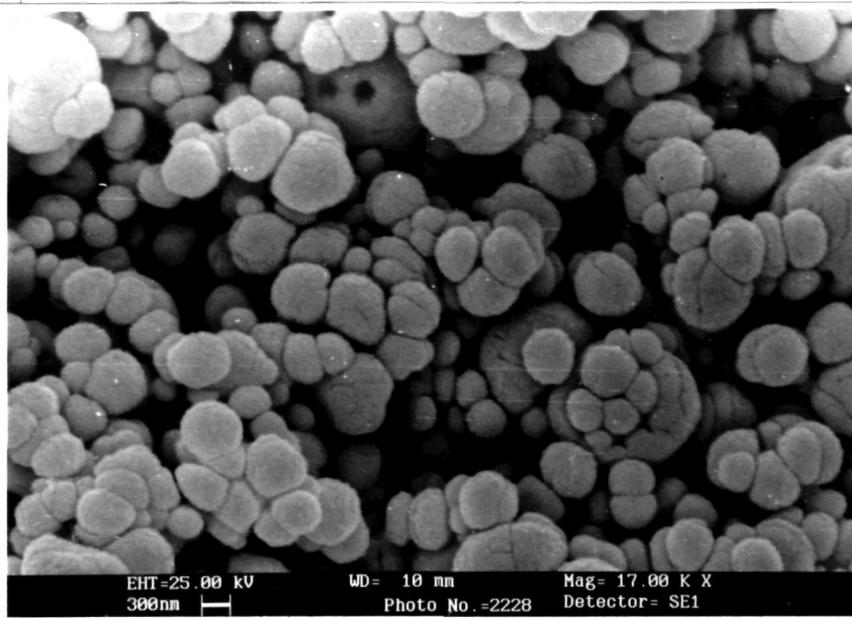
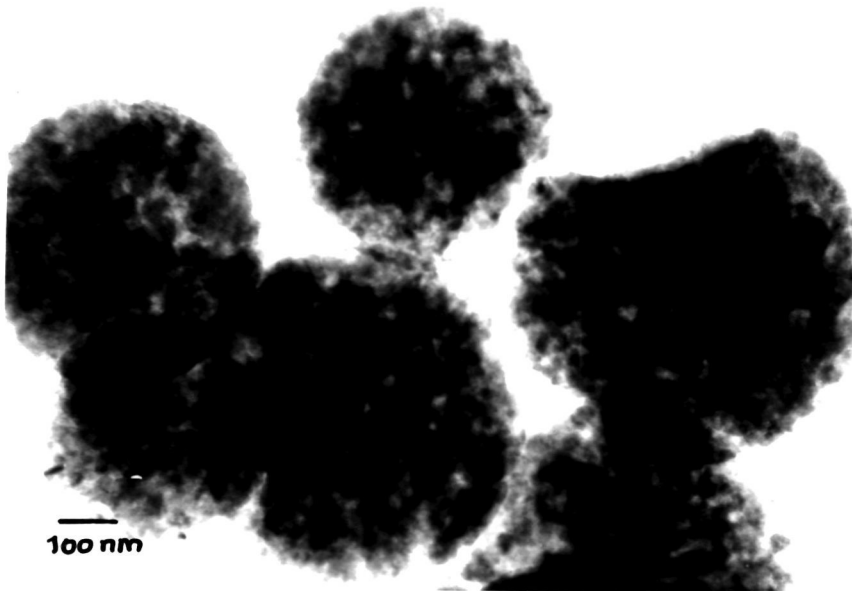


Fig.1.10. X-ray diffraction patterns of alumina powders.

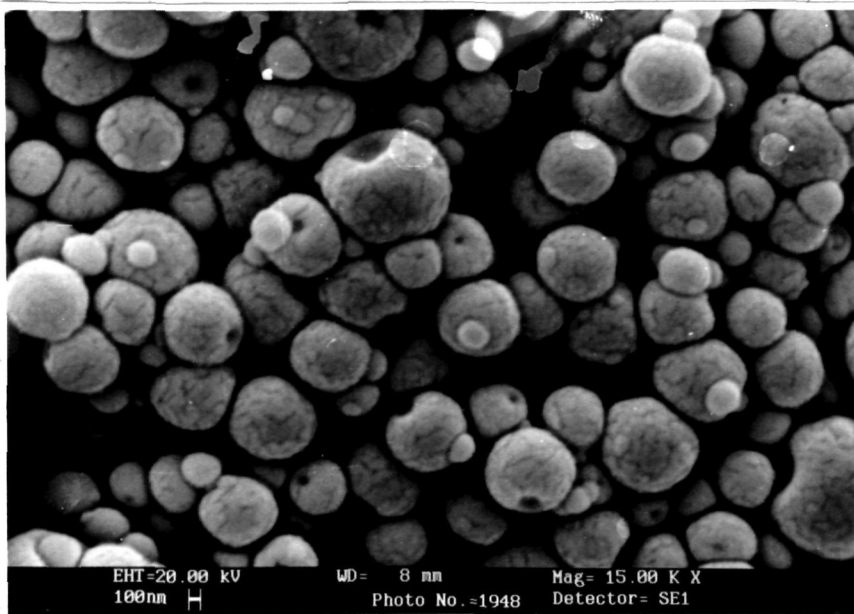


(a)

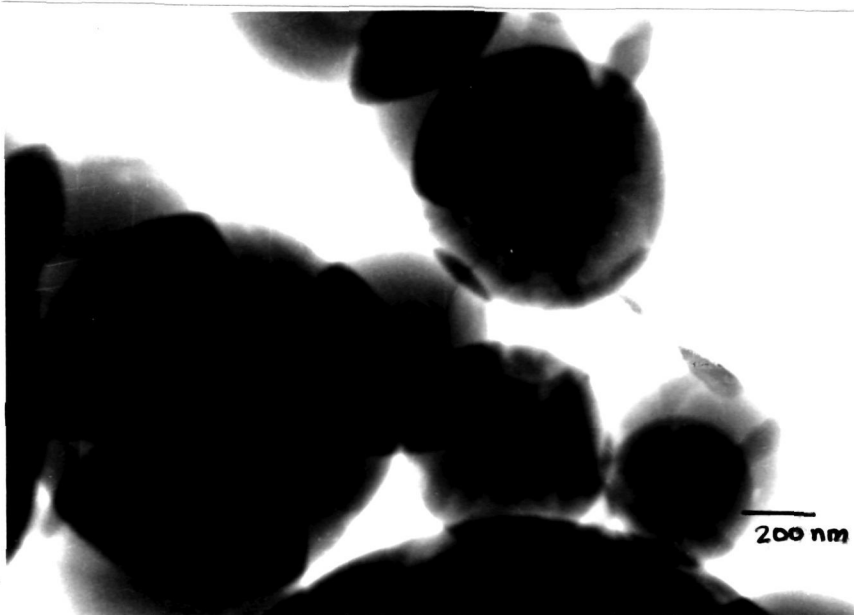


(b)

Fig. 1.11. a) SEM and b) TEM micrographs of alumina particles calcined at 1473 K for 24 hours.



(a)



(b)

Fig. 1.12 a) SEM and b) TEM micrographs of as prepared particles of mullite.

The TEM micrograph of these particles is shown in fig 1.12b which shows the particles to have a smooth surface. The particle sizes have a gaussian distribution with maximum number of particles in the range of 200-400 nm fig 1.13. The particles have a rough surface morphology and it does not change upon calcination. The particles are hollow and have pores on their surfaces as in other systems. The powder crystallized after calcining the as prepared sample at 1473 K for 24 hours. The SEM and TEM micrographs of the calcined sample are shown in figs. 1.4a and 1.14b respectively. The X-ray diffractogram is shown in fig 1.15. The first peak correspond to silica which was phase separated during calcining. The TEM micrographs also show the presence of two phases. The X-ray pattern shows broad peaks confirming the small size of the constituent particles and the their values estimated by the Scherrer's equation is 37.8 nm. The chemical composition of the particles was confirmed by energy dispersive X-ray analysis and it showed Al : Si ratio to be 3 : 1 (fig 1.16).

1.3.4. $\text{PbZr}_{0.5}\text{Ti}_{0.5}\text{O}_3$

The particles produced by the nebulized spray pyrolysis of the precursor solution (table 1.1) were spherical and uniform. The SEM and TEM images of the powders of PZT as obtained by pyrolysis at 673 K are shown in figs 1.17a and 1.17b respectively. The particle size distribution is shown in fig 1.18 in which we see that the maximum number of particles are centered around 300nm. This powder is amorphous as revealed by the electron and X-ray diffraction pattern. The latter is shown in fig 1.19a. After heating the amorphous powder at 823 K for 12 hrs, it transformed into the stable tetragonal phase with $a = 4.0655 \text{ \AA}$ and $c = 4.0646 \text{ \AA}$.

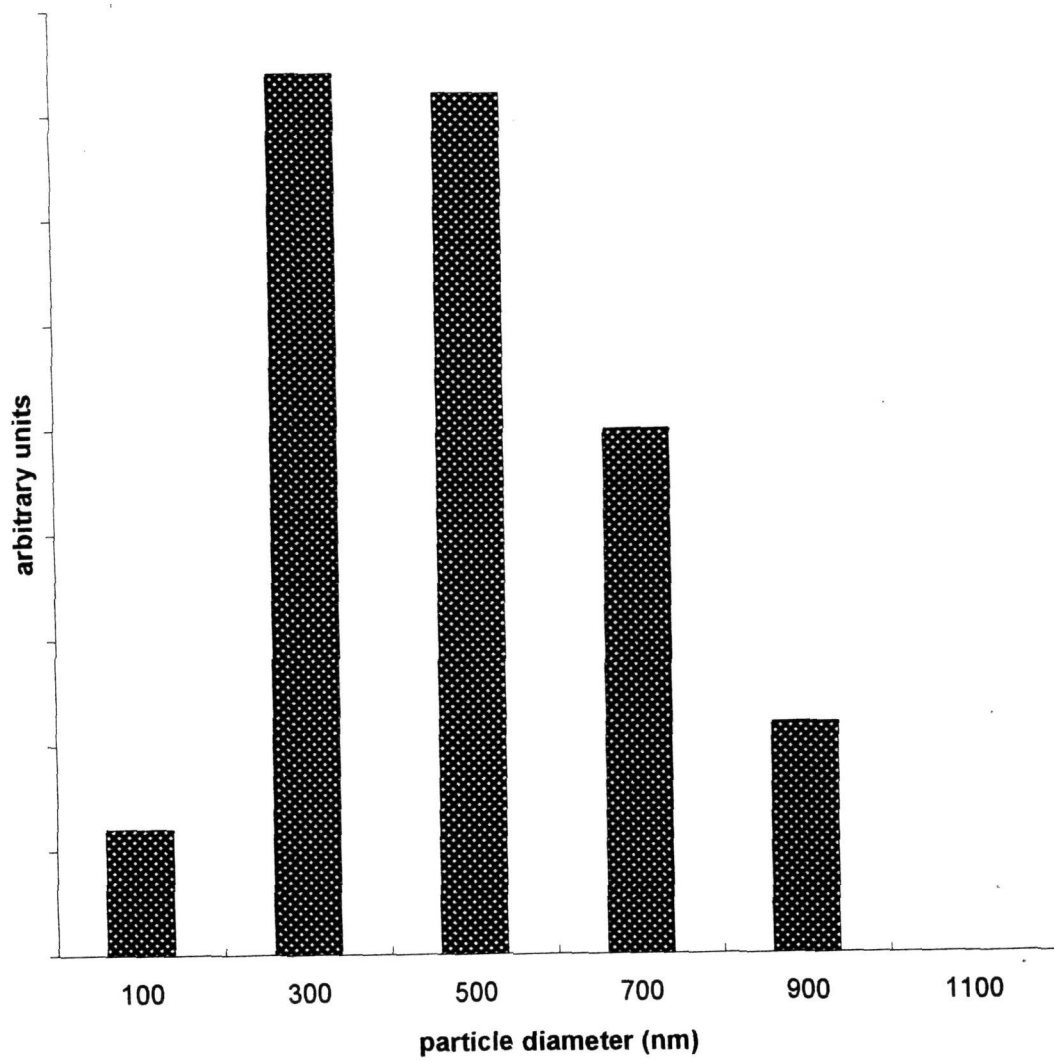


Fig 1.13. Particle size distribution of mullite particles

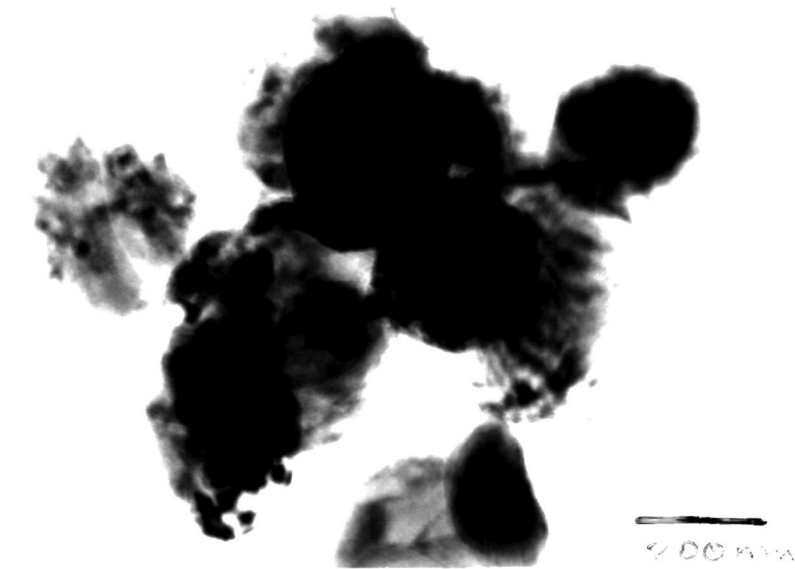
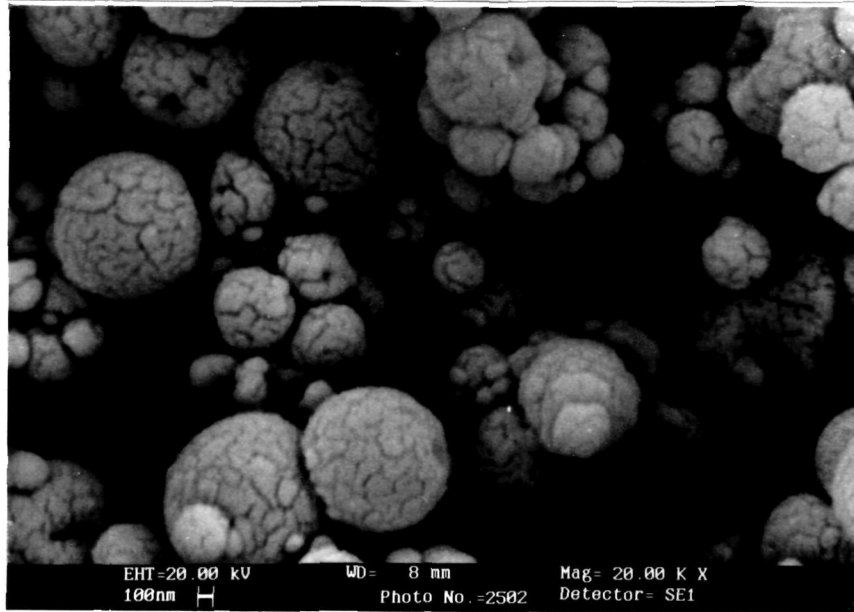


Fig.1.14.a) SEM and b) TEM micrographs of mullite particles calcined at 1473 K for 24 hours.

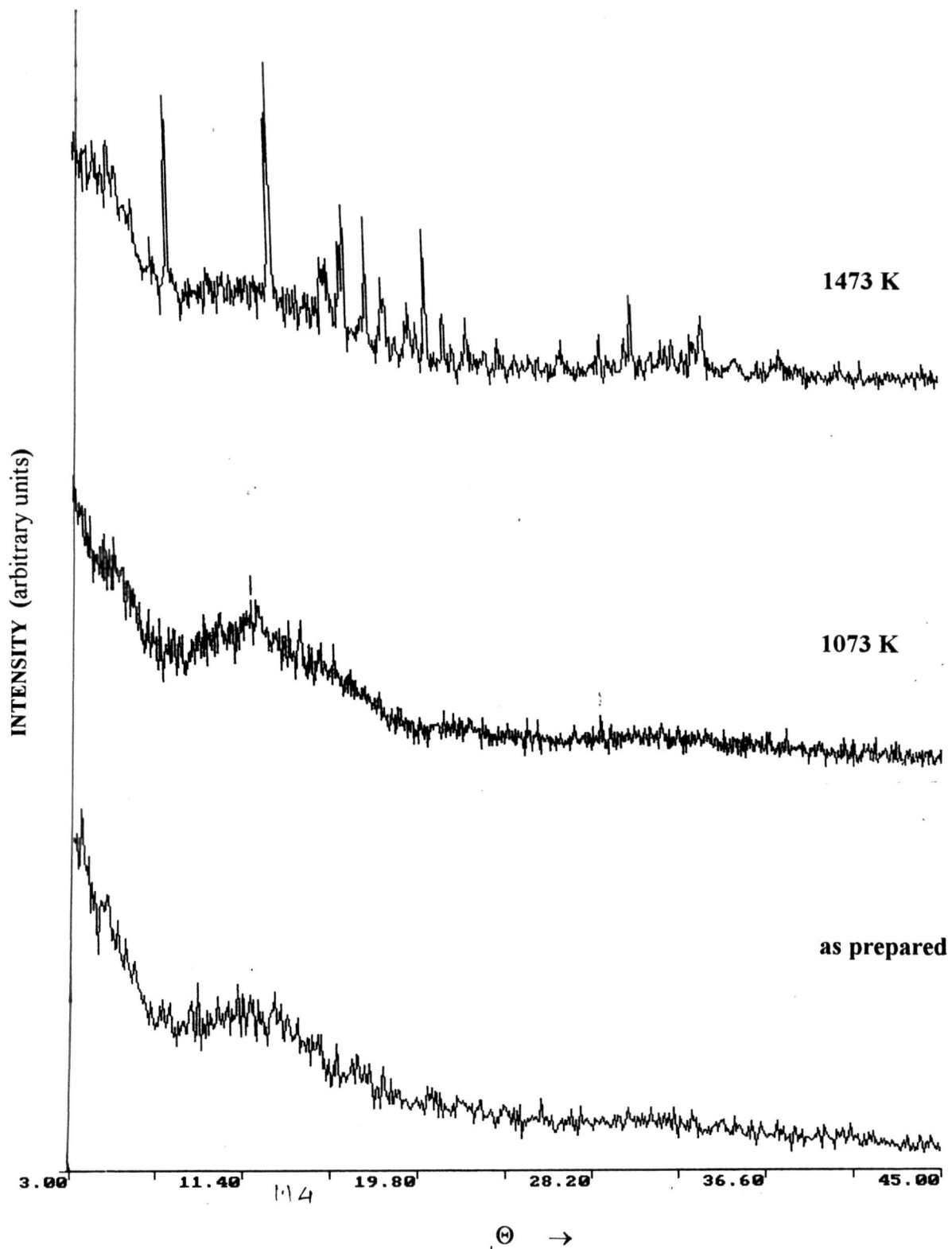


Fig.1.15. X-ray diffraction patterns of mullite powder.

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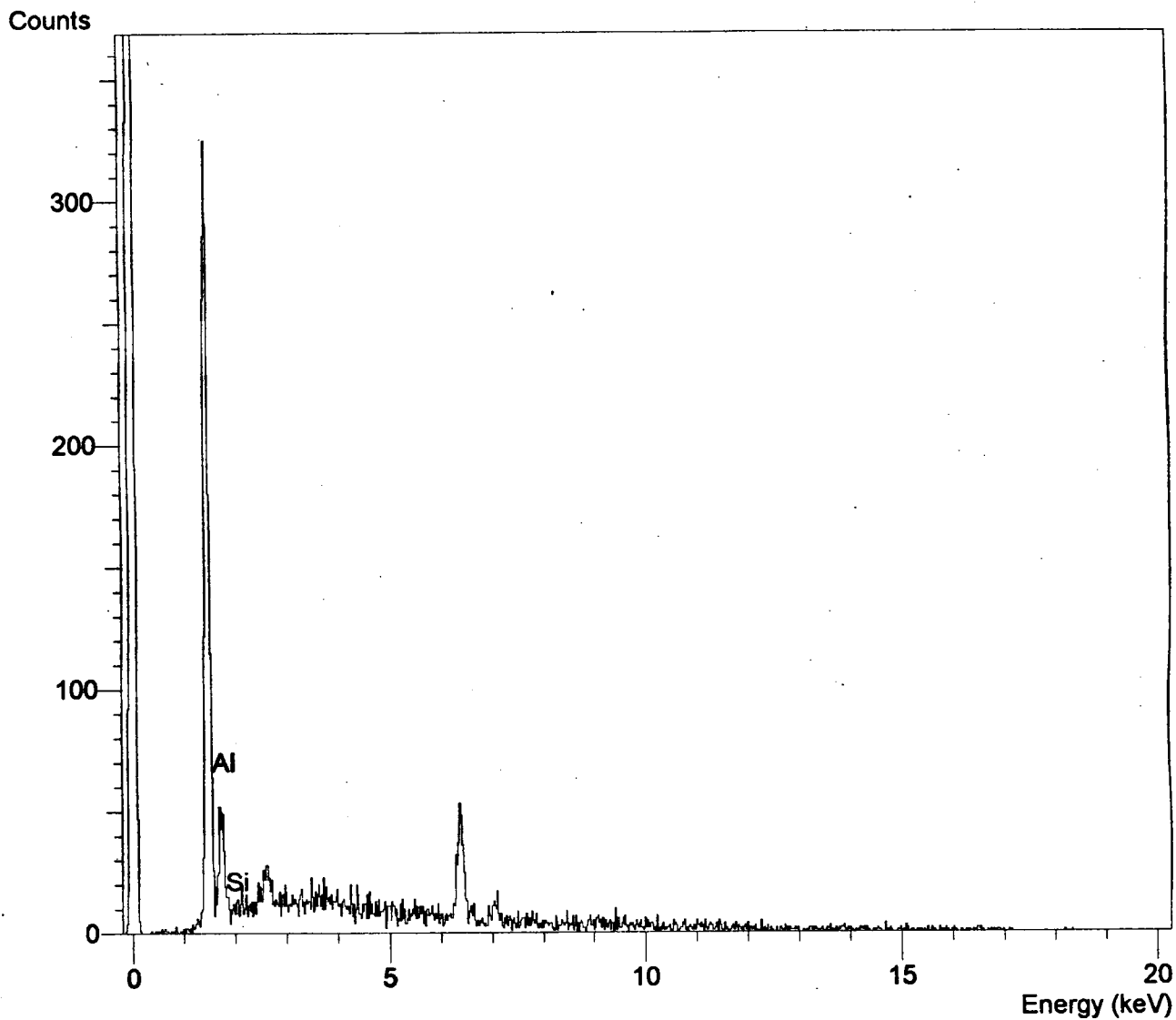
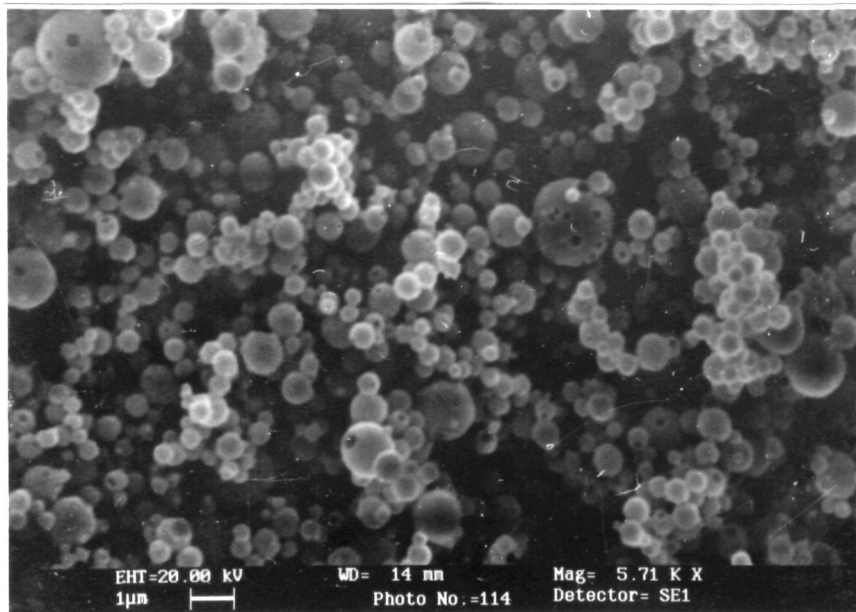
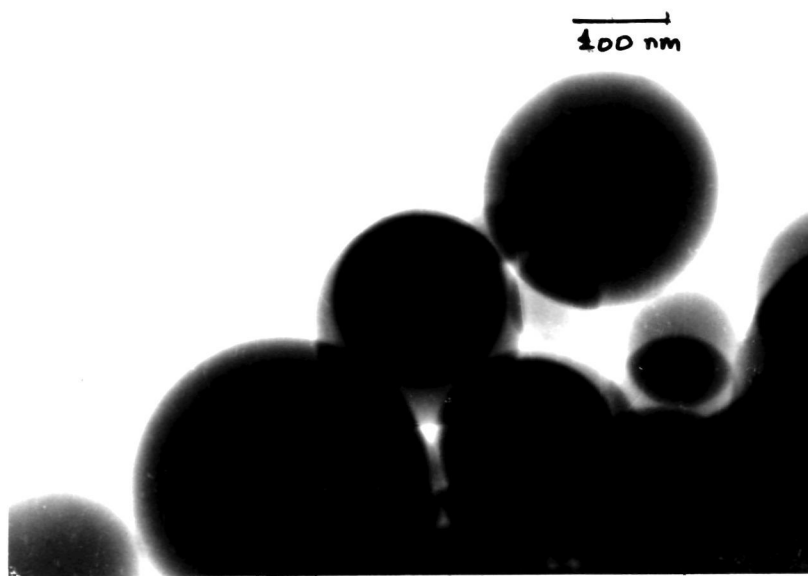


Fig.1.16. EDX spectrum of mullite powder.



(a)



(b)

Fig. 1.17. a) SEM and b) TEM micrographs of as prepared particles of PZT.

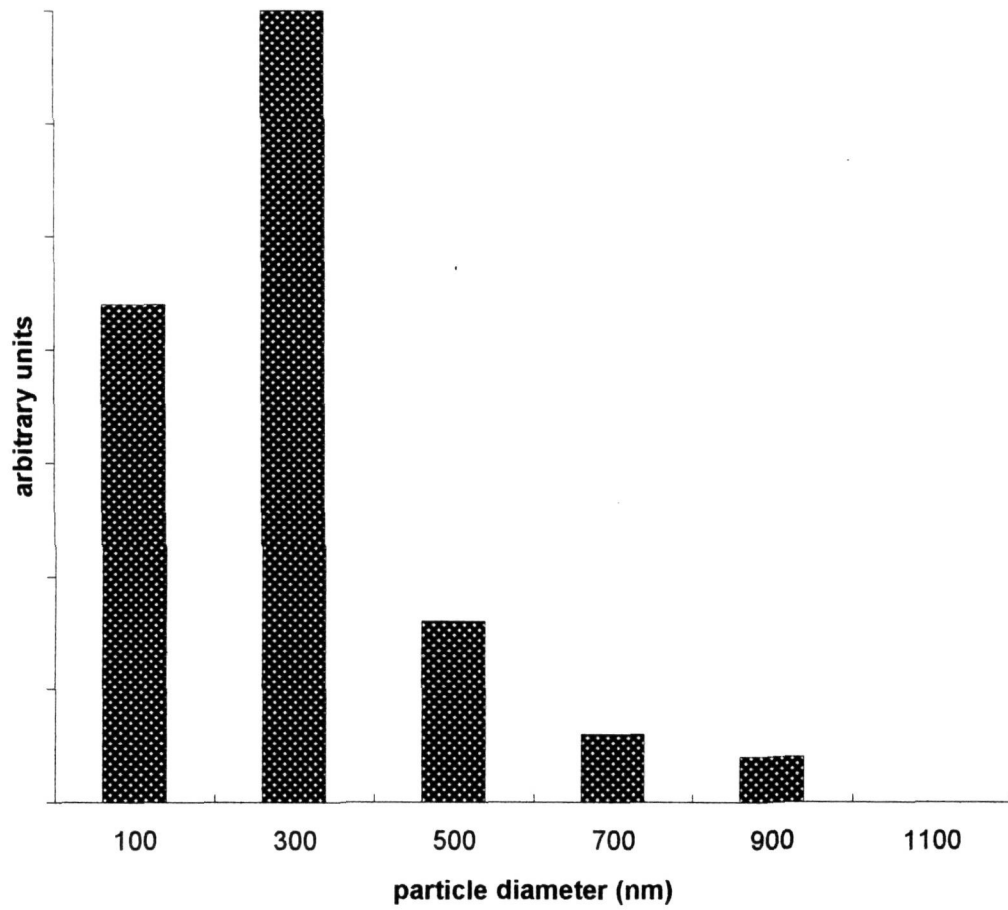


Fig. 1.18. Particle size distribution of PZT powder.

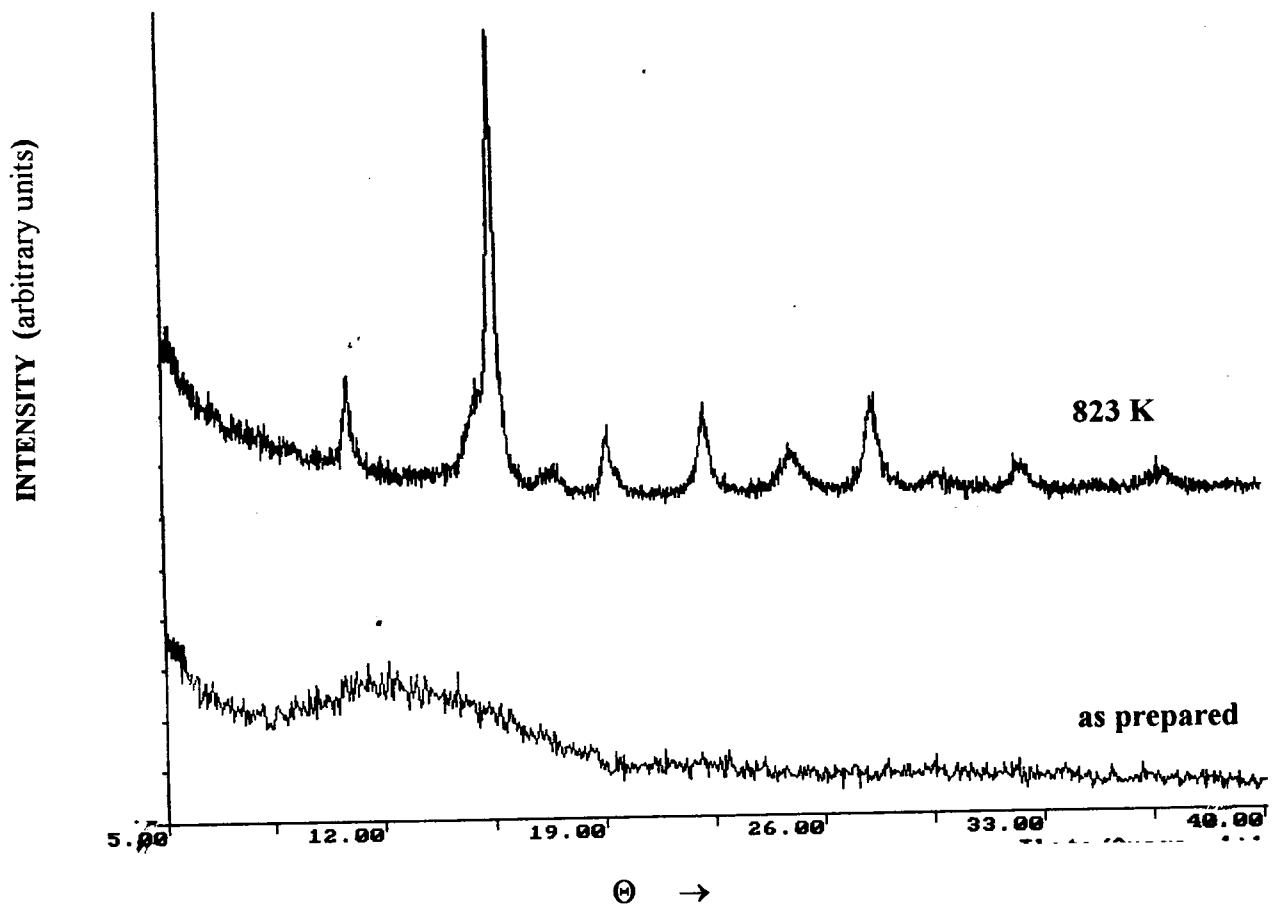


Fig.1.19. X-ray diffraction patterns of PZT powder.

The X-ray diffraction pattern of the powder heated to 823K is given in fig 1.19b. The SEM and TEM micrographs of these particles in figs 1.20a and 1.20b show them to be spherical even after crystallization. The large spherical particles are composed of tinier particles just as in the case of Al_2O_3 and ZrO_2 . The particle size calculated from the line widths is 29.5 nm. Energy dispersive X-ray analysis (fig 1.21) of the PZT powder gave the ratio of Pb : Zr : Ti to be 1 : 0.5 : 0.5 confirming the composition as $\text{PbZr}_{0.5}\text{Ti}_{0.5}\text{O}_3$.

It is interesting to note that upon diluting the concentration of the precursor the thickness of the hollow shell decreases and at 0.001M concentration the particles adopt shapes varying from spherical to hemispherical. A TEM micrograph of such a sample is shown in fig. 1.3.

1.4. CONCLUDING REMARKS

The present study of the preparation of the metal oxide powders by the nebulized spray pyrolysis of metal-organic precursors establishes the efficacy of the method. It has certain noteworthy features as detailed below:

- (i) The use of metal-organic precursors ensures complete decomposition at relatively low temperatures.
- (ii) The particles as-obtained from nebulized spray pyrolysis are spherical and have diameters in the 0.1-1.6 μm range. The hollow nature can be clearly seen in the TEM image of PZT shown in fig 1.3.
- (iii) The as prepared particles have a smooth surface if the precursors are organic derivatives and are seen to have rough surface if the precursors are inorganic nitrates.

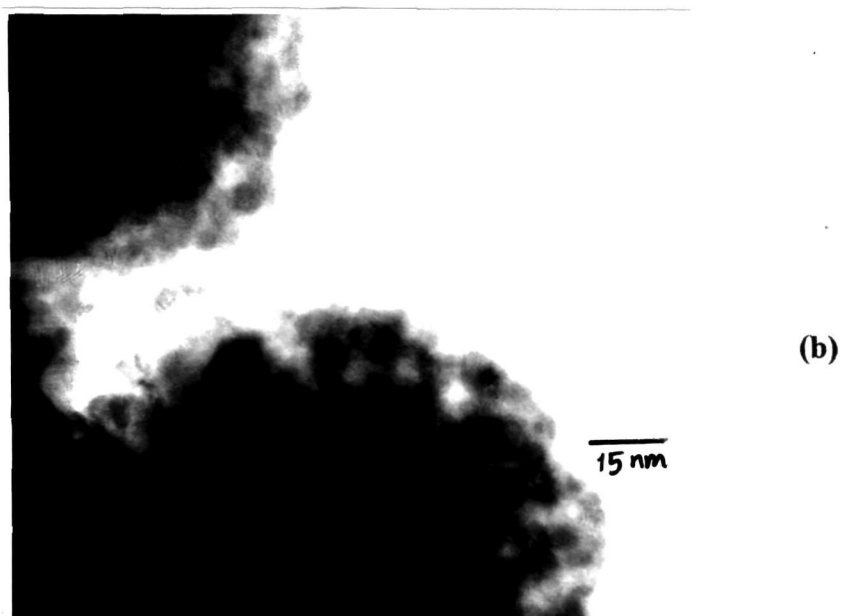
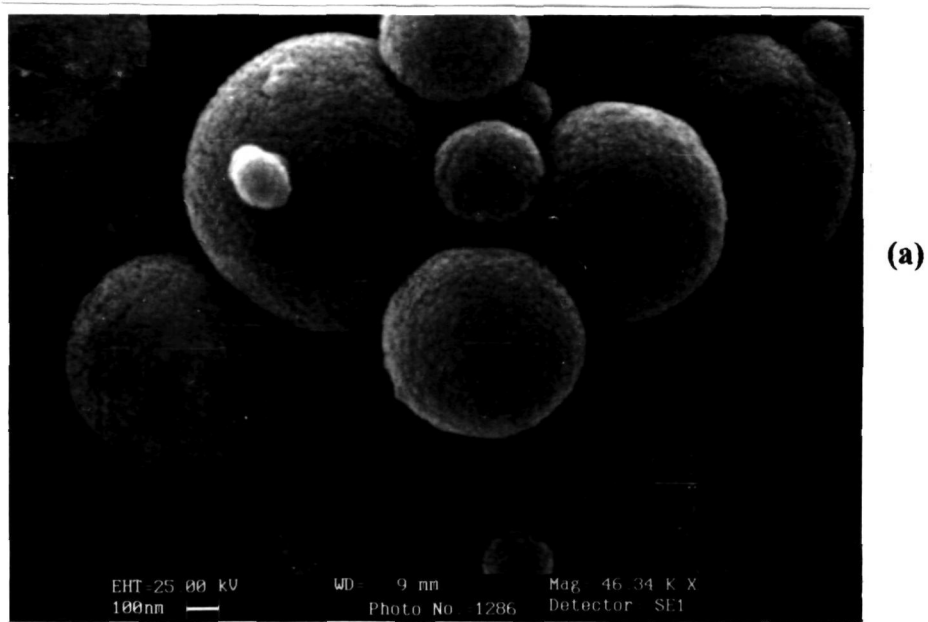


Fig. 1.20. a) SEM and b) TEM micrographs of as PZT powders calcined at 823 K for 12 hours.

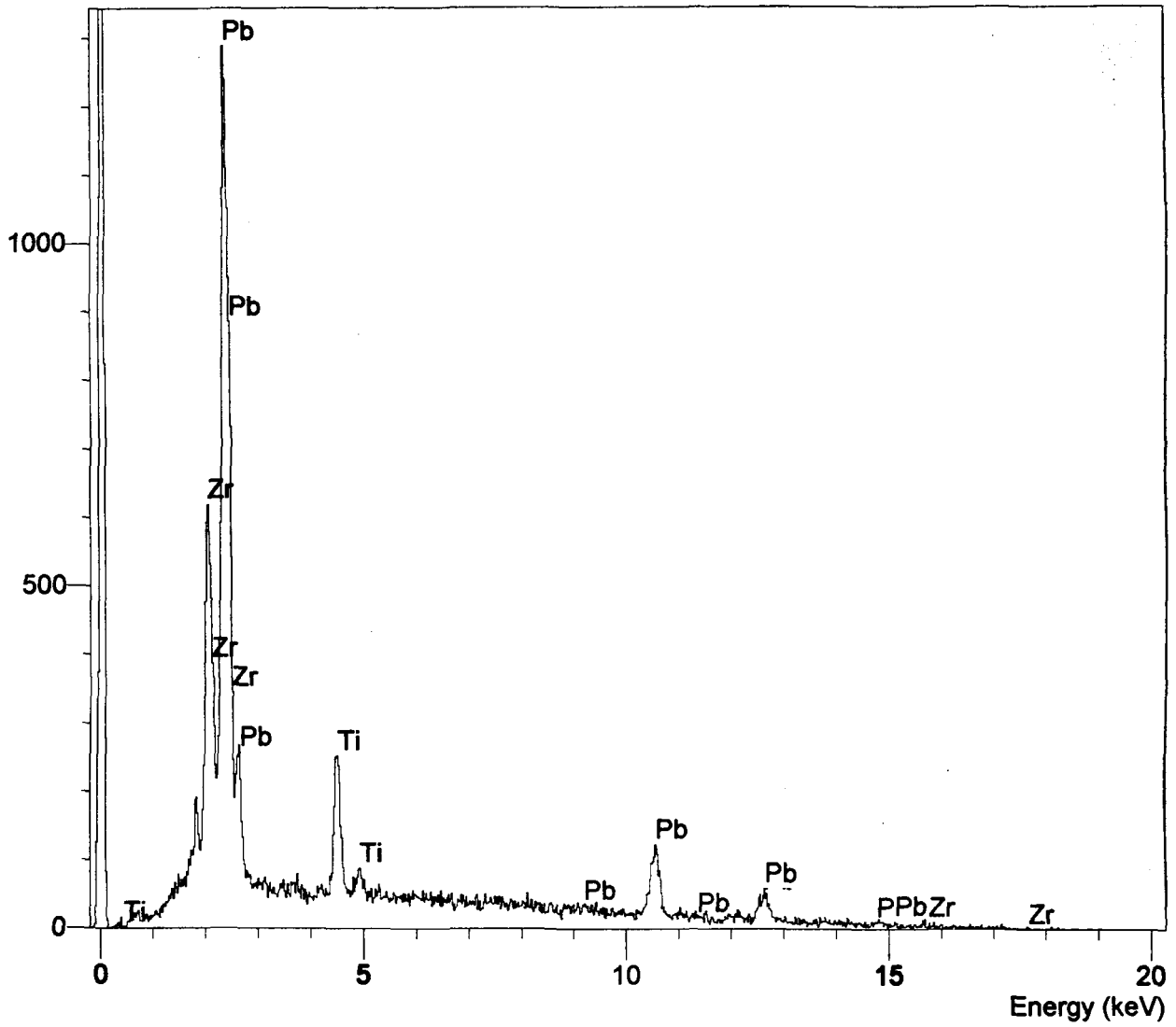


Fig.1.21. EDX spectrum of PZT powder.

(iv) The hollow spherical particles obtained by pyrolysis are generally composed of smaller particles as mentioned earlier. This is clearly seen from figs 1.10b and 1.21b where we show the high magnification SEM images of the crystalline particles of Al_2O_3 and PZT. It appears that although the particle size distribution in figs 1.5, 1.9, 1.15 and 1.18 give diameters going upto 1 μm or more, the real size of the particles is much smaller. Thus, the size of the larger spherical particle Al_2O_3 in fig 1.10b and of PZT in fig 1.21b are in the 0.5-1.5 μm range, but the small particles composing these are fairly uniform with mean diameters of 0.1 μm or less.

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PART II

NANOPARTICLES BY SONOCHEMICAL SYNTHESIS

II.1. INTRODUCTION

It has been recognized for many years that power of ultrasound has great potential for uses in a wide variety of processes in the chemical and allied industries. Reported¹⁻³ applications include cleaning, sterilization, flotation, drying, degassing, defoaming, soldering, plastic welding, drilling, filtration, homogenization, emulsification, dissolution, deaggregation of powder, biological cell disruption, extraction, crystallization and of course as a stimulus for chemical reactions.

The sonic spectrum can be broadly divided into four regions a) infrasonic b) audible (human), c) power ultrasonic and d) high frequency ultrasonic. Infrasonic region is the frequency range below the human threshold of hearing (about 20 Hz). The human audible range comprises of frequencies between 20 Hz to 20 kHz. The power ultrasonic range is from 20 kHz to 100 kHz and the high frequency ultrasonic is from 1MHz to 100 MHz. The term 'power ultrasonic' is coined to the region of 20 kHz to 100 kHz because maximum sound energy can be transmitted into a system at the lower frequencies and this induces cavitation, which is the origin of sonochemical effects.

It is certain that sonochemical effects cannot be the result of direct coupling of the sound field with the chemical species on the molecular level since the sound frequencies employed (20-100kHz) are too low even for the excitation of rotational motion. Hence the

chemical effects produced are due to some other phenomena. This phenomena is the formation and collapse of micro bubbles which is known as cavitation. During cavitation the temperature and pressure raise to 5000 K and 1000 atm respectively⁴ and an alternative electrical theory claims that lower temperature and pressures are involved but electrical discharges accompany the collapse of the cavitation bubble⁵.

Since cavitation is responsible for sonochemical effects it would be useful to study the factors affecting cavitation. A lot of parameters affect cavitation and most prominent of them are discussed below.

Frequency : If the frequency is low large bubbles would be formed and low energy is sufficient to induce cavitation. On the other hand if the frequency is very high, in the range of MHz then the attenuation would be high and weak or no cavitation would occur as the time period is too short to create bubbles.

Intensity : As the cavitation varies inversely as the frequency, it is necessary that higher intensity is applied when high frequency is used. Infinite increase is limited by the material and its dimensions.

Solvent : Higher vapor pressure of the solvent would result in less violent collapse of the bubbles as the penetration of vapor into the bubbles would increase. For this reason induction of cavitation is more difficult in the case of solvents with low vapor pressure. As the ease of bubble formation varies inversely as the surface tension and viscosity of the solvent the same trend is followed.

Nature of the bubbled gas : The temperature accompanying the collapse is proportional to $(\gamma - 1)$, where γ is (C_p/C_v) , and hence it is advantageous to use gases with high. The thermal conductivity of the gas should be lower for greater cavitation temperatures. The

dissolved gas acts as cavitation nuclei, therefore, higher solubility would enable facile cavitation.

External temperature : The rise in temperature would increase the vapor pressure of the gas hence it would reduce the intensity of cavitation.

External pressure : The increase in external pressure decreases the vapor pressure and hence increase the intensity of cavitation.

II.a. SCOPE OF THE PRESENT STUDY

Titania is an industrially very important material. It is a photocatalyst and also an excellent support for other oxidic materials which are used in gas sensing. Superfine particles of this material would alter the electronic structure and hence the properties which arise due to it. The importance of zirconia has been discussed in the part I of this thesis.

We have prepared these powders as a first step to study the effect of particle size on the catalytic properties of these materials.

II.2. EXPERIMENTAL

The schematic of the experimental setup is shown in fig-2.1. It consists of two independent parts. The titanium horn through which ultrasound is introduced into the system and the reaction vessel which is a glass vessel containing the precursor. For the reaction we chose tetradecane as the solvent because it has high viscosity, molecular mass, surface tension compared to other common solvents and it is inert being an alkane. The gas passed was oxygen which was introduced through a side port and the vent was fed to the exhaust.

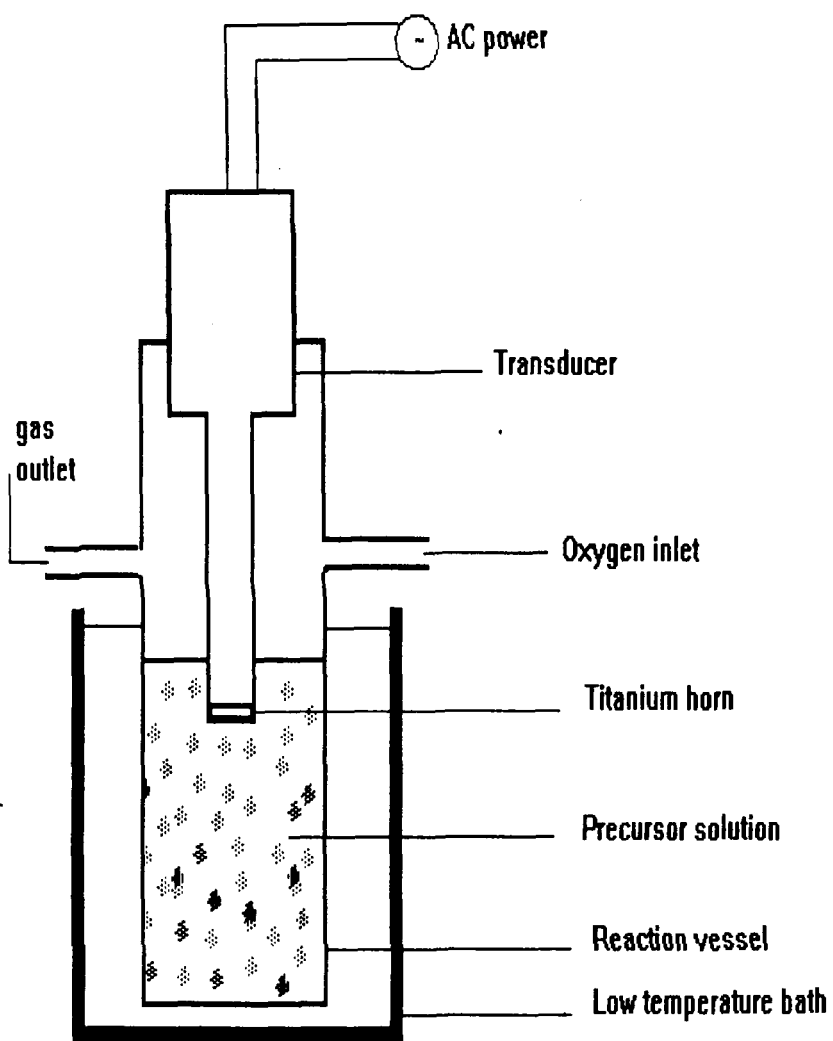


Fig. 2.1 Schematic diagram of the apparatus used for sonochemical synthesis of metal oxides.

Oxygen was introduced at the rate of two bubbles per second. The reaction vessel was maintained at a temperature of -10°C with a help of a low temperature bath. Sonication was carried out for 6-8 hours depending on the system by a 600 watt ultrasound generator operating at a frequency of 20 kHz.

II.2.1. TiO_2

To prepare TiO_2 , titanium(IV)isopropoxide was dissolved in tetradecane (50% v/v) and sonicated in O_2 atmosphere for 8 hours at -10°C . The precipitate was centrifuged at 1500 rpm for 10 minutes and the supernatant was decanted. The precipitate was washed with CCl_4 five times to remove the solvent. The precipitate was dried at 348 K in an oven for 12 hours and the powder annealed at 623 K for 12 hours.

II.2.2. ZrO_2

For the preparation of ZrO_2 , 50% v/v of zirconium propoxide in tetradecane was used. The reactants were sonicated in oxygen atmosphere for 6 hours at . The precipitate formed was separated as before and the product was clacined at 673 K for 12 hours and studied by employing SEM and TEM and X-ray diffraction.

II.3. RESULTS AND DISCUSSION

II.3.1. TiO_2 .

The SEM image of the calcined sample is shown in fig. 2.2. The SEM image shows the particle sizes to be in the range of 150 - 200 nm and shows coagulation of these particles. The sample was dispersed in CCl_4 by sonicating in an ultrasonic bath and the colloid was

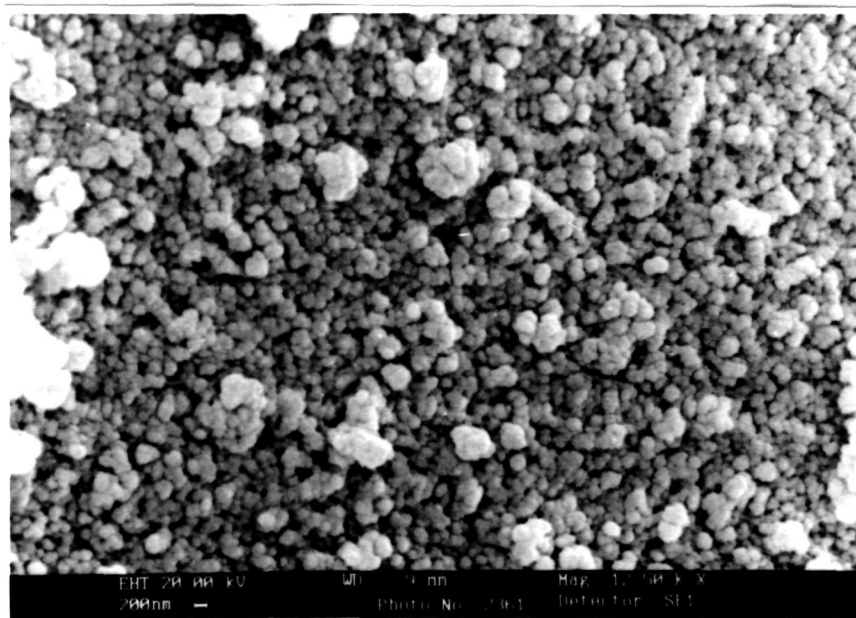


Fig.2.2. SEM micrograph of the titania powders prepared by sonochemical route.

loaded on carbon grids for TEM analysis. The TEM image of the annealed sample shown in fig 2.3 reveals that the 200 nm particles are in fact clusters of smaller particles of the dimensions of 10-15 nanometers. It is interesting to note that the clusters are of uniform size and contain almost a constant number of smaller members. The anatase phase was formed after heat treating the powder at 350 °C for 12 hours. The X-ray diffractogram is shown in fig 2.4 The particle size estimated from the line widths is found to be 19.5nm.

II.3.2. ZrO₂.

The SEM image of the as prepared ZrO₂ sample is shown in figs 2.5 The SEM image shows the particle sizes to be in the range of 150 - 200 nm and shows coagulation of these particles. The sample was dispersed in CCl₄ by sonicating in an ultrasonic bath and analyzed using TEM. The TEM image of the annealed sample is shown in fig 2.6 reveals that the 200 nm particles are in fact clusters of smaller particles of the dimensions of about 20 nanometers. The monoclinic phase and the tetragonal phases coexisted after heat treating the powder at 673 K for 12 hours. The X-ray diffractogram is shown in (fig 2.7). The particle size estimated from the line widths of the diffraction pattern is 31.5 nm.

II.4. CONCLUDING REMARKS

Nanoparticles of titania and zirconia were prepared employing a locally built apparatus using ultrasound of 600 watts operating at 20kHz. This setup is less sophisticated and consumes less power. The experiment produces particles of uniform size. The particles are uniform in size and cluster together to form agglomerates of almost uniform size. These particles are 15-20 nanometers in size. So this method has proven to be an elegant way to produce superfine particles for advanced applications.

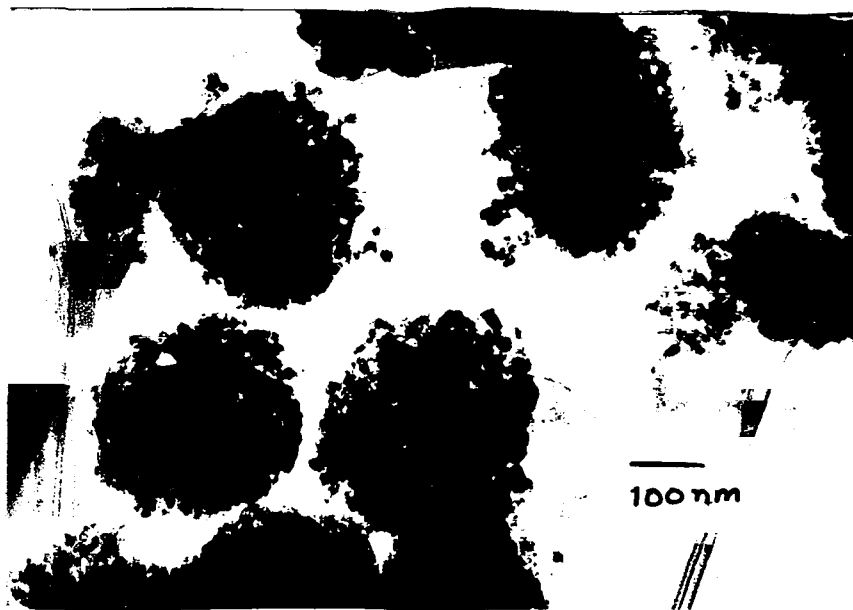


Fig.2.3 TEM micrograph of the titania powders prepared by sonochemical route.

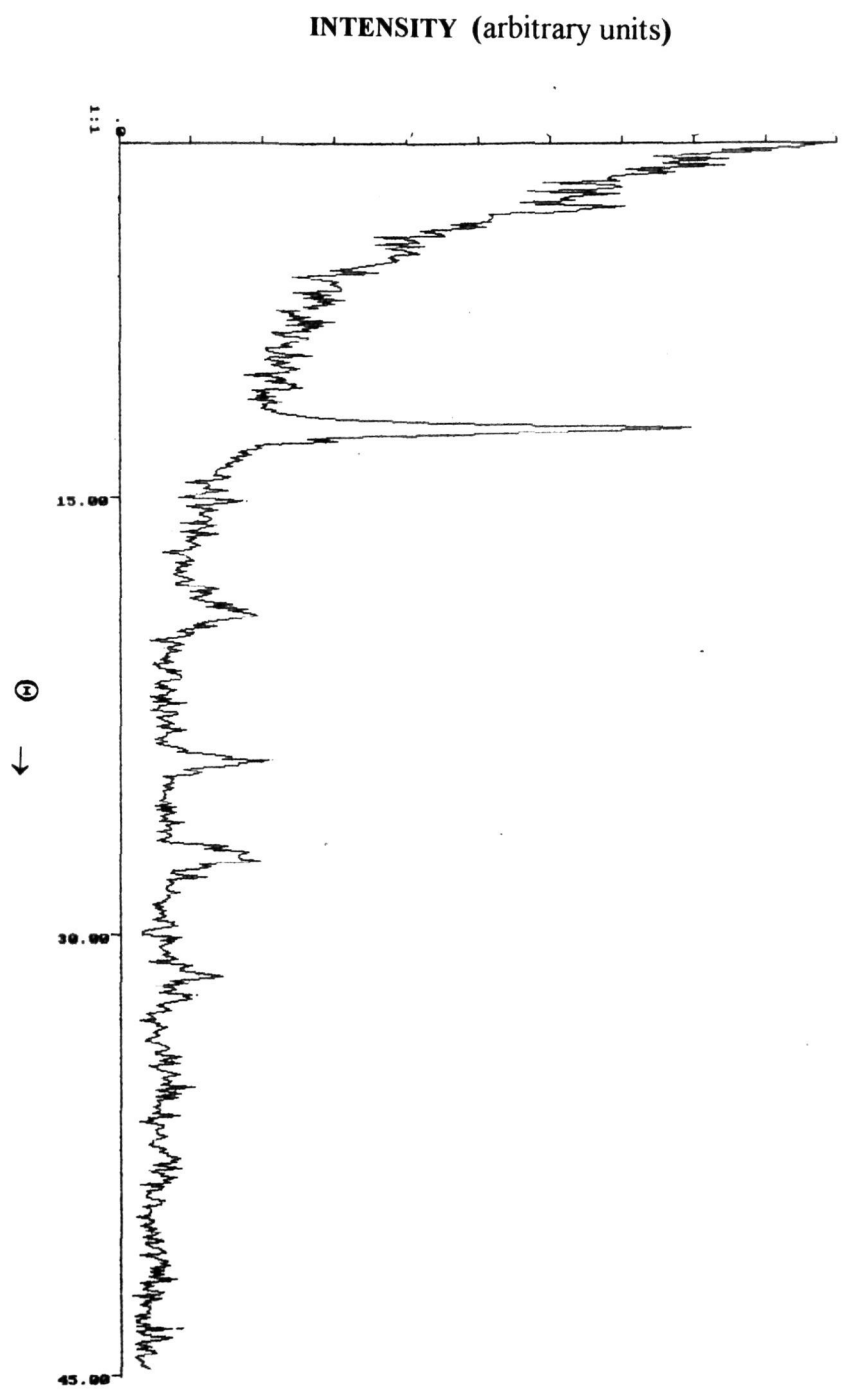


Fig. 2.4. X-ray diffraction pattern of the titania powders calcined at 623 K for 12 hours.

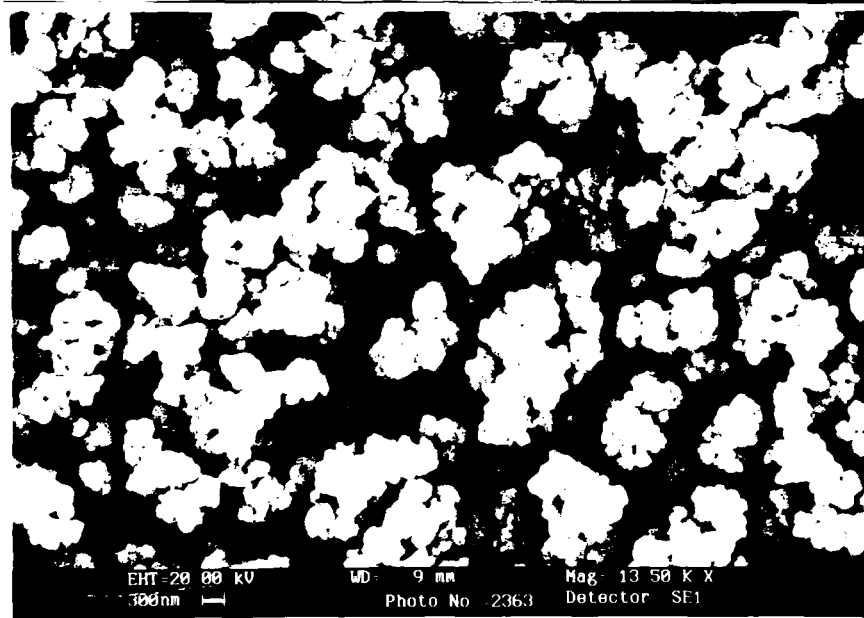


Fig.2.5. SEM micrograph of zirconia particles prepared by the sonochemical route.

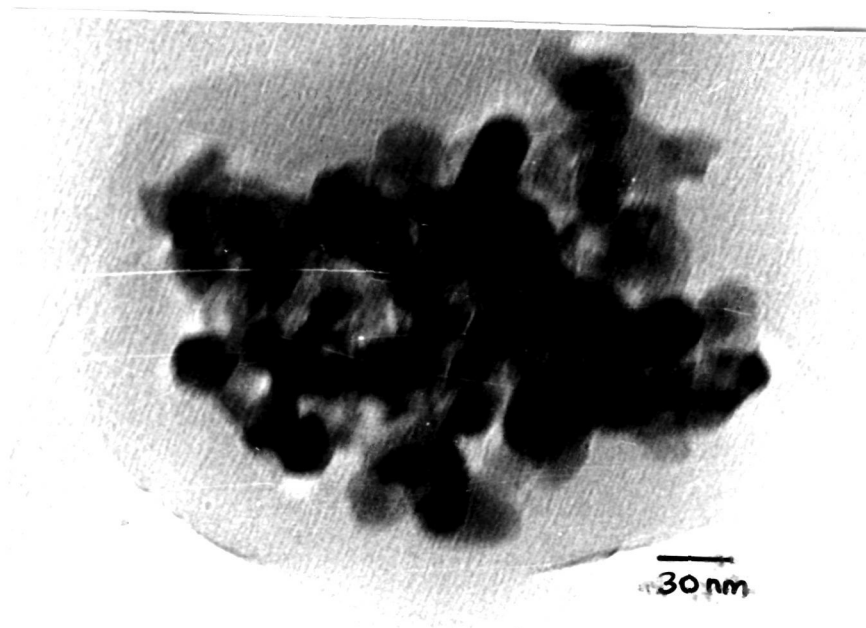


Fig.2.6. TEM micrograph of zirconia particles prepared by the sonochemical route.

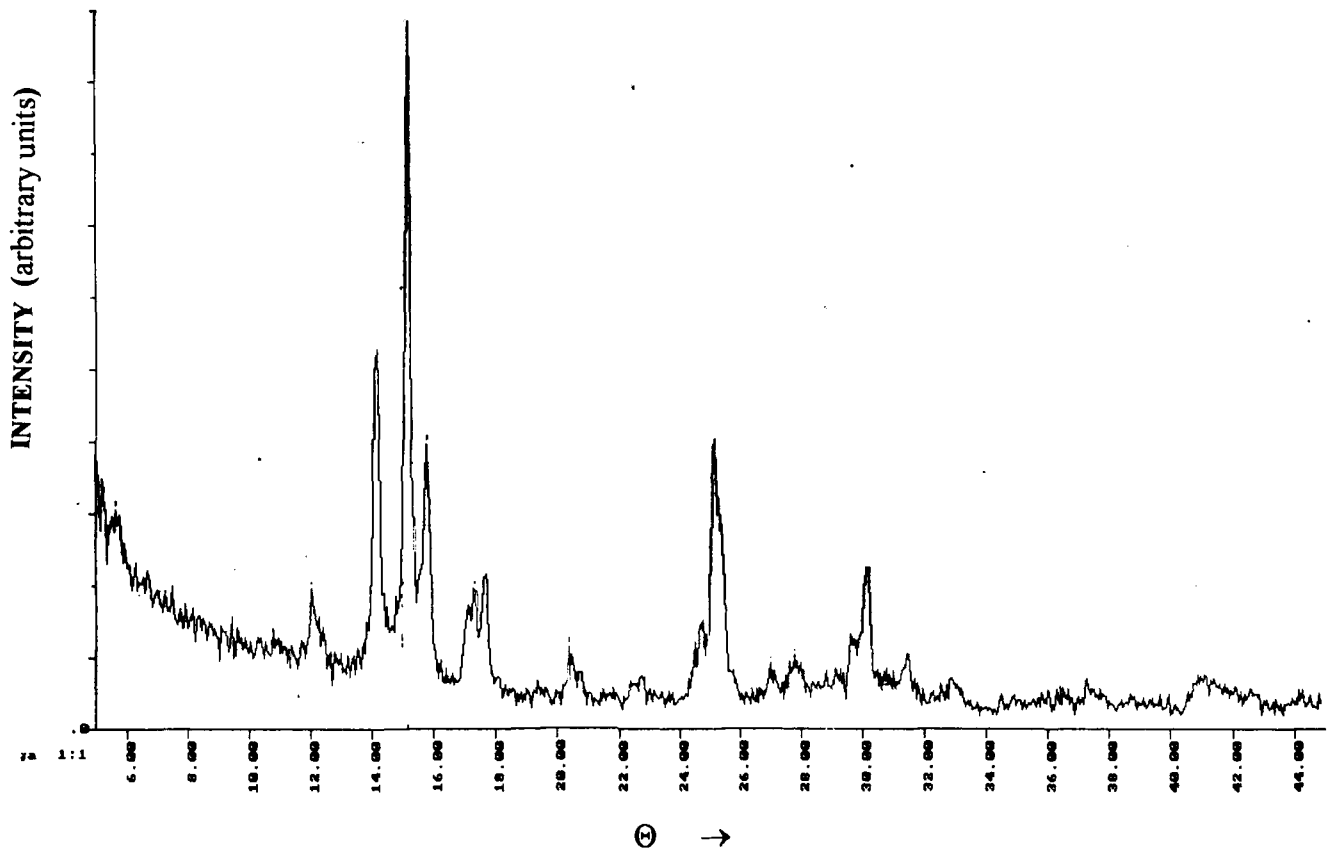


Fig.2.7 X-ray diffraction pattern of zirconia calcined at 673 K for 12 hours.

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