SOL - GEL SYNTHESIS OF OXIDE PARTICULATE CERAMICS

THESIS SUBMITTED TO THE UNIVERSITY OF KERALA
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FOR THE DEGREE OF

DOCTOR OF PHILOSOPHY
IN CHEMISTRY

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OCTOBER, 1994

DEDICATED TO

MY PARENTS AND TEACHERS

CERTIFICATE

This is to certify that the Thesis entitled "Sol-Gel Synthesis of Oxide Particulate Ceramics" is an authentic record on the research work carried out by Mr. T.V. Mani under my supervision in partial fulfilment of the requirement for the Degree of Doctor of Philosophy of the University of Kerala, and further, that no part thereof has been presented before for any other degree.

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DECLARATION

I, T.V. Mani, hereby declare that this Thesis entitled "Sol-Gel Synthesis of Oxide Particulate Ceramics", is a bonafide record of research work done by me and that no part of this Thesis has been presented earlier for any degree or diploma of any other University.

(**T.V. Mani**)

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(T.V. MANI)

SYNOPSIS

Title: Sol-gel Synthesis of Oxide Particulate Ceramics

The thesis is related to novel preparative techniques for fine oxidic ceramic powders such as alumina, aluminium titanate and Bi-based superconductors. The powders have been characterized in detail. Studies on methods of deagglomeration of fine powders are dealt with. Further, high temperature densification of such powders and development of microstructures have also been investigated. The topic was selected in view of the emerging importance on the property specific fine ceramic powders for high temperature sintered ceramics. Powders with properties such as fine particle size, uniform size distribution, high purity and good surface properties to result low sintering temperature and desirable microstructure are some of the requirements.

The total work has been presented in two parts. Part I consists of preparative aspects of fine powders of alumina and aluminium titanate through hydrolysis gelation technique. The condition of gel formation and thermal decomposition of the gel on the properties of the powders have been dealt with. Part II consists of preparative aspects of Bi-Pb-Sr-Ca-Cu-O superconductor through acrylic acid polymer precursor route and also by microwave technique. The thermal decomposition characteristics of the precursor to obtain superconducting phases and further refinement of sintered microstructures have been dealt with.

Chapter I consists of a brief review of the chemical methods of preparation for fine ceramic powders with emphasis on sol-gel as well as microwave decomposition techniques. Chapter II gives experimental details on the preparation of materials such as fine alumina, aluminium titanate and Bi-Pb-Sr-Ca-Cu-O superconductors. Treatments for deagglomeration of the powder and characterization of such powders are also presented. Methodology for obtaining alumina having fine grained microstructure have been dealt with in Chapter III. The salient features of aluminium titanate as a low thermal expansion ceramic based on the preparation of transparent gel from a mixture of titanium isopropoxide and boehmite sol, gelation characteristics in different media and phase formation with temperature of calcination are presented in Chapter IV. Characteristics of sol-gel derived aluminium titanate powder are also discussed. Thermal analysis, specific surface area (BET) and XRD data along with microstructural features of the powders have been presented.

Chapter V deals with the preparation aspects of Bi-Pb-Sr-Ca-Cu-O superconductor through organic polymer precursor route as well as microwave decomposition method. Further, the formation characteristics of the high-Tc phase in both the methods are studied in detail and compared. The texturing studies in Bi-Pb-Sr-Ca-Cu-O system have been achieved through novel zone melting-refining methods and presented in this chapter.

Chapter VI refers to the detailed discussion and comparison of the results of novel findings in the work. The conclusions of this study are highlighted in Chapter VII.

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5. **T.V. Mani**, P. Krishna Pillai, K.G.K. Warrier and A.D. Damodaran, Dependence of Calcination Conditions of Boehmite on the Alumina Particulate Characteristics and Sinterability, Mater. Lett., 19(5), 237-41 (1994).

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10. **T.V. Mani**, A.D. Damodaran and K.G.K. Warrier, Zone melting-refining in Bi-Pb-Sr-Ca-Cu-O superconductor prepared through the sol-gel method, J. Mater. Sci. (In print).

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CHAPTER I

INTRODUCTION TO PARTICULATE CERAMICS

1.0 Introduction

Ceramic materials include metallic oxides, silicates, nitrides, carbides and similar systems which generally are stable towards high temperatures(1). These are presented as mono or multicationic systems. Table 1.1 indicates some of the ceramic materials which are of much technical importance. Ceramic objects are generally formed by mixing the starting powders with binders, solvents, plasticizers, dispersants etc. and casting followed by densification at temperatures around two-third of their melting point(2). On the other hand, conversion of starting material to a liquid phase and shaping by subjecting to cooling-solidification process are adopted in the case of glasses. With the development of technologies all around, further innovations in processing of ceramics have emerged. Advanced ceramics are divided into two categories, (i) structural ceramic and (ii) functional ceramic. The structural ceramics covers ceramics in mechanical application, coatings, membranes for catalysis and filtration, abrasives, thermal shock resistors etc. The latter term covers ceramics that serve for electronic, electrooptic, electrochemical, optical or magnetic functions. For example, materials like mullite, lithium alumino silicate, aluminium titanate etc.

Table 1.1 Various ceramics of technical importance in different categories

Functional group	Compounds
Single Oxide	Al_2O_3, TiO_2, ZrO_2, MgO, SiO_2, UO_2, CeO_2, ThO_2, BeO etc.
Binary Oxide	$3Al_2O_3.2SiO_2$, Al_2TiO_5, $FeTiO_3$, $SrTiO_3$, $MgAl_2O_4$, $2MgO.SiO_2$, $CaSiO_3$
Multioxidic Systems	Cordierite ($2MgO.2Al_2O_3.5SiO_2$), Silica glasses, Leucite ($K_2O.Al_2O_3.5SiO_2$) $YBa_2Cu_3O_7$, BPSCCO systems
Carbides	SiC, WC, Al_4C_3
Nitrides	Si_3N_4, AlN, BN
Mixed Systems	$SiO_2.CdS$, SiO_2-AgCl, SiAlON

have lower thermal expansion coefficient and have found applications where thermal shock is experienced(3). Electronic materials(4,5), ceramic superconductors(6-8), negative and positive temperature coefficient (NTC, PTC) materials(9) outweigh their mechanical properties with electrical properties. Use of ceramic materials in optics like optical fibres are common today(10,11). Ceramics such as Zirconia, Alumina, Silicon carbide, Silicon nitride, Aluminium carbide etc. are of greater attraction as structural materials due to their high strength and lower density and other electrical and mechanical properties(12,13). Ceramic engine components are made out of some of these materials(14,15). Proper selection of starting ceramic powders with the required properties as well as following novel low temperature processing of ceramics have been felt important(16-18).

Ceramic powder which is the basic starting material, may be produced by conventional size reduction processes. But detailed analysis of such materials showed considerable impurity pickup during the size reduction step. Hence alternate methods of preparation of powders have been identified. Not only ceramic particulates are designed by controlled growth of molecules or basic crystals to colloidal range, powder particles are further graded by elutriation processes to different size and weight(19).

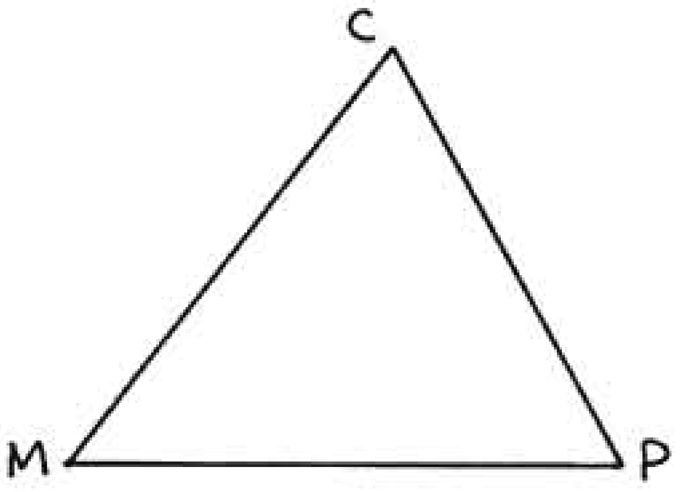
Fine powders which undergo sintering at lower temperatures are called active powders, the activity of which depends on factors such as defects, surface area, particle size, shape etc(20). Powders of 1000°A size are said to sinter 10^8 times faster than that of micrometer size powders(21). It has been well understood that ceramic powder should have characteristics such as higher activity and fine grains with narrow size distribution. The powders should be homogeneous in composition and should resist the compositional variation with time(22,23). They should not contain agglomerates which sinter invariably to theoretical density at lower temperatures introducing a non-uniform shrinkage pattern at the final stage of sintering(24,25). Attempts in the preparation of successful ceramic powders resulted in selection of wet chemical processes with the involvement of basic elements of chemistry(26-29).

1.1 Composition-Microstructure-Property Relationship

A triangular relationship exists between composition, microstructure and property in materials. The composition of the starting powder and microstructure of a ceramic have been understood to be extremely important in deciding the ultimate performance because they are inextricably related(30-34). The presence of minor additives or impurities can be detected or controlled due to sophisticated analytical techniques(35-40). Figure 1.1 shows a triangular relationship between composition(C), microstructure(M) and property(P).

Uniquely homogeneous structure, extremely fine scale

Fig. 1.1 Composition-Microstructure-Property relationship



Composition(C)	Microstructure (M)	Properties (P)
Pure Al_2O_3	Dense, fine grained	High mechanical strength, good insulator
$Al_2O_3+Na_2O$	β-Al_2O_3	Solid electrolyte
ZrO_2		Oxygen sensor
ZrO_2+ | CaO, CeO_2 Y_2O_3	Stabilized ZrO_2	High toughness
ZnO+BaO	Large grains	Low voltage varistor
$ZnO+Bi_2O_3$	Restricted grain growth	High voltage varistor
SiC	Powders/wiskers	Electronic properties, composites etc.
Al_2O_3, ZrO_2, TiO_2	Porous materials	Filters, membranes, catalysts
Al_2O_3+MgO	Liquid phase restricted grain growth of Al_2O_3	Complex structure lead to lower thermal conductivity
$BaTiO_3$ + Rare semiconduction earths		(n,p) type

(100°A) second phase and controlled surface composition gradient in a ceramic are often referred as ultrastructure. Figure 1.2 represents the approach of ultrastructure processing via modified powder goemetry by introduction of chemical methods(41,42). Figure 1.2 also reveals that ultrastructure is obtained by powders which are processed under controlled conditions. The control should be imposed even from the starting materials, processing steps and upto the production of final ceramic. This can be achieved by resorting to non-conventional methods(43,44).

1.2 Desired characteristics of ceramic particulates

Although finely divided and uniformly distributed narrow range ceramic powder is most suited for achieving high density ceramic at lower temperatures, they are also associated with problems in its preparation. One of the problems is the surface hydroxyl groups undergoing coalescence on calcination to result in hard agglomerates(45). Thus some of the desired properties of ceramic powders in general are,

(i) Uniform particles in submicrometer range
(ii) Particles with narrow size distribution
(iii) Absence of impurities
(iv) Knowledge of compositional levels
(v) Tailormade grain surface
(vi) Devoid of agglomerates

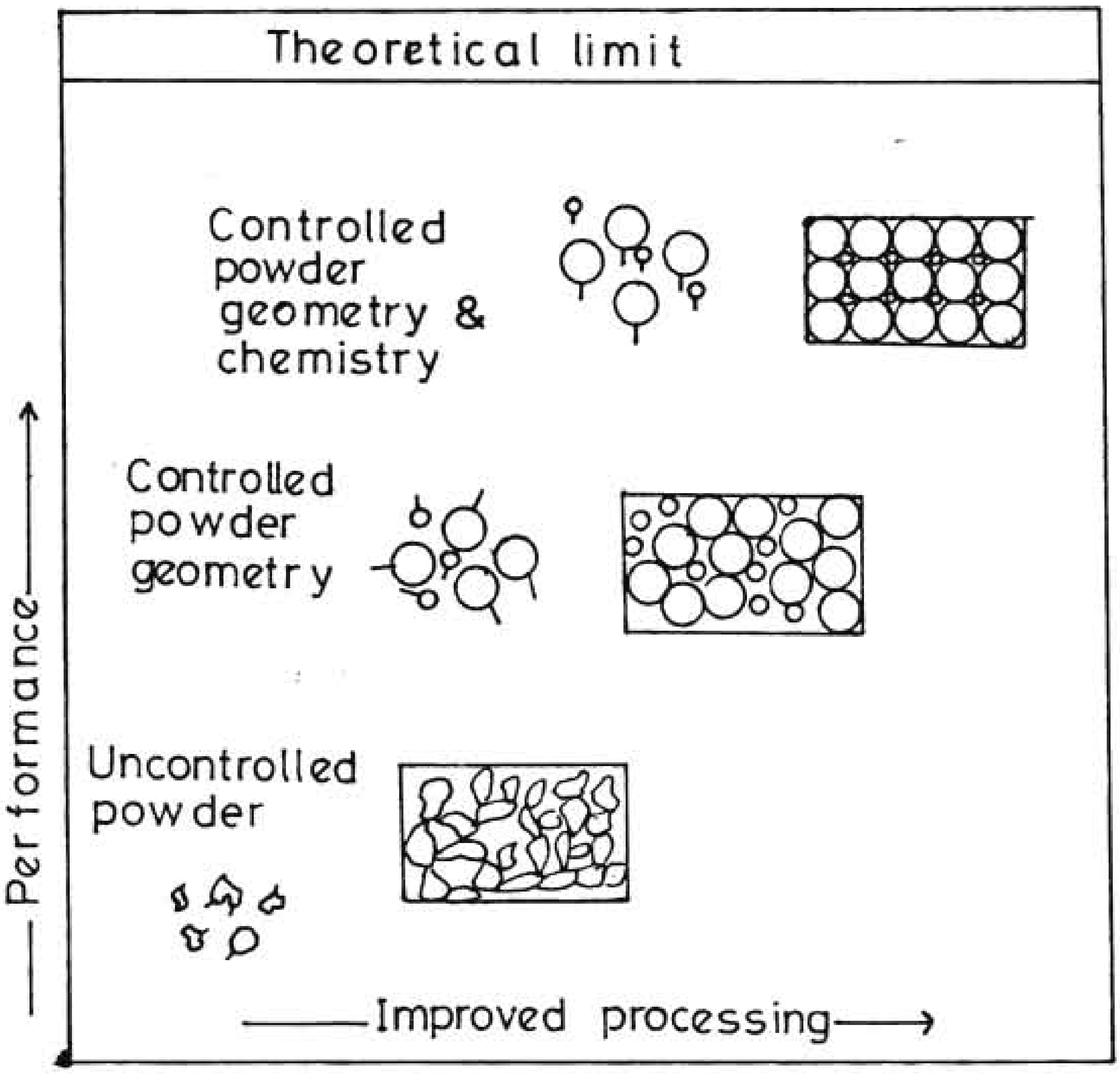


Fig.1.2 Approach of ultrastructure processing.

1.3 Chemical methods for powder preparation

To achieve the above objectives, conventional powder preparation methodologies are quite inadequate. But chemical methods which are further divided into different categories have proved successful in producing powders of desired qualities.

In general, the chemical routes are divided into three categories.

(i) Solid state decomposition
(ii) Wet chemical methods
(iii) Vapour phase synthesis

A method is chosen based on specific requirements of powders. Wet chemical route is preferred more often(46).

1.3.1 Solid state decomposition technique

Solid state decomposition involves heating of a material to high temperature to decompose it to oxide. Many metal salts such as nitrates, sulphates, chlorides etc. are used in decomposition. Two major problems generally addressed are grain growth beyond control and inadequate homogeneity of phases specially in multicomponent systems.

1.3.2 Vapour phase synthesis

The ceramic powder is formed by the vapour phase reactions of reactant(s), where relatively unagglomerated high purity powder results. Silicon carbide powders are synthesised by decomposing volatile organometallics such as $(CH_3)_2SiCl_2$ or $(CH_3)SiH_3$ at high temperatures in vacuum(47). Fine powders of silicon nitride are produced by reacting $SiCl_4$ and NH_4 at high temperatures. The nonavailability of suitable volatile precursors limits this method for the preparation of all ceramic powders(48).

1.3.3 Wet chemical methods

Wet chemical techniques include a variety of methods of powder preparation, a few of which are given below:

(a) Evaporation:

Evaporation technique is used to separate the solvent and dissolved species from a solution or a suspension. Evaporation causes crystallisation of dissolved species and hence is most suited for single component systems. However, in multicomponent systems, this leads to compositional inhomogeneity due to differential solubility of the components. In such cases, spray drying is adopted since evaporation takes place from fine droplets(49-51). The solution is atomized into a hot zone with the help of compressed air and the solid particles are collected in another chamber using a cyclone generator. A schematic representation of a spray drier is shown in Fig.1.3. An extension of the spray drying is spray calcination where the spray dried powder is instantaneously calcined to fine oxide powders(52-54). Spray drying is also used to granulate fine powders in order to improve flowability and packing(55).

(b) Freeze drying:

Fine spherical powders with relatively low agglomeration results by this method(56). The main steps are, (a) atomize the solution into fine droplets, (b) freeze these droplets by dry ice-acetone or liquid nitrogen and (c) dry these spheres by evacuation keeping the temperature below the lower eutectic of water salt system.

(c) Precipitation technique:

Precipitation technique has been one of the conventional methods for powder preparation(57-60). Mainly insoluble hydroxides are prepared by hydrolysis by deprotonation of the solvated metallic ion. Various intermediates are formed during the hydrolysis process due to various extent of deprotonation and is a function of pH. The general reaction is written as,

$$xM(H_2O)_a^{z+} + (y+b-ax)H_2O \longrightarrow M_x(H_2O)_b(OH)_y^{(xz-y)} + yH^+$$

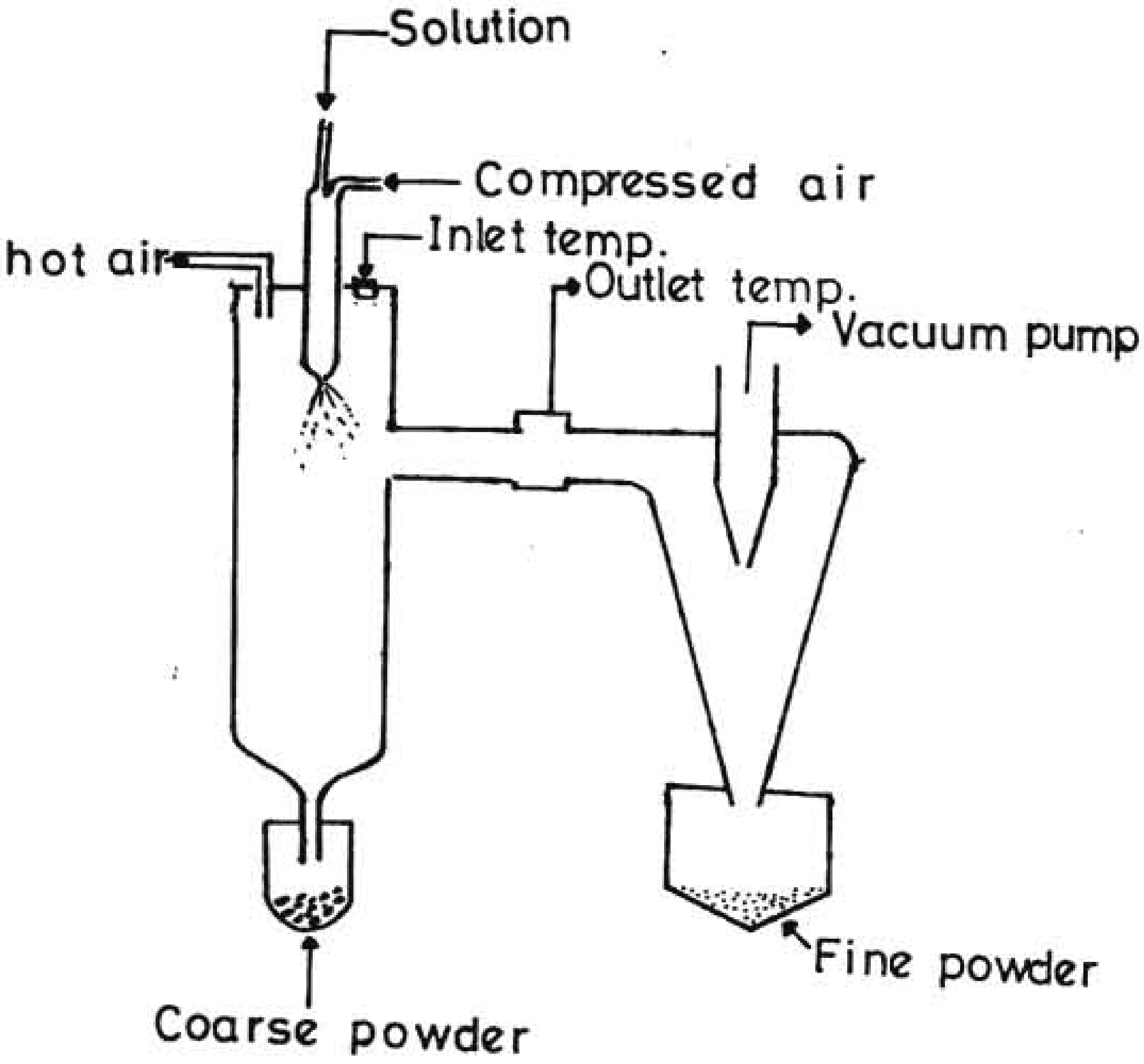


Fig.1.3 .Spray drier set up (schematic)

where 'a' the coordination number of hydrated cation, 'z' the oxidation stage of cation. The precipitation pH of a particular species depends on the extent of dehydroxylation and its solubility. Thus the precipitation pH of cation varies with respect to the solubility of the hydroxides. This prevents the simultaneous precipitation of various hydroxides. Precipitation reactions are used to coat a species over the other. Alkoxides are either hydrolysed to hydroxides or to oxides by changing the conditions of precipitation like temperature, pH or extent of water(61). Doped titania powders containing SrO or BaO are precipitated by cohydrolysis of alkoxides(62). Forced precipitation technique followed by Matijevic et. al. has shown to produce a number of metal ions containing species with various morphological features(63). A few typical reactions for precipitation of some species are given below:

$\text{Al salts} + NH_4OH \xrightarrow{T,pH} \text{Al-hydroxides}$

$\text{Sod. aluminate} + CO_2 \longrightarrow \text{Bayerite}$

$\text{Metal alkoxide} \xrightarrow{H+/OH-} \text{Oxide, hydroxides}$

$\text{Metal salt solution} + (NH_4)_2C_2O_4 \longrightarrow \text{Metal oxalate}$

$\text{Aq. metal salt solution} + \text{urea} \xrightarrow{T\ 90°c} \text{metal hydroxide}$

Hydrothermal processing of metal salts is yet another important method for obtaining fine ceramic powders and has been used in the synthesis of oxides such as monoclinic zirconia, hafnia, hexagonal anorthite(64-66). Two approaches in the preparation of monosized, equiaxed powder are the homogeneous and heterogeneous nucleation techniques. Homogeneous nucleation was utilized by Matijevic(67) and Barringer and Bowen(68) to prepare the particle of fine size.

1.3.4 Sol-gel method

A sol is a colloid where solid is dispersed in a liquid and a gel is with a three dimensionally interconnected network containing the dispersed medium uniformly distributed in pores and the process of gel formation is called gelation. This method is found to evolve powders with high purity and homogeneity at reasonably lower temperature(69-72). The versatility of sol-gel process applied in ceramic technology is clear from Fig.1.4. Eventhough the history of gels started in 19th Century, the sol-gel technology was made popular in ceramics only during the 80's and 90's(73-90). Xerogel is formed from water as the dispersion medium, and alcogel from alcohol medium. Gels when dried under hypercritical conditions undergo minimum shrinkage, contain pores filled with air, are known as aerogel(91-93). Sol-gel processing has resulted in glass with novel composition and properties without subjecting to usual melting-cooling processes(94-99).

(a) Alkoxide precursors for sol-gel particulates:

Alkoxides are alcohol derivatives of metals with R-O-M

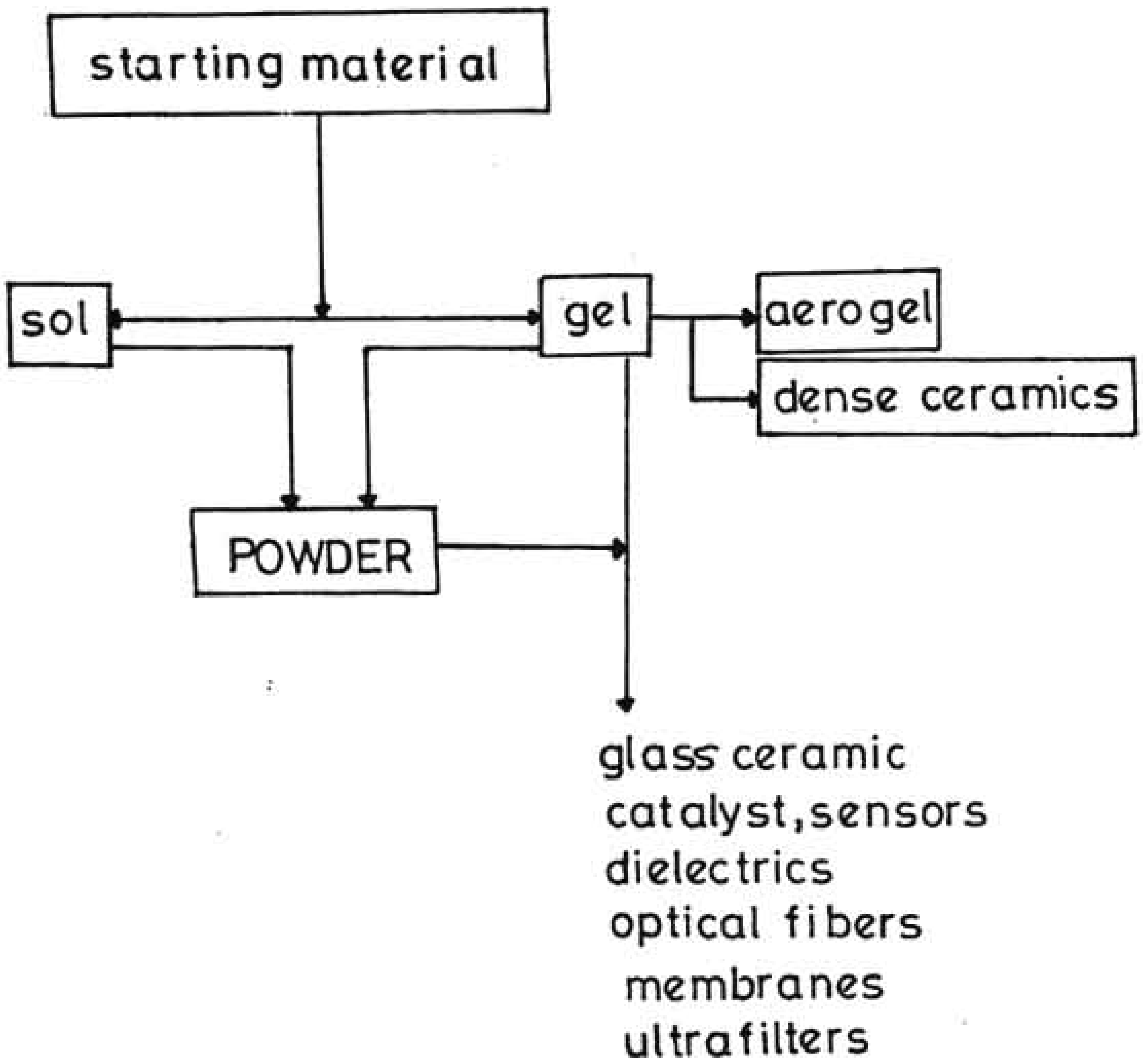


Fig.1.4. Multifaceted sol-gel process

bonding. Most of the alkoxides are highly unstable towards water and hence the nature of products depends on processes such as hydrolysis, condensation-polycondensation and gelation(100-103). These processes are pictoriously represented in Fig.1.5.

Usual procedure for hydrolysis of alkoxides is by dissolving in a proper non aqueous medium followed by addition of water or water with acid or base under controlled manner. As a result, the system passes from a solution stage to a sol and then to a gel. Linear or crosslinked polymer results according to the reaction conditions like pH, temperature, and water content since the mechanisms of hydrolysis are different.

The reactivities of alkoxides are made use not only in single components but also in multicomponent systems as well, which are otherwise very difficult to prepare. Preparation of mullite, corderite etc. are easily made by adopting to sol-gel method(104,105). Alkoxides which have transient existence in presence of water undergoes hydrolysis due to absorption of atmospheric moisture. Presence of acetic acid or acetyl acetone results in forming more stable metal-oxy bonds(106).

$$\mathrm{Ti(O\text{-}isoPr)_4 + HOAC \longrightarrow Ti(O\text{-}isoPr)_3(OAC) + PrOH}$$

$$\mathrm{Ti(O\text{-}isoPr)_4 + Acetyl\ acetone \longrightarrow Ti(O\text{-}isoPr)_3(acac) + PrOH}$$

In general, the modifying ligands are more

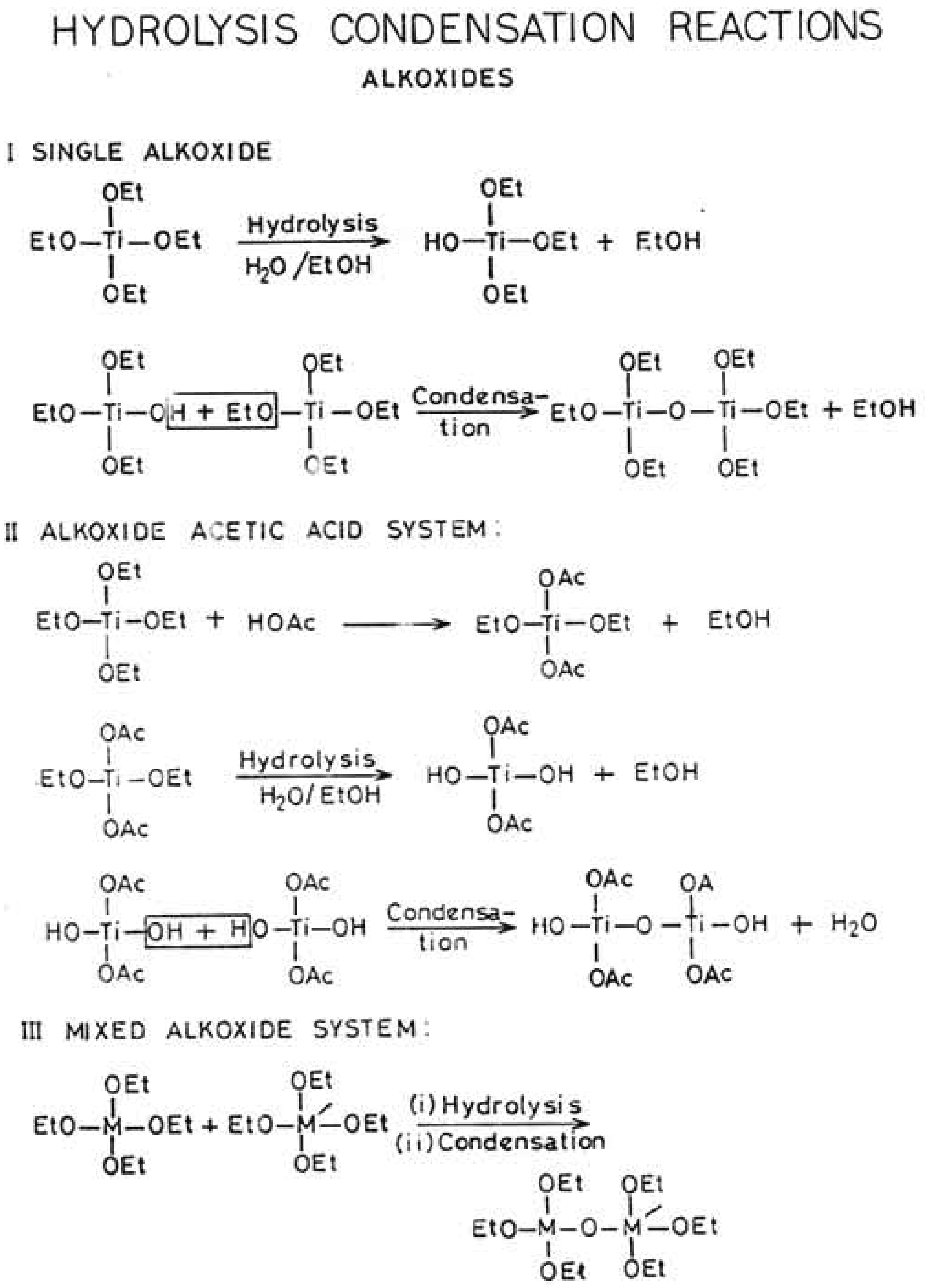


Fig. 1.5 Hydrolysis - condensation of alkoxide

electronegative and are removed slowly.

(b) Metal salts as precursor to sol-gel particulates:

Apart from alkoxides, metal salts are also used as precursor for sol-gel processing(57,58,67,107,108). Metal salts soluble in water produce hydrated cations. During change in pH, removal of the water of hydration and hydroxylation take place and gel is formed. For example, above pH 2, aquo ions of Zr(IV) spontaneously hydrolyse and undergo olation to form the $(Zr_4(OH)_8(OH_2)_{16})^{8+}$ poly cation. At higher pH, further hydrolysis takes place resulting in a rapid condensation yielding gelatinous precipitates. Al^{3+} ion has a co-ordination number of 6 and exists as $(Al(H_2O)_6)^{3+}$ in aqueous medium. This ion undergoes hydrolysis above pH 3 and may be represented as

$$(Al(OH_2)_6)^{3+} + n\ OH^- \longrightarrow (Al(OH)_n(OH_2)_{6-n})^{(3-n)+} + n\ H_2O$$

where 'n' is called molar ratio of hydrolysis. Depending on the pH conditions, the product varies from boehmite to Bayerite. The hydrolysed gelatinous precipitates are washed to remove the anion and the precipitate can be peptized by addition of required amount of acids like HCl or HNO_3(107).

Sols obtained by peptization of hydroxides are also gelled by various methods like forced flocculation and removal of solvent molecules to reach the percolation threshold. Gel structures are controlled by the balance between electrostatic repulsion and vanderWaal's force of attraction.

One of the demerits in this case is the introduction of anionic impurities. Anions like chlorides, sulphates etc. introduce problems during further processing to sintered materials. Another factor is the excess water which create problems due to the surface hydroxyls. But in the case of alkoxide derived ceramics, impurity of carbon is cited.

(c) Organic polymers as precursors in sol-gel synthesis:

Apart from inorganic polymers, organic polymers are also used in ceramic processing. Here a metal ion or hydroxide or oxyhydroxide is trapped in an organic gel matrix by chelation(109). Pechni method has been commonly used in ceramic powder preparation(110), including $YBa_2Cu_3O_{7-x}$ superconductors(111). The effectiveness of gelling agent depends on the number of active sites present in a molecule and in this respect a comparison citric acid and acrylic acid molecules has been reported(109). The problem of carbon residue formed after decomposition of the gel is addressed as one of the problems in using organic gelling agents but vacuum calcination reduces this problem considerably.

1.4 Microwave processing of ceramics

Microwaves are electromagnetic waves with wave lengths ranging from 1 m to 1 mm, with a frequency range 0.3 to 300 GHz. The electric and magnetic field vectors of microwaves interact with matter. This interaction induces translational motion of electrons and ions and rotational motion of dipoles. The inertial, elastic or frictional forces induce resistance to the motion of charges, causing the loss of electric field and hence create volumetric heating. This is mainly by eddy currents(112). The microwave interaction with matter also depends on temperature. Materials like CuO, NiO, Co_2O_3, MnO_2 etc. absorb microwaves even at room temperature but materials such as Al_2O_3, MgO, SiO_2 etc. are transparent to microwaves at room temperature and have a critical temperature above which they become microwave active. Some of the advantages of microwave heating are, it creates volumetric heating, short time of processing, potential to heat large section uniformly, rapid removal of water, binder etc. without cracking, heating of selected zones, densification at lower temperatures. Some of the characteristics which are utilized in microwave processing of materials are penetration radiation, field distribution, dielectric loss and acceleration with temperature, differential coupling and self limitation(113).

These advantages and characteristics of microwaves are extended to various fields of materials processing. One recent application in polymers is the curing of polyimide thin films. It is commonly used in processing of wood and food materials. Heat treatment of glasses below glass forming temperature for the formation of glass ceramics has been achieved effectively by microwaves. Preparation of intricate shapes is achieved by joining different parts and microwave joining is carried out efficiently in various ceramics such as Al_2O_3. Surface modification of glasses by diffusion of different ions is carried out efficiently by microwave because electrically heated diffusion is different from that of microwave heated one. Another area of wide microwave use is in ceramic powder preparation. Combustion synthesis is easily carried out in microwave oven by which oxide or non oxide powders are prepared. YBCO superconductor powder has been prepared by microwave decomposition of constituent metal nitrates(114). Alumina-zirconia composite powders are prepared by pyrolysis of $Al(OR)_3$ and $Zr(OR)_4$ mixture. Microwave sintering produces dense ceramic with uniformly distributed fine grained microstructure and with enhanced properties within very short time(115).

1.5 Introduction to the system under study

1.5.1 Alumina

Aluminium oxide usually known as alumina (Al_2O_3) is one of the most technologically important ceramics due to its versatile properties like low electrical conductivity, high thermal conductivity, high melting point and chemical inertness even at higher temperatures(116). Compared to any other ceramic counterpart, alumina is available in plenty due to the large deposits of Bauxite. Table 1.2 shows application of alumina in various fields of science and technology.

Table 1.2 Application of alumina as a ceramic material

Properties	Uses
1. Mechanical	Thread guides, wear resistant applications, catalyst carriers, abrasives, cermets, turbine blade, etc.
2. Thermal	Good thermal conductivity, Thermal shock resistant, Substrate for electronic materials, etc.
3. Electrical	Very good insulator in pure form. Low dissipation factor. β-Al_2O_3 acts as solid state electrolyte, alumina coating as electrical insulators.
4. Optical	Good opacifier in pigments due to high retractive index. Induce flourescence with a very little Cr^{3+} ion. It forms various coloured compounds. $CoAl_2O_4$ (Dark Blue) $CuAl_2O_4$ (Light Green), $FeAl_2O_4$ (Black), $ZnAl_2O_4$ (Violet).
5. Chemical	Coating on metals, ceramics etc.
6. Prosthetic	Dental ceramic, Artificial bone
7. Nuclear	Nuclear element composite

Commonly alumina is prepared by calcination of hydroxides of aluminium. The various forms of aluminium hydroxides as reported are given in Table 1.3. The mode of conversion of these hydroxides to alumina during heat treatment is also shown in Table 1.3.

Among various hydroxides, boehmite and diaspore are both monohydroxy oxides of aluminium with different crystal structures and are of particular importance because the former one is easily dispersible in water around pH 3-4 range and the latter undergoes conversion to α-Al_2O_3 around 500-600°C region due to its structural characteristics(116). As shown in Table 1.3 boehmite undergoes transformation to γ, δ, θ aluminas before getting converted to α- Al_2O_3. Except in diaspore, other hydroxides develop α-Al_2O_3 only above 1150°C. But seeding of α-Al_2O_3 in hydroxides have shown that crystallization of α-Al_2O_3 occurs at low temperatures(117,118).

Usually alumina is sintered above 1600°C. But many reports are available about sintering of alumina at lower temperature with and without liquid phase formers(119-121). MgO is commonly added as liquid phase forming agent which forms spinel, $MgAl_2O_4$(122). Presence of trace impurities and sintering atmospheres have profound effect on the electrical and optical properties of alumina(123-125).

Behaviour of a powder compact at higher temperature is controlled by intrinsic and extrinsic properties. The former covers exclusively the powder characteristics and the latter

Table 1.3 Decomposition of various Al-hydroxides to α-Al_2O_3

Gibbsite($Al_2O_3.3H_2O$) $\longrightarrow$ Chi $\longrightarrow$ Kappa $\longrightarrow$ Alpha

Boehmite($Al_2O_3.H_2O$) $\longrightarrow$ Gamma $\longrightarrow$ delta, theta Alpha

Bayerite($Al_2O_3.3H_2O$) $\longrightarrow$ eta $\longrightarrow$ Alpha

Diaspore($Al_2O_3.H_2O$) $\longrightarrow$ Alpha

---

500 600 700 800 900 1000 1100 1200

Temperature (°C)

include temperature, pressure, atmosphere, time etc. Thus the nature of powder decides the fixing of extrinsic properties of sintering parameters. Table 1.4 indicates a reported study(126) where it is shown that the sintered density, microstructural features, porosity etc. depend on grain size and nature of impurities. Based on chemical methods, transparent alumina was prepared by Yoldas(127-129). Agglomeration of fine alumina powder has shown adverse effect on sintering(130) and hence powder deagglomeration processes are necessary to have uniform packing in the green compacts. Recent studies on high tech alumina are mostly carried out from boehmite(131-137) derived from either alkoxide or aluminium salts.

1.5.2 Aluminium Titanate

Aluminium Titanate (Al_2TiO_5, AT) is widely known due to its very low thermal expansion coefficient and very high melting point, 2700°C(138,139). It exhibits thermal expansion anisotropy along the crystallographic directions(140) and hence on cooling from sintering temperature, Al_2TiO_5 undergoes anisotropic shrinkage leading to microcracking along the grain boundaries and thus causing considerable decrease in mechanical properties.

Aluminium Titanate is formed by the equimolar reaction between alumina and rutile.

Table 1.4 Effect of powder characteristics on properties of sintered alumina

Purity	Alumina samples			
	I	II	III	IV
Al_2O_3	99.7	99.95	99.97	99.97
Dia (μm)	0.52	0.55	0.58	0.53
Na (ppm)	594	59	22	35
Si (ppm)	93	75	34	39
Fe (ppm)	90	17	18	18
Mg (ppm)	300	300	8	234
Apparent sintered density (g/cc)	3.89	3.94	3.89	3.96
Porosity (%)	2.51	1.01	2.26	0.50
Grain size (μm)	4.60	4.02	12.18	7.19

$$\underset{\text{(alpha alumina)}}{Al_2O_3} \quad + \quad \underset{\text{(rutile)}}{TiO_2} \xrightarrow{t\ >1400^{\circ}C} \underset{\text{(aluminium titanate)}}{Al_2TiO_5}$$

The reaction is endothermic in nature(141,142). While α-Al_2O_3 has density 3970 kg/m^3 and rutile 4250 kg/m^3, aluminium titanate has a density of 3700 kg/m^3. This introduces 11% molar volume increase. Aluminium titanate exists in two polymorphic forms, Aluminium titanate, the low temperature form, is stable upto 1800°C and Aluminium titanate, the high temperature form which is stable above 1800°C to the melting point(138). Aluminium titanate phase undergoes a reversible decomposition around 1200-1000°C range during cooling from sintering temperature and many attempts have been made to bring the decomposition under control(143). Hamano et. al. doped various oxides like MgO, SiO_2, ZrO_2, Fe_2O_3 etc. to study their effect on the decomposition(144). Kajiwara has stabilized Al_2TiO_5 with CaO and SiO_2 and studied mechanical properties(145). Detailed studies on the use of rare earth oxide for controlling the decomposition and microcracking phenomenon were reported(144). Microcracks in Al_2TiO_5 are grain size dependent and a critical grain size of 1-1.2 µm exists above which the grains undergo microcracking(146,147). Table 1.5 indicates the 'd' values as given in JCPDS file.

Thus the problems addressed in Al_2TiO_5 ceramic can be viewed from two angles. The first one relates to synthesis of

Table 1.5 Standard 'd' values Al_2TiO_5*

d	I/Io
4.818	11
4.714	42
3.356	100
3.169	6
2.754	3
2.654	64
2.117	13
1.904	24

* JCPDS File

Al_2TiO_5 below 1400°C. Secondly a method has to be evolved to prevent decomposition of Al_2TiO_5 phase into Al_2O_3 and TiO_2 during cooling. Answers to these will solve the problem of low mechanical properties.

1.5.3 Bi-based superconductor

Discovery of a ceramic superconductor by Muller and Bednorz was a breakthrough in the field of superconductivity(148). The three major superconducting ceramic compounds of interest are Yttrium based $YBa_2Cu_3O_{7-x}$ (Tc 92K)(149), Bismuth based Bi-Pb-Sr-Ca-Cu-O(150) and Thallium based Tl-Ba-Ca-Cu-O(151). The Bi-based system has been selected in this study due to its interesting problems and possibilities such as higher Tc ($\approx$110K), high current carrying capacity, Jc, higher stability towards magnetic field and enhanced environmental stability. The long heat treatment time required for forming the 110K superconductor and the very large crystal anisotropy are the observed major problems(152-154).

Bi-system (BSCCO) mainly consists of three compounds with general formula $Bi_2Sr_2Ca_{n-1}Cu_nO_x$. They are $Bi_2Sr_2CuO_{6+x}$ (2201, Tc $\approx$ 17K), $Bi_2Sr_2CaCu_2O_{8+x}$ (2212, Tc $\approx$ 85K) and $Bi_2Sr_2Ca_2Cu_3O_{10+x}$ (2223, Tc $\approx$ 110K)(155-157). The formation temperature of these phases are approximately 700°C, 820°C and 850°C and these temperatures vary depending on the precursor, methods of preparation, atmosphere of heat treatment etc. Some of the intermediates and corresponding temperatures of formation are indicated below:

$$Bi_2O_3 + CaO + PbO + CuO \xrightarrow{600°C} Bi_2Sr_2CuO_6 + Ca_2PbO_4$$

$$Bi_2Sr_2CuO_6 + Ca_2PbO_4 + CuO \xrightarrow{800°C} (BiPb)_2Sr_2CaCuO_8 + CaCuO_2$$

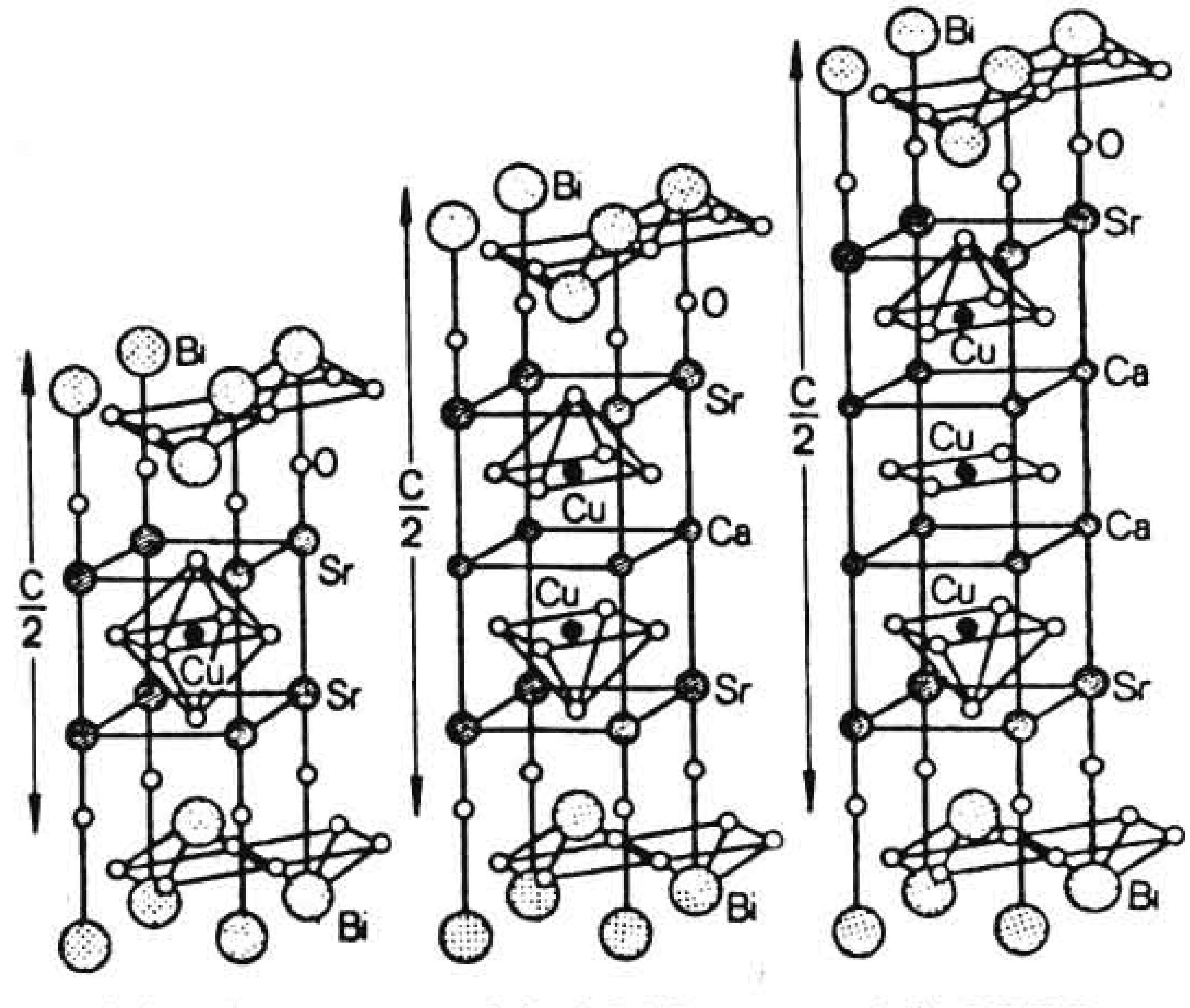
$$Bi_2Sr_2CuO_8 + CaCuO_2 \longrightarrow Bi_2Sr_2CaCuO_8$$

$$(BiPb)_2Sr_2CaCuO_8 + CaCuO_2 \xrightarrow{850°C} Bi_2Sr_2Ca_2Cu_3O_{10}$$

$$(BiPb)_2Sr_2CaCuO_8 + CaO + CuO \xrightarrow{850°C} Bi_2Sr_2Ca_2Cu_3O_{10}$$

The three major phases are identified by XRD and the 'd' values are provided in Table 1.6. Figure 1.6 represents the approximate crystal structure of these three phases.

Since many intermediates are involved in the reactions, the role of homogeneity, particle size etc. are of extreme importance. Thus a suitable chemical method of preparation is needed to prepare BPSCCO superconductor fine powders. The long heat treatment time required to obtain 110K phase is due to sluggish solid state reactions involving many intermediate compounds. Lead (Pb) was found as a suitable dopant which reduced the total time of processing(158). Eventhough exact role of Pb is still ambiguous, it has been stated that Pb^{2+} ions occupy some Bi^{3+} lattice sites and impart increased stability to 2223 phase(159). The system doped with 'Pb' is denoted as



(a) 2201 (semiconductor phase) (b) 2212 (low Tc phase) (c) 2223 (high Tc phase)

Fig.1.6 Schematic representation of crystal structure Bi-based superconducting systems

Table 1.6 'd' Values of 2201, 2212 and 2223 phases*

2201		2212		2223	
d	(hkl)	d	(hkl)	d	(hkl)
12.3	(002)	15.41	(002)	4.77	(002)
5.264	(111)	3.855	(008)	9.250	(004)
4.100	(006)	3.586	(113)	6.167	(006)
3.447	(113)	3.251	(115)	4.625	(008)
3.075	(008)	3.085	(0010)	3.700	(0010)
2.960	(017)	2.870	(117)	3.390	(105)
2.688	(200)	2.707	(200)	3.093	(107)
2.023	(208)	2.572	(0012)	2.697	(110)
1.899	(220)	2.444	(1111)	3.0790	(0012)
1.606	(315)	2.034	(2010)	2.643	(0014)
				2.313	(0016)

*(Powder Diffraction, Vol.5, No.1, March 1990)

BPSCCO.

The BPSCCO grains are of flaky morphology with very large anisotropy with respect to electrical conduction. Processing of superconductors are aimed at grain alignment and various reports are available in this subject(160,161), most of them being concentrated on powder-in-tube processes or thin films. Very few reports are available on the bulk compact processing with grain alignment. Thus major problems that remain to be tackled appear to be developing a chemical route for preparing 110K phase with shortest time of processing and arriving at a powder processing technique to achieve bulk compact with a-b plane grain orientation.

1.6 Definition of the problem

The present work has been selected based on certain important advanced ceramic systems and also on the appropriate powder synthesis techniques. The materials of research have been alumina, aluminium titanate and the Bi-based high-Tc superconductor. They are qualified by the fact that alumina is a single component, aluminium titanate is a binary and Bi superconductor is a multicomponent system.

Some identified problems in the preparation of alumina are, (i) use of a cheaper precursor like Al-nitrate for the preparation of boehmite, (ii) study of the effect of calcination conditions of boehmite gel to obtain an easy sinterable powder for sol-gel alumina and (iii) study of the powder characteristics of alumina obtained from boehmite gel modified by various treatments.

The problems identified in aluminium titanate system are, (i) use of a molecularly mixed gel system to attain maximum homogeneity of phases, (ii) study on the aluminium titanate phase formation with respect to different gel preparation and drying methods and (iii) comparison of the characteristics of aluminium titanate powder obtained from various treated gels.

The present work in BPSCCO is aimed at (i) to evolve a chemical route of synthesis for this multicomponent system, to reduce the total time of formation of 2223 phase, (iii) to study the behaviour of the precursor powders towards calcination temperature and (iv) to optimise a processing technique such as zone melting refining for bulk BPSCCO for introducing a-b plane orientation.

1.7 Conclusion

Powder preparation and processing are vital parts of high technology ceramic because powder form is the easiest to work with. At the same time the efficiency of a ceramic depends on the characteristics of powder which in turn depend on the nature of starting materials. Among the various methods of powder preparation, wet chemical route imparts most of the desired qualities to the powders. Wet method also imposes some basic problems such as agglomeration and volume handling.

Sinterability and resulting microstructure are the best evaluation methods of a powder because low temperature sinterability and fine uniform microstructure are the ultimate aims.

Literature survey on the advanced ceramics converged to selection of three typical ceramic systems such as single component alumina, binary aluminium titanate and multicomponent Bi superconductors for the present study and some basic problems involved in these systems are dealt with.

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PART I

STUDIES OF ALUMINA AND ALUMINIUM TITANATE POWDER PREPARED BY SOL-GEL TECHNIQUE

ABSTRACT

Single component alumina (Al_2O_3) and binary aluminium titanate (Al_2TiO_5) oxide fine powders have been prepared by sol-gel method. The gel formation, oxide phase evolution at higher temperature and the effect of various solvent treatment and drying conditions on the reactivity and powder characteristics were studied in both cases.

Boehmite (AlOOH) has been prepared from aluminium nitrate as a transparent gel. The evolution of transition alumina from boehmite xerogel and their characteristics such as specific surface area, morphology, compaction-sinterability are studied. The effect of solvents such as acetone and isopropanol on the evolution of alumina phase as well as characteristic of alumina powder obtained are also studied. Treatment with solvents appear to have reduced the α-Al_2O_3 formation temperature. A maximum specific surface area of 310 m^2/g is obtained for gel treated with iosopropanol and calcined at 400°C. XRD studies of the boehmite gel calcined at 1000°C indicated a mixture of transition aluminas which get converted to alpha alumina at higher temperatures. Sintered density of boehmite gel without any solvent treatment has been $\simeq$98% at

1600°C compared to that of $\approx$96% density at 1450°C in the case of solvent treated gels.

Spray drying method has been used to attain spherical alumina powders with fine size. Boehmite sol after spray drying and calcination at 1000°C resulted in spherical alumina powders of size $\simeq$ 1 µm particle. These powders also show high specific surface area and enhanced densification.

Aluminium titanate has been prepared from a mixed gel obtained from boehmite and stabilized Ti-isopropoxide. Aluminium titanate phase formation occured at 1370°C. The powder characteristics such as specific surface area, particle size distribution and compaction-densification were also evaluated. The effect of anionic impurities, different solvents and microwave drying on aluminium titanate phase evolution is studied by thermal analysis. Aluminium titanate formation at 1347°C is observed for the gel washed thoroughly to remove almost all of the anionic impurities.

The gelation studies of aluminium titanate precursor sol by using nephelometric (light scattering) technique. Water based sol took around 30 h to complete the gelation but that with dioxane and isopropanol took 5-10 h only.

The surface area measurements show that a drastic decrease in the specific surface area upto 0.5 m^2/g after calcination at 1400°C. This is mainly due to the reaction of alumina and titania to form aluminium titanate and followed particle growth. Particle size analysis showed an average particle size of about 2 µm.

CHAPTER II

EXPERIMENTAL AND CHARACTERISATION TECHNIQUES

2.A EXPERIMENTAL TECHNIQUES FOR FINE POWDER SYNTHESIS

2.A.1 Salient features of sol-gel synthesis adopted under the present study

(a) Alumina

In the present study boehmite gel is prepared by following way. Aqueous solutions of aluminium nitrate ($Al(NO_3)_3.9H_2O$) were prepared by dissolving in double distilled water in different concentrations of 5, 10, 15 and 20 wt% in separate experiments. Precipitation of aluminium hydroxide was done from these solutions using NH_4OH (10% aq. solution) as precipitating agent under various conditions of temperature and pH. First of all, the effect of temperature was studied by doing the precipitation at 27°C and 95°C. Secondly, the precipitation was done at pH ranges from 7 to 9.5. In all these cases, NH_4OH solution was added to aluminium nitrate solution under vigorous stirring. The gels were washed thoroughly to remove the anionic impurities and were characterised by XRD. The gel after washing was peptized at pH 4 and aged for 24 h at 28°C. It was then dried at 40°C for 48 h in an air oven. The scheme adopted is pictoriously

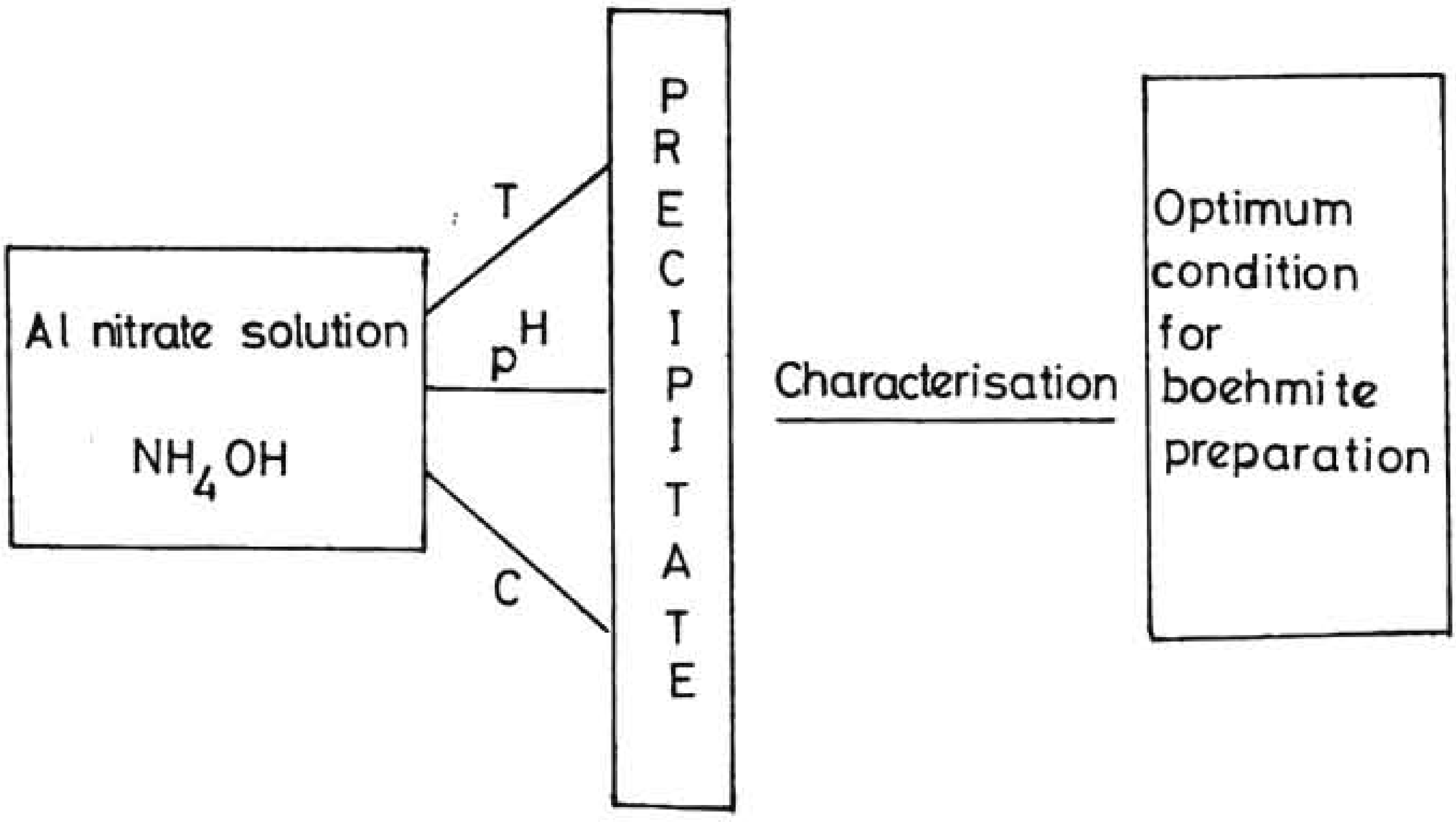

Fig. 2.1 Scheme for boehmite preparation

represented in Fig.2.1. The gel was calcined at various temperatures and the powder characteristics were studied. The boehmite gel is also treated with various solvents and the powder obtained after calcination was also characterized.

(b) Aluminium Titanate

Many methods are available in literature for the preparation of Al_2TiO_5 powder and the methods are summarised in Table 2.1. Generally adopted system is to co-fire a mixture of TiO_2 and Al_2O_3 around 1400°C for long hours to complete the reaction(1).

In the present experiment, titanium isopropoxide (Aldrich Chemicals, England) was diluted with same amount of isopropanol which was distilled and dried over $CaCl_2$. This solution was estimated for TiO_2 gravimetrically. The standard titanium isopropoxide solution was kept in air tight bottles closed with septum and stored in cold conditions. Whenever the solution was required, the required quantities were withdrawn using a syringe. These precautions introduce minimum hydrolysis of the alkoxide solution. Known amount of Ti-isopropoxide was added to glacial acetic acid kept at ice cold conditions with stirring. The molar ratio of alkoxide to acetic acid was kept at 0.16. The standard boehmite sol was mixed slowly with the alkoxide solution keeping the temperature below 10°C. The molar ratio of alkoxide to water, isopropanol and acetic acid in the mixture were 0.009, 0.03 and 0.16

Table 2.1 Chemical methods adopted for Al_2TiO_5 powder preparation

Methods	Literature
1. Heat treatment of a mixture of coarse and fine α-Al_2O_3 and anatase at 1450°C	B. Fruedenberg and A. Mocellin, J. Am. Ceram. Soc., 70(1) 33 (1987) and J. Am. Ceram. Soc., 71(1) 22 (1988)
2. Hydrolysis of Ti- and Al-isopropoxide in hexane and heating the powder at 800°C and sintering at 1600°C	M.K. Morrow, C.E. Holocombe and C.A. Cromer, NTIS Report, No.Y-1831 (1972)
3. Hydrolysis of Ti and Al isopropoxide by aqueous ammonia at room temperature	O. Yamaguchi, T. Hitoshi and K. Shimizu, Science and Engineering Review of Doshisha University, 22, 26 (1981).
4. Hydrolysis of Ti-isopropoxide in alumina sol	H. Okamura., E.A. Barringer and H.K. Bowen, J. Am. Ceram. Soc., 69, C22 (1986).
5. Oxidation of Al_2Br_6 and $TiCl_4$ in argon-oxygen plasma	M.J.J. Gami and R. McPherson, J. Mater. Sci., 15, 1915 (1980).
6. Hydrolysis of aerosols of Ti-ethoxide and Al-sec butoxide	B.J. Ingebrethsen, E. Matijevic and R.E. Tartch, J. Colloid and Interface Science, 95, 228 (1983).

7. Gas phase hydropyrolysis	W.F. Klading and H. Mayer, J. J. Mater. Sci., 25, 1973 (1990).
8. Calcination of the powder obtained from evaporation of the solvent from aqueous solution of Ti and Al-sulphate	E. Kato, K. Daimon, J. Takahashi, R. Kato and K. Hamano, Report of the Research Laboratory of Engineering Materials, Tokyo Institute of Technology, No.9, 75 (1984).
9. Chemical vapour decomposition (CVD)	S. Hori and R. Kurita, Int. J. High Tech. Ceramics, 1, 59 (1985).
10. Hydrolysis of a mixture of Ti-butoxide and Al-sec butoxide after refluxing in butanol	T. Woigner, L. Lespade, J. Phalippou and R. Rogier, J. Non. Cryst. Solids, 100, 325 (1988).
11. Heating a mixture of Al_2O_3 and TiO_2 at 1450°C after ball milling	M. Kajiwara, Br. Ceram. Trans. J., 86, 77 (1987).
12. Dispersing equimolar mixture of Al_2O_3 and anatase with 2 wt% Mg-acetate in ethanol and heated to 1450°C after drying and consolidation	I. Stomenkovic, Ceramic International, 15, 155 (1989).

respectively. The temperature of the reaction system was kept below 10°C with gentle stirring for one hour. The mixed sol was poured into petridishes of 14.5 cm diameter and allowed to gel for 5 days at 25°C. The gel turned to a transparent solid mass after gelation. The gel underwent cracking on further drying. These gels were calcined at higher temperatures to study the phase evolution by XRD. Characteristics of powders obtained from decomposition of transparent gel is studied. The gel is modified with organic solvent by washing and microwave drying. Effect of all these processes were evaluated on the basis of thermal analysis studies and powder characteristics.

(c) Bi-based superconductor

Like other ceramic materials the ceramic superconductors are also generally prepared by mixing and firing of the constituent oxides(2). Many wet chemical methods have been followed to enhance the homogeneity of the cations involved and hence to decrease the time of total reaction(3). This involves use of alkoxide(4), oxalate gel(5), acetate gel(6) etc. where one possibility is molecular level of mixing. Organic complexing agents like naphthanoic acid(7), has also been used for making the precursor gels for BPSCCO system. The effectiveness of gelling agent in a system depends on available active sites in this compound. A comparison of citric acid and acrylic acid showed that acrylic acid has more active sites than the former(8). In a similar way, microwave techniques in systems of ceramic precursors has been used with advantage(9,10) and hence has been attempted here.

Processing of superconductors has been a problem due to its brittleness and unstability towards many chemicals. But various methods like oxide powder in tube (OPIT), melt texturing, injection moulding, slip casting etc are some processes adopted for superconductor fabrication(11-14).

(i) Synthesis of acrylate gel for BPSCC precursor powder:

In the present study, the approaches are made for gel preparation. First one is the use of acrylic acid and second is use of microwave activator and microwave heating. In a typical experiment for acrylate gel preparation, 7.761 g of Bismuth nitrate ($Bi(NO_3)_3.5H_2O$) (AR Grade, E. Merck, India) was dissolved in 48 ml of 5:1 acrylic acid-water mixture which resulted in a golden yellow solution. To this solution 1.3248 g lead nitrate ($Pb(NO_3)_2$), 4.2326 g strontium nitrate ($Sr(NO_3)_2$), 4.723 g calcium nitrate ($Ca(NO_3).4H_2O$) and 7.248 g copper nitrate ($Cu(NO_3)_2.3H_2O$) were added keeping the cation ratio of Bi:Pb:Sr:Ca;Cu as 1.6:0.4:2:2:3 respectively. 20 ml of water is also added to dissolve all the nitrates completely to get clear bluish green solution. This solution was heated on a water bath at 80°C. On concentration, brown fumes of oxides of nitrogen evolved and resulted in a green gel and was dried in air circulating oven at 120°C for 24 h. This gel is used for the preparation of high-Tc BPSCCO superconductor powder.

(ii) Microwave synthesis of precursor powder for BPSCCO superconductor:

Nitrates of bismuth, lead, strontium, calcium and copper were used in the microwave decomposition studies. A mixture of cations in $Bi_{1.6}Pb_{0.4}Sr_2Ca_2Cu_3O_{10+x}$ stoichiometry was ground in an agate mortar to a homogeneous paste and was introduced into a microwave oven having 2.45 GHz and 600W power and exposed for 60, 120, 180, 240 and 600 sec. in separate experiments. Another set of experiments were done by incorporating 7.5 wt.% of starch to the nitrate mixture. The percentage of starch was arrived by trials. The mixture started melting to give a uniform bluish coloured solution, then evolved brown fumes with foaming. At the end of 180 sec. of exposure, the mass got converted to a pale green gel which immediately decomposed with a glow to result in black powder. This precursor was subjected to thermogravimetric analysis in a Schimadzu TGA unit with a heating rate of 10°C/min. in air. All these powders were further heat treated upto 50 h in powder form in air. X-ray diffraction as well as SEM data at various stages have been taken and analysed.

The precursor powders obtained in both cases were used for calcination studies and superconductor phase formation. The characteristics of superconductor phase powder obtained from both experiments were also characterized and properties are compared.

2. B. CHARACTERISATION TECHNIQUES USED IN THE PRESENT STUDY

2.B.1 Introduction

Characterization of the raw materials and the powders are important to determine various parameters like chemical composition, particle size distribution, morphological feature, density, surface area etc. Figure 2.2 represents the relationship between characterization features and ceramic processing features(15-21). Various instrumental methods used during the present study are briefly described below:

2.B.2 Chemical Analysis: Estimation of Alumina

Procedure: Transferred 20 ml of standard aluminium solution (0.02 M) to a 250 ml flask, added 25 ml EDTA and a drop of methyl orange solution followed by ammonia (1:3) dropwise until the colour of the indicator changes from red to yellow. Add 10 ml of buffer (pH 5.3) and heated to boiling for 5 min. Cooled and added 5 ml of buffer (pH 5.3) and titrated with zinc acetate (0.02 N) using a few drops of xylenol orange indicator. The end point was noted as the yellow colour changed to orange. Then added 1 gm of NaF and boiled for 5 min, cooled, added 10 ml of buffer (pH 5.3) and titrated with zinc acetate (0.02 N). The equivalent Al_2O_3 for 1 ml of zinc acetate (0.02 N) was found out by dividing the amount of alumina present in 20 ml by the titre value of zinc acetate. Similarly, the boehmite sol digested with sulphuric acid was used for estimation and the following

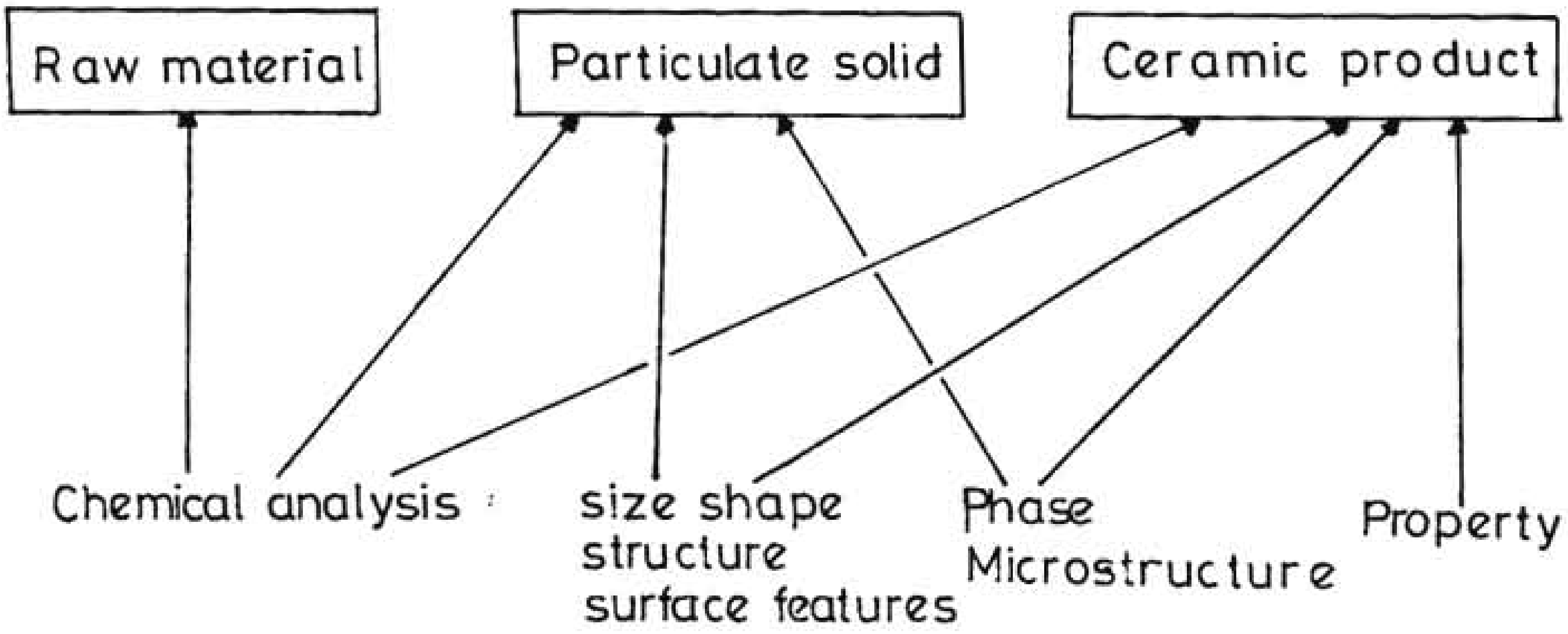

Fig. 2.2 Relationship between characterisation and ceramic processing

equation is used for calculation percentage of alumina =

$$\frac{a \times V \times M}{W} \times 100$$

a = volume of boehmite sol

V = titre value in ml of zinc acetate solution

M = equivalent of Al_2O_3 in gm per ml of zinc acetate solution

W = wt. in gm of the sample present in 250 ml of the stock solution

2.B.3 Flame Photometer: Estimation of Sodium

A Flame Photometer can be used for quantitative analysis of cations which impart colour to the flame. In the present case sodium content of the alumina was measured using flame photometer. Absorbance for a series of standard sodium chloride solutions were obtained first and the graph plotted as a function of concentration and absorbance from which the concentration of test solution was calculated.

Standard sodium solutions of 200 ppm was made by dissolving 0.2542 gm of dry NaCl in double distilled water and diluted to 500 ml in a calibrated flask. Solutions of 10 ppm, 20 ppm, 50 ppm and 80 ppm were made from this with proper dilution and drawn a calibration curve. The boehmite sol digested with sulphuric acid was also used for the test and the concentration of sodium was obtained from the calibration graph.

2.B.4 X-ray Diffraction (XRD) Studies

XRD is usually used to characterize crystalline materials and is described based on Bragg's equation where λ is the wavelength of X-rays, angle of diffraction from a lattice plane with spacing 'd' and 'n' an integer or order of diffraction. X-ray specimen can be a single crystal or a powder or a polished surface. The latter two are commonly used for a polycrystalline material. The intensity of diffracted X-rays are plotted against 2θ values. The identification of phases are done by calculating the 'd' values for each peak and comparing it with the standard values given in JCPDS file. If the diffraction pattern is new, computerised programmes are available to find out the plane of diffraction, 'd' values and crystal structure of that new compound.

In the present study, X-ray diffraction patterns were obtained from a Rigaku model (Japan) X-ray diffractometer with CuK using nickel as a filter. The samples for XRD were prepared by smearing the powder on glass plates coated with paraffin. The powder was pressed using another clean glass plate to get a plane surface.

XRD pattern, in the present study, was used to study the crystallinity and amorphous nature of gels. The amorphous nature of sol-gel derived boehmite and evolution of various transition aluminas during calcination was studied by XRD. XRD data are used to study the chemical reactions taking place in aluminium titanate formation. The effect of calcination and reaction temperature in Bi based superconductor was also studied by XRD pattern. Texturing of BPSCCO grain in its bulk compact was analysed by (001) reflection in XRD Pattern.

2.B.5 Thermal Analysis

Thermal analysis included Thermogravimetric Analysis (TGA) and Differential Thermal Analysis (DTA) with respect to the present investigation.

i. TGA: Thermogravimetric analysis mainly consists of a furnace, highly sensitive balance and set up for measuring temperature and weight change during heating. Thermogravimetric analysis presently consists of a plot of weight change vs temperature called thermogram or TGA curve. TGA curve provides information about vapourization, oxidation, decomposition etc. processes. In the present study a Shimadzu TGA (H 50 model, Japan) was used. Heating rate adopted was 5°C/min in air.

TGA results were used to study the decompositior patter of gel precursors made under various conditions in order to adopt the right calcination conditions.

ii. DTA: In DTA, highly sensitive thermocouples detect the difference in the temperature (ΔT) due to some chemical or physical processes occuring in the sample and is plotted against temperature. Thus the exothermic and endothermic processes and a quantitative knowledge of the energy changes can be obtained from DTA curves. The reference sample used is alpha alumina which undergoes no enthalpy change till its melting point.

Schimadzu DTA H50 model was used in the present study. The heating rate was fixed to 5°C/min under atmosphere conditions. All the samples were dried at 100°C for 2 h and cooled in a desiccator before the thermal analysis. The data obtained from DTA curves were used to study the temperature of nucleation of crystallites from gels, formation of transition aluminas from gels processed under various conditions by identifying the exothermic and endothermic peaks. Aluminium titanate phase formation from its precursor gels were also studied by DTA peaks.

2.B.6 Particle Size Analysis

Commonly used techniques for particle size measurements are sieving, sedimentation, laser diffraction, light intensity fluctuation technique etc. Among these, sedimentation technique is widely used in ceramics. Stoke's law is the basic principle of sedimentation technique. Stoke's law uses to determine Stoke's diameter 'a' of a particle by correlating the terminal velocity 'V' of particle settling under gravity in a medium of viscosity .

$$a = \sqrt{\frac{18\eta V}{(D_P - D_L)\,8}}$$

where D_P and D_L are the densities of particle and liquid. To prevent the particle agglomeration, suitable surfactants are used during dispersion and is dispersed ultrasonically.

In the present study a particle size analyser (Sedigraph 5000D, Micromeritics, USA) was used where the particle sedimentation is monitored by X-ray. A plot of cumulative mass percentage vs equivalent spherical diameter is obtained from which the average particle size could be calculated easily. The powder suspensions were made in glycerol-water system by ultrasonically dispersing it.

The data obtained from particle size analysis are used to compare the particle size distribution in alumina and aluminium titanate obtained from gel prepared under various conditions. The packing characteristics, sinterability under various of these powders were correlated with particle size distribution.

2.B.7 Microscopic Techniques

The Scanning Electron Microscopy (JEOL 35C, Japan) was extensively used to study the morphological features of powders, microstructure of green and sintered compacts and texturing of BPSCCO compacts. The samples for SEM were prepared by depositing a thin film of powder from a dilute dispersion on a brass stud. The fractured surface of sintered specimen are made by making a fresh fractured surface and fixing it on a brass stud. The samples for SEM were coated with gold in ion sputtering unit (JEOL, Finecoat JFC 1100, Japan) to make the sample conductive.

2.B.8 Density Measurements

The tap density of powders were found out using a densitometer (Indian Equipment Corporation, Bombay, India) and graduated cylinders. Powders of known weight were taken in graduated cylinders and tapped for 15 min with a tapping rate of 25 taps/min. The resultant volume of the taped powder was measured and the density was calculated. The density of sintered specimen were found out using Archemedes principle.

2.B.9 Surface Area Analysis

The specific surface area, in the present study, was measured using a surface area analyser (GEMINI 2360, Micromeritics, USA) working on the principle of BET equation after attaining the dynamic equillibrium of gas adsorption on the surface.

In the present study, the samples were evacuated at 150°C and then cooled to liquid nitrogen temperature before nitrogen gas adsorption. The specific surface area results were measured in the P/Po range 0.03 to 0.5.

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CHAPTER III

STUDIES OF SOL-GEL DERIVED ALUMINA

3.1 PREPARATION OF ALUMINA POWDERS FROM BOEHMITE GEL

(a) Gel calcination-characterisation studies

Boehmite gel obtained after optimising the condition of precipitation (Chapter II(a)) was peptized to boehmite sol at pH 4 by adding 1:1 HNO_3. The sol was aged for 24 h at 28°C and was estimated for alumina, Fe_2O_3 and soda content by wet chemical analysis methods.

The transparent hard gel of boehmite obtained after drying was subjected to thermal analysis with a heating rate of 10°C/min. The gel was calcined at 200, 400, 600, 800, 1000 and 1200°C in an electric muffle furnace and evolution of transition aluminas were monitored by XRD. The calcined powders were dry ground in a mechanical grinder (Retsch, Germany) for 30 min. Specific surface area of these powders were determined. They were compacted into discs of 10 mm dia and 2 mm thickness uniaxially at 200 MPa pressure. These discs were sintered at 1600°C for 2 h in an electric muffle furnace (Nabertherm, Germany). Sintered densities of these samples were measured by Archemedes principle. Fractured surface of these sintered discs were observed under Scanning Electron Microscope for morphological characterisations.

(b) Preparation of spray dried powders

Another batch of boehmite sol was spray dried in a Buchi minispray drier (Switzerland) to obtain spherical powders. The characteristics of the sol used and conditions of spray drying are provided in Table 3.1.

The spray dried powders were carefully collected so as to prevent contact with moisture and then calcined at temperatures ranging from 200 to 1200°C. These powders were also characterised.

(c) Preparation of solvent treated powders

Boehmite gel was redispersed in solvents such as isopropanol and acetone by sonication and filtered after a residence time of 30 min. The weight ratio of gel to solvent was 1:5 and the washing was done for five consecutive times. The washed gel was dried in an air oven at 80°C for 24 h. Similarly the spray dried powders were also washed using isopropanol and acetone. The powder to solvent weight ratio is reduced here to 1:2 due to the consideration of lower water content in the spray dried powder. All the treated powders were characterized by TGA and DTA. The powders calcined at various temperatures of 200 to 1200°C were characterized for specific surface area, morphology and sinterability at temperatures of 1450, 1500 and 1600°C.

Finally, a comparison of the results of characterization of alumina powder obtained from various

Table 3.1 Spray drying conditions

1. Constituent of sol		Boehmite
2. Colour		Bluish tinge
3. Solid content		3 M AlOOH
4. Temperature		
	Inlet	= 170°C
	Outlet	= 100°C
5. Feed rate		= 15 ml/min.
6. Nozzle Size		= 0.5 mm dia

treatments were made to arrive at a low temperature processable powder.

3.2 RESULT AND DISCUSSION

3.2.1 Alumina from nontreated boehmite gel

(a) Boehmite gel preparation:

Al^{3+} ions undergo various extent of hydrolysis to different hydroxides in presence of OH^- ions(1). Depending on the pH conditions, the hydroxide may be either $Al(OH)_3$ or AlOOH(2). In the present case, as the concentration of Al-nitrate is increased above 10%, the viscous gel formed at the gelation point around pH 7 would be so thick that it creates stirring problems and hence affect the homogeneity. Thus as an optimum condition, 10% aluminium nitrate was used for precipitation reactions. Table 3.2 summarises the effect of pH and T on the nature of precipitation.

Thus boehmite preparation from the requires a temperature above 90°C and careful control of the pH in between 7 and 7.5. The presence of boehmite is observed with its bluish tinge. The gel obtained under above described conditions was washed to remove nitrate ions completely. A study on the filtration rate was carried out which indicated that the gel at pH 8 has maximum rate of filtration. But the quantity of filtrate collected for longer time of filtration was higher in the case of those prepared at pH 7. It was noted that presence

Table 3.2 Optimum conditions for boehmite preparation

Concentration of Al-nitrate solution (Aqueous)	T°C	pH	Physical appearence of gel	XRD data
10% (by wt)	28	7-7.5	Bluish tinge precipitate turns white on aging	Boehmite to Bayerite conversion occured
,,	28	8	White precipitate	Bayerite
,,	95	7-7.5	Gel with Bluish tinge	Boehmite
,,	95	8	White crystalline precipitate	Bayerite

of small amount of alcohol like isopropanol has made the boehmite stable towards higher pH ranges.

(b) Thermal analysis of the gel:

The peptized gel on drying converted to a clear transparent gel. Thermal analysis data of the xerogel is presented in Fig.3.1. The gel appears to undergo three stages of decomposition (Fig.3.1a). First decomposition at 200°C is the liberation of free water present in the gel pores and is predominantly endothermic as supported by DTA results (Fig.3.1b). The weight loss occuring at around 300°C is very sharp and is exothermic in nature. The exothermic nature indicates the decomposition of nitrate ions. A further weight loss taking place after 300°C to 500°C range is a broad one. The broad exothermic peak ranging from 400 to 800°C is due to crystallization of gamma alumina. The results are supported by XRD data also. The alpha alumina crystallization is indicated by the exothermic peak in DTA at 1120°C. In fact, this peak ranges over a temperature of 1000 to 1150°C, which shows that crystallization of different transition aluminas were also taking place in this range and are also exothermic in nature.

Comparison of TGA-DTA of gels treated with solvents like acetone and isopropanol are presented in Figs. 3.2 and 3.3 respectively. The total weight loss is considerably lower indicating that the pore water in the gel are removed during washing. The weight loss registered at 400-800°C range in gel

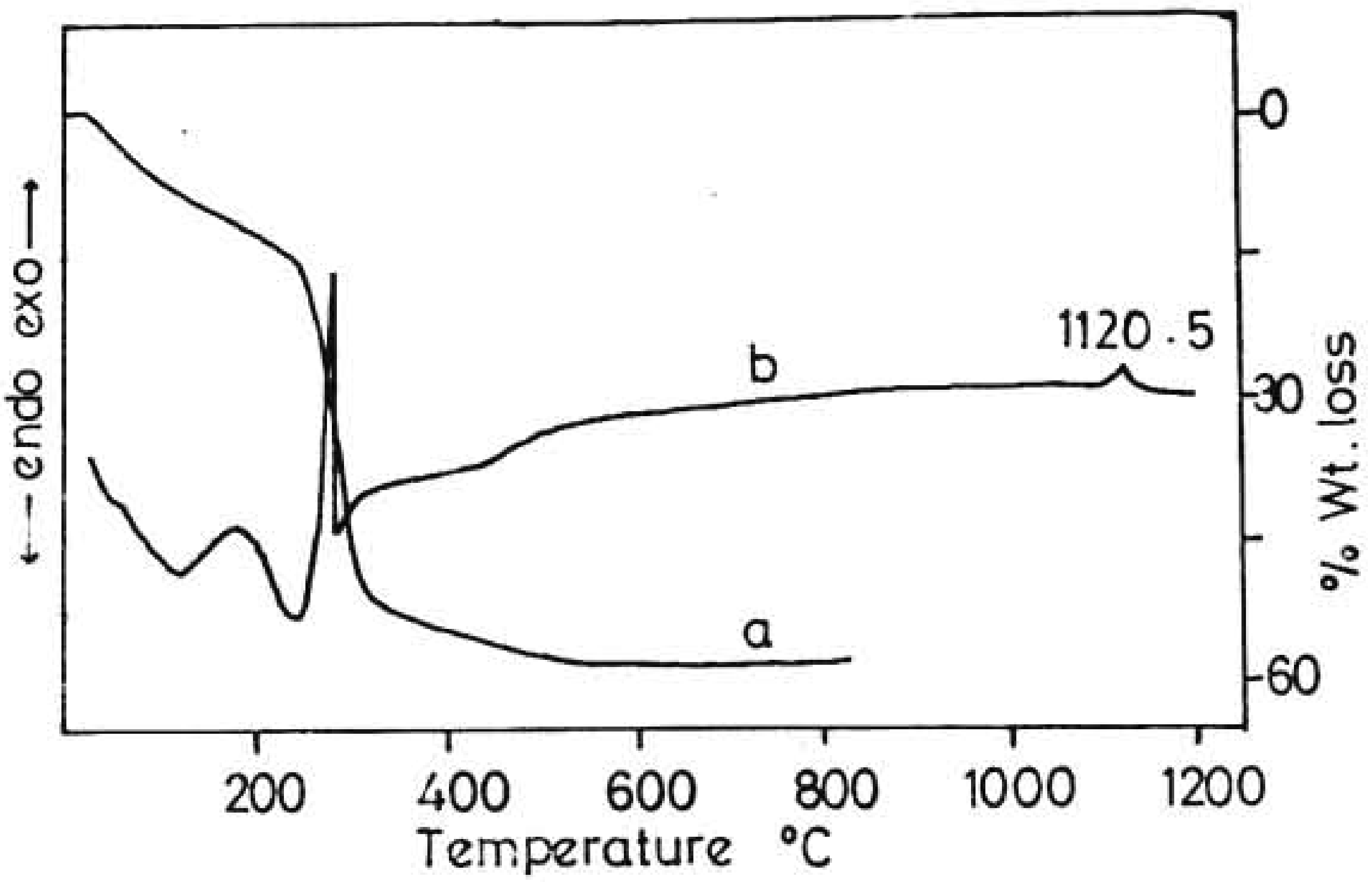


Fig.3.1 Thermal anlysis curves of boehmite gel
(a) TGA (b) DTA

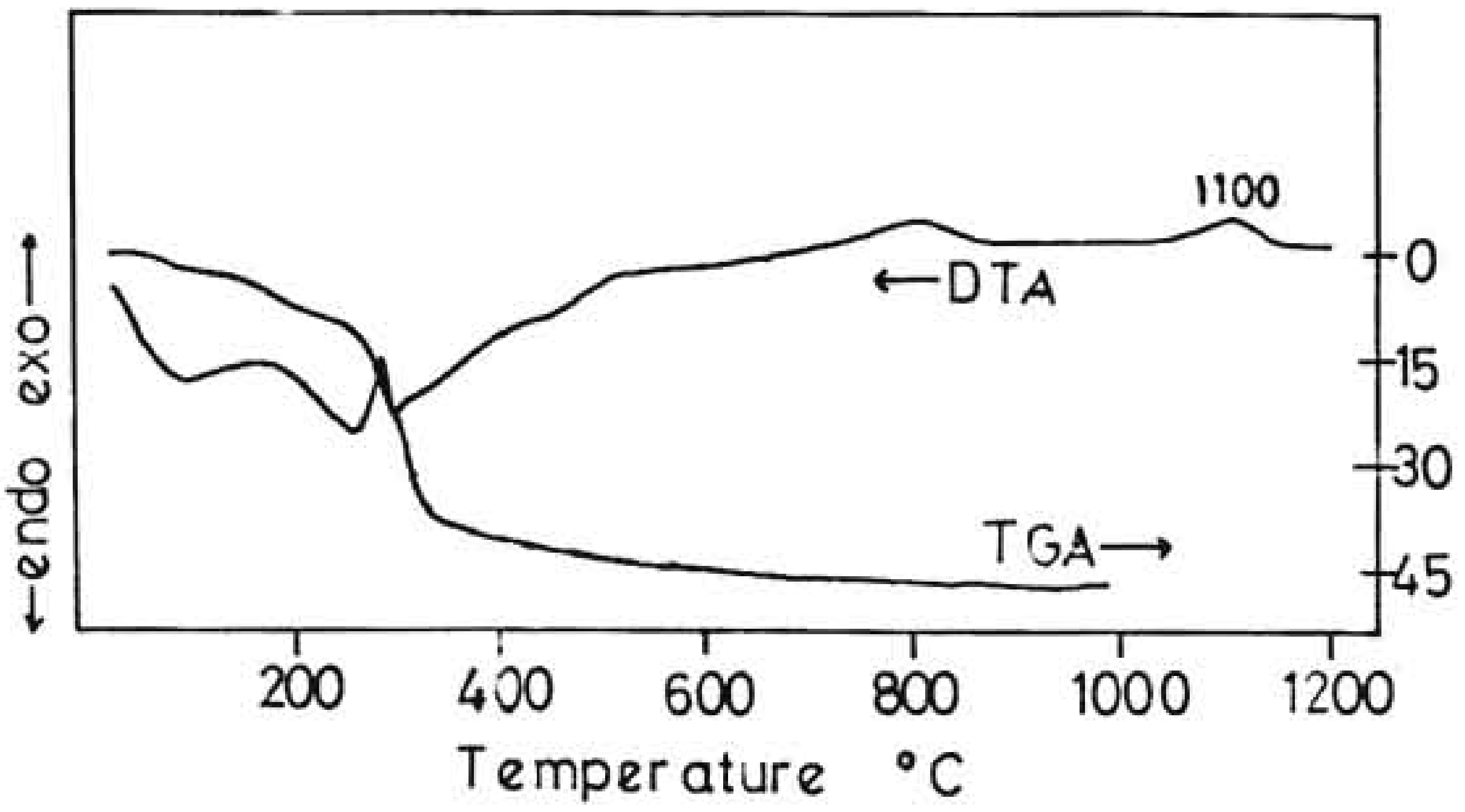


Fig .3.2 TGA - DTA Curves of acetone treated boehmite gel

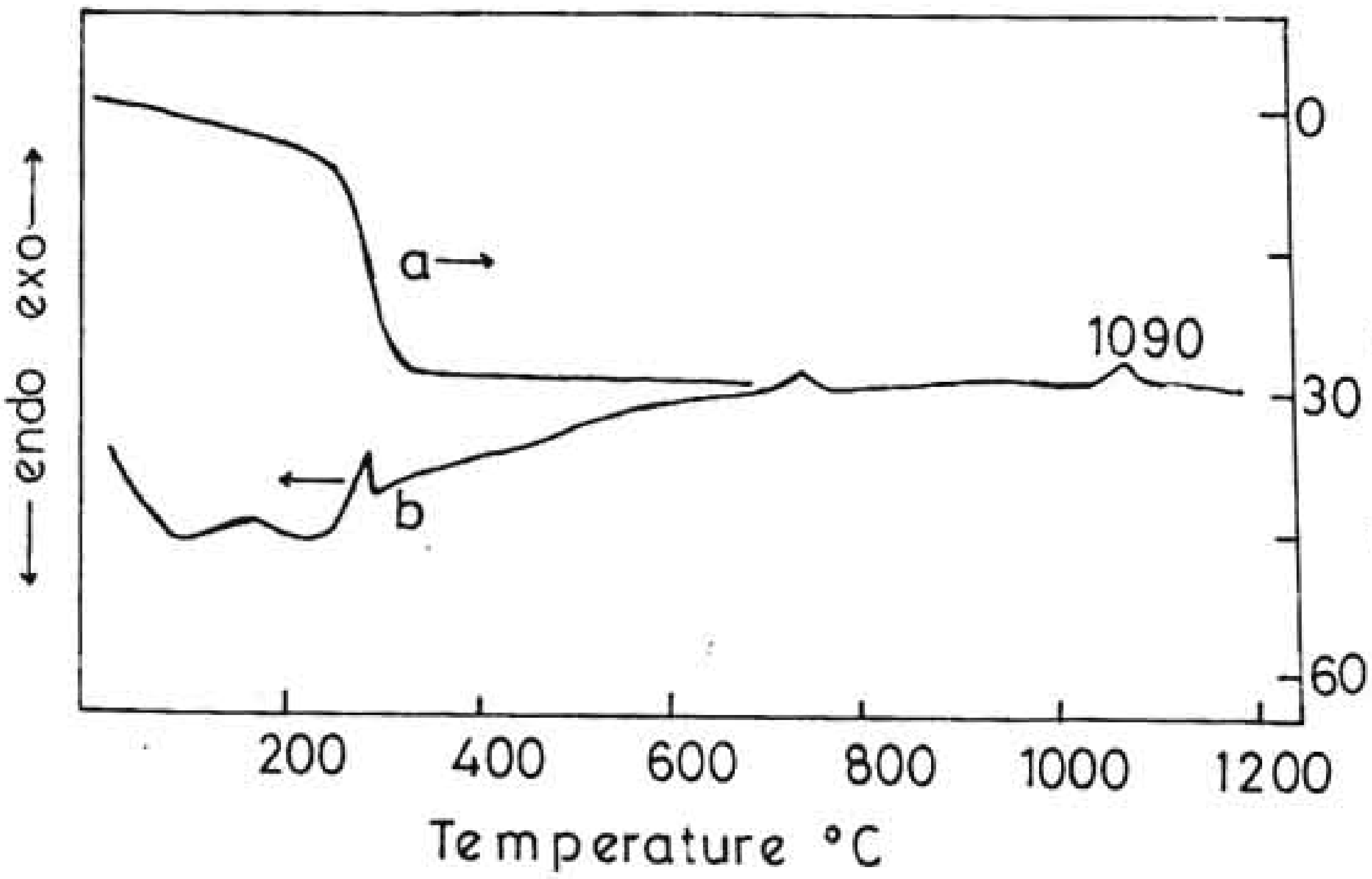


Fig. 3.3 TGA-DTA curves of isopropanol treated boehmite gel.

without solvent washing is not observed in the solvent treated gels. This indicates that the surface hydroxyls are replaced by solvent groups to large extent. This, of course, should lead to lower extent of agglomeration during further calcination of the gels. The alpha alumina formation has been reduced by 50-60°C in treated gels when compared to non treated gels. The solvent treatment has changed the gel network and hence the decomposition pattern of gel may be the reason for lowering of formation temperature. Perhaps, the enhanced surface energy of the unagglomerated gamma Al_2O_3 makes it less stable converting it to alpha Al_2O_3 at low temperature.

(c) X-ray diffraction studies:

The gel and oxides obtained after calcination at various temperatures were analysed by powder X-ray diffraction. The gel dried at room temperature shows no specific X-ray pattern due to the amorphous nature but on drying at 100°C (Sample A) for 24 h shows the broad peaks of boehmite indicating the slight crystallization of boehmite (Fig.4a). However, on calcining at 200°C (Sample B) sharp peaks are identified which are due to crystallisation of boehmite phases. The gel on further heating to 400°C (Sample C) get decomposed completely to γ-Al_2O_3. XRD shows no characteristic peaks of either boehmite or bayerite at this temperature range. The XRD pattern of sample C is very broad indicating that the γ-Al_2O_3 exists as fine crystallites. When heated to 600°C (Sample D) and 800°C (Sample E) the

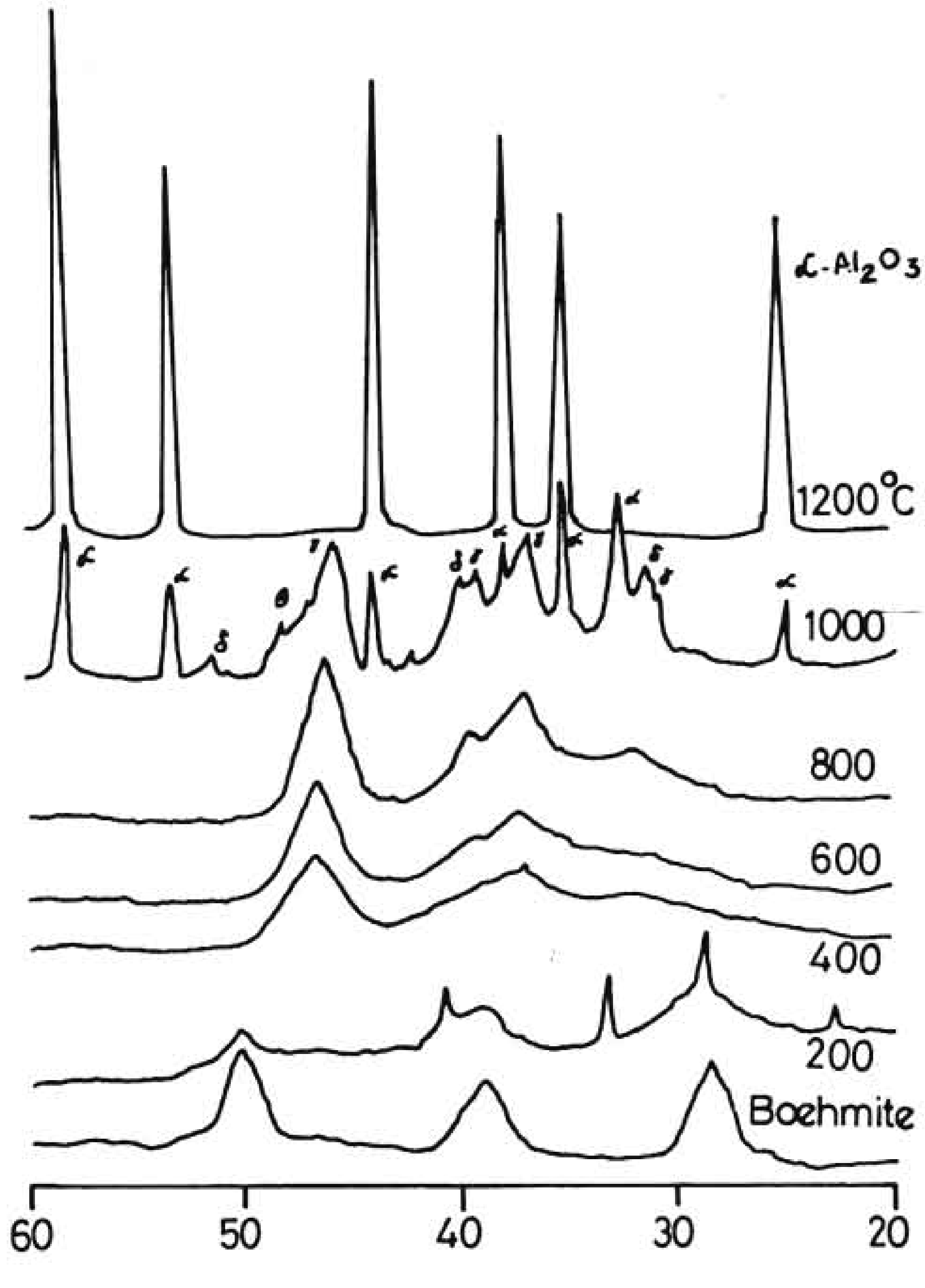


Fig.3.4 XRD Pattern showing evolution of alumina from boehmite

sharpness of the characteristic peaks of γ- Al_2O_3 increases indicating its grain growth. This situation is further indicated in DTA curves. The XRD peaks of γ-Al_2O_3 is not very sharp even at calcination at 800 or 1000°C. This may be due to the spinel structure of γ- Al_2O_3(3) powder obtained after heating the gel at 1000°C has given an XRD pattern given in Fig.3.4f (Sample F) where there is the coexistence of transition aluminas like γ, δ, θ and α. But on heating to 1200°C for 8h (Sample G) all of the γ- Al_2O_3 and other transition aluminas are consumed and α-alumina phase is formed. The exothermic peak as developed from 1000°C onwards indicates the transition aluminas like γ, θ and δ from γ Al_2O_3 matrix are formed above 1000°C. The α-Al_2O_3 crystals could be evenly distributed in the γ- Al_2O_3 matrix which may have a seeding effect of α-Al_2O_3 in γ-Al_2O_3 matrix. The XRD of sample F indicates the presence of α- Al_2O_3 by very sharp peaks and the XRD pattern of 1200°C calcined powder with intense peak of α- Al_2O_3 again indicating the grain growth of α. Al_2O_3.

(d) Surface area measurements:

Figure 3.5 indicates the specific surface area of boehmite and oxide obtained after calcination at various temperatures. On calcination at 400°C, the specific surface area increases to 275 g/m^2 and on further heating at higher temperatures it gets reduced. Obviously this is due to the grain growth and agglomeration. A sudden decrease in the specific surface area takes place in between 600 and 1000°C indicating very high extent of grain coarsening at these ranges of temperatures.

(e) Compaction-sintering behaviour:

Table 3.3 summarises the compaction behaviour of alumina powder obtained after calcining at various temperatures. There is a general increasing trend in the green density with calcination temperature upto 1200°C. However, the powder calcined specifically at 1000°C has attained higher density on sintering at 1600°C compared with other samples. The sample calcined at 1200°C obtained slightly higher green density. Since the densification kinetics also depends on the nature of porosities present in green compacts, two identical compacts with similar green densities vary in the pore distribution. This leads to different paths of pore removal mechanism leading to different sintered densities. However, the densification of sample F to higher densities may be attributed by the insitu conversion of the low temperature transition phases to alpha alumina. The mechanism could be that the small quantities of alpha alumina uniformly distributed in powder compacts act as nuclei for former conversion and densification. Effect of physical seeding of alumina in boehmite gel has shown early sintering(4,5). Further, the present observation is rather similar to the transformation assisted densification in TiO_2 system(6). The lower densities

Table 3.3 Comparison of compaction and sintered densities of powders from boehmite calcined at various temperatures

Sample (Temp.) of Cal. (°C)		Green density (kg/m^3)	Sintered density (kg/m^3)
B	200	1230	3296
C	400	1380	3455
D	600	1400	3514
E	800	1410	3700
F	1000	1540	3900
G	1200	1660	3720

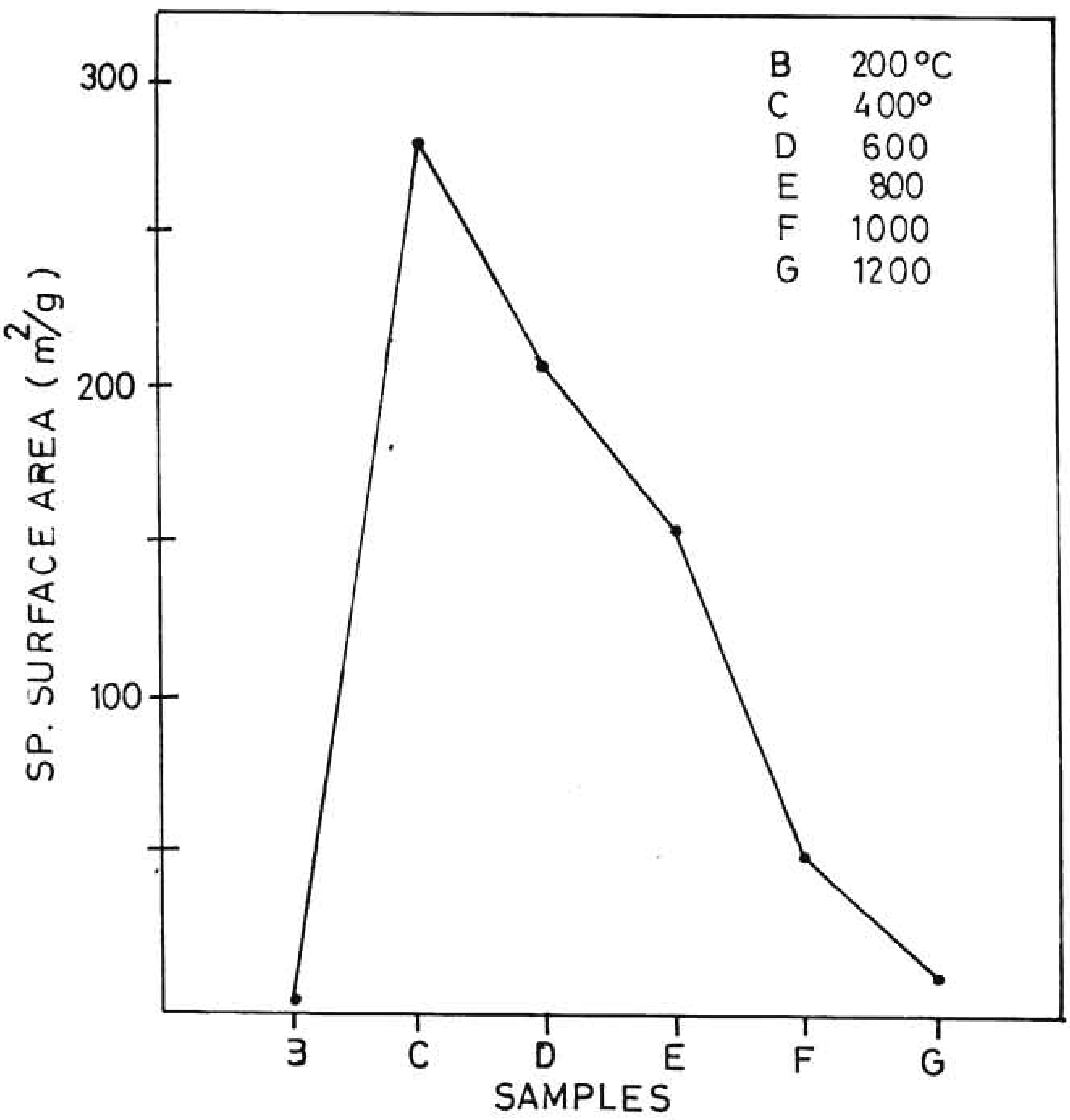


Fig.3.5 Variation of specific surface area

obtained on calcined gel at 800°C could be due to insufficient nucleating sites and also incomplete decomposition of the boehmite. This is further indicated by the IR spectral data (Fig.3.6) of samples calcined over various temperatures. However, the densification of sample F to higher values may be contributed by the insitu conversion of the low temperature phase to α-Al_2O_3. Figure 3.7 shows the variation of sintered density of powders calcined at various temperatures.

Figure 3.8 indicates the fractographs of sintered alumina from compacts of gels calcined at 1000° and 1200°C. While the former appears to be nearly dense having average grain size of 2-2.5 µm and with least inter or intragranular porosity, the latter appears to have larger grains and porosities.

3.1.2 Characterisation of alumina powder from solvent treated boehmite

Figure 3.9 indicates the IR spectra of alumina obtained from solvent treated gels calcined upto 800°C. The hydroxyl groups get removed at as low as 400-500°C compared to 800-900°C in the case of untreated gel(Fig.3.6).

Table 3.4 shows the variation in surface area of isopropanol and acetone treated powders. Specific surface areas of 310 m^2/g and 65 m^2/g are obtained for isopropanol treated gel calcined at 400°C and at 1000°C respectively. However, the gel treated with acetone and calcined at 400°C had

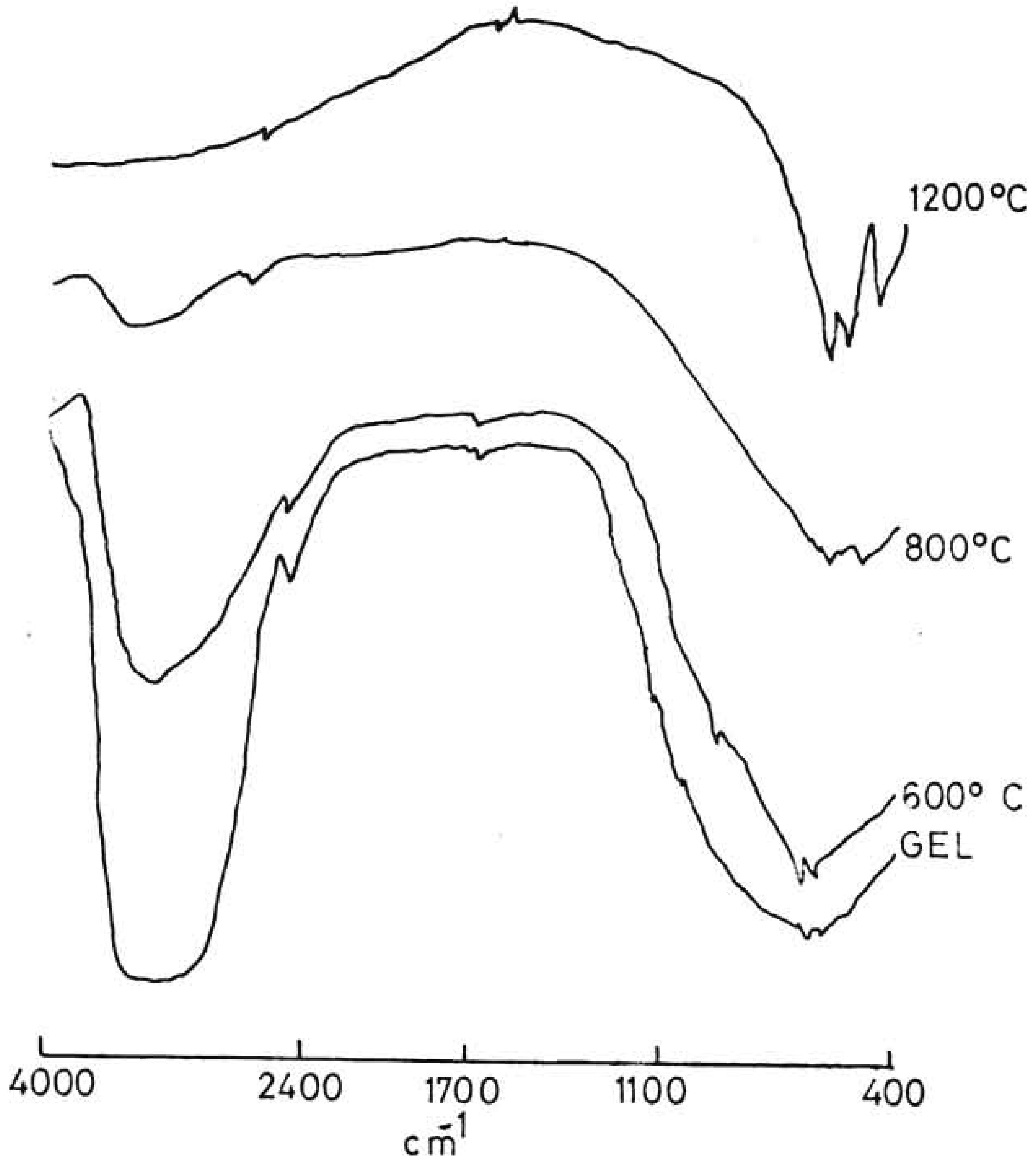


Fig.3.6 IR Spectra of boehmite gel heated to vaious temperatures

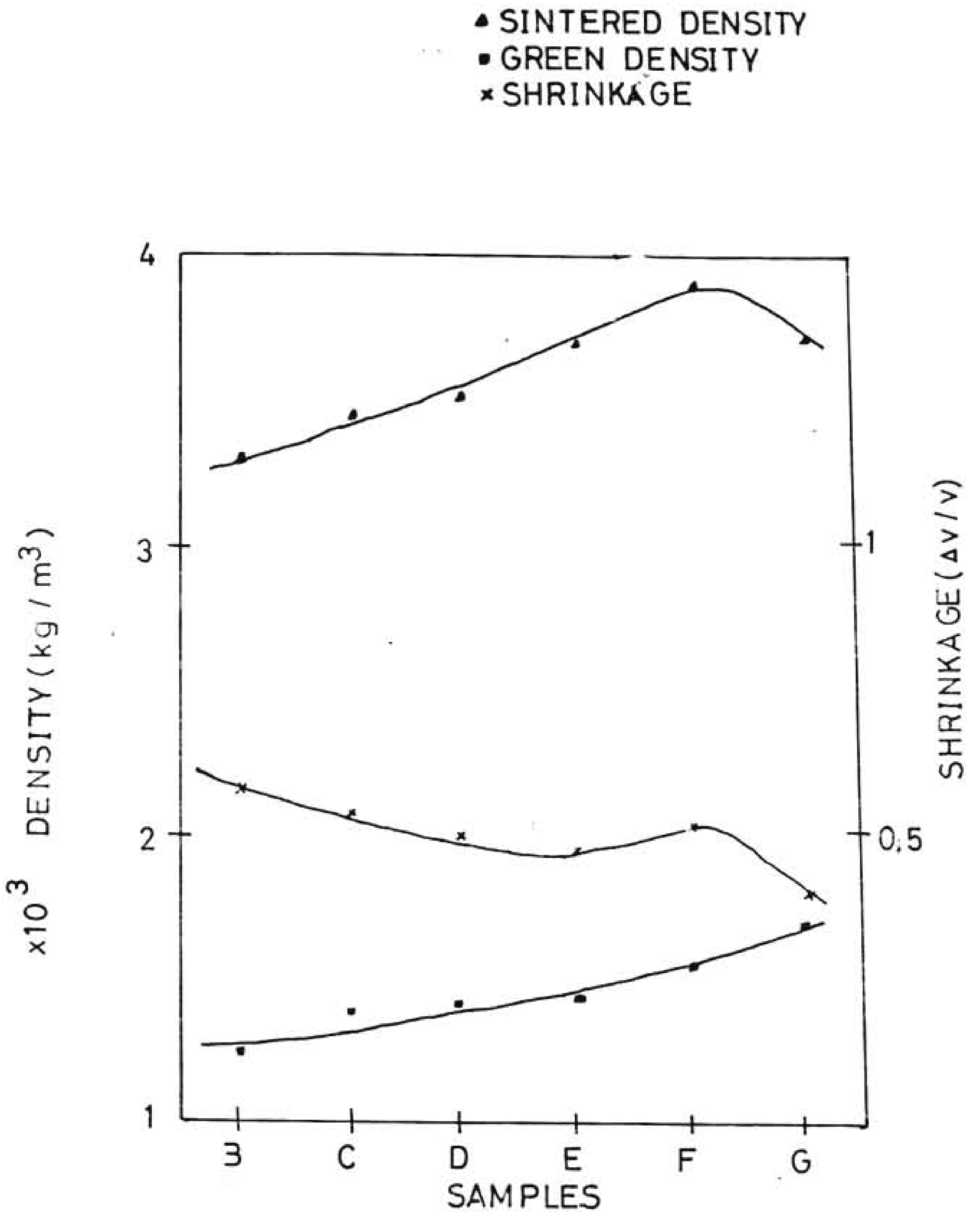


Fig. 3.7 Density variation in boehmite calcined at various temperatures.

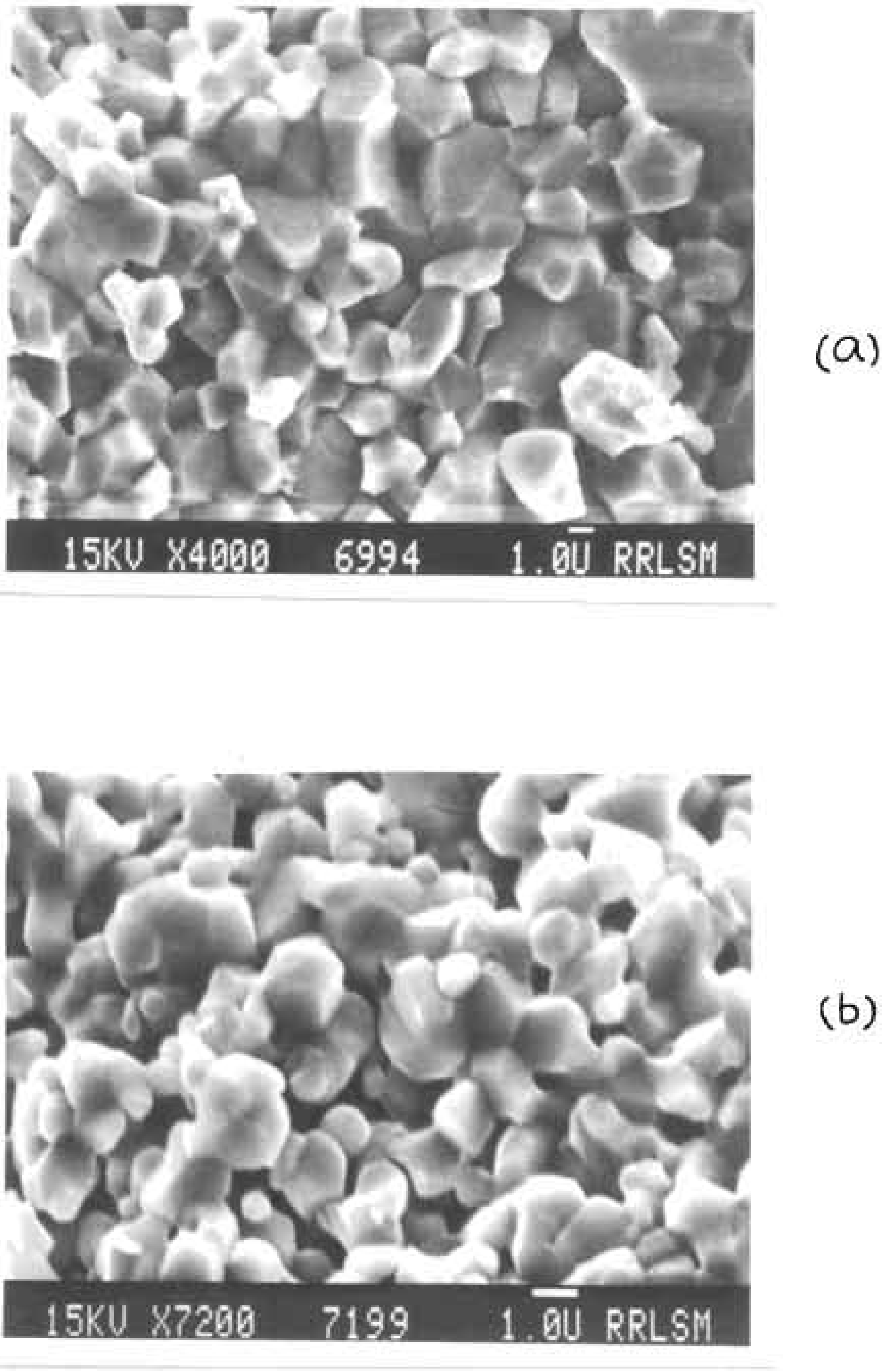


Fig. 3.8 SEM fractographs of alumina sintered at 1600°C from powders calcined at (a) 1000°C and (b) 1200°C

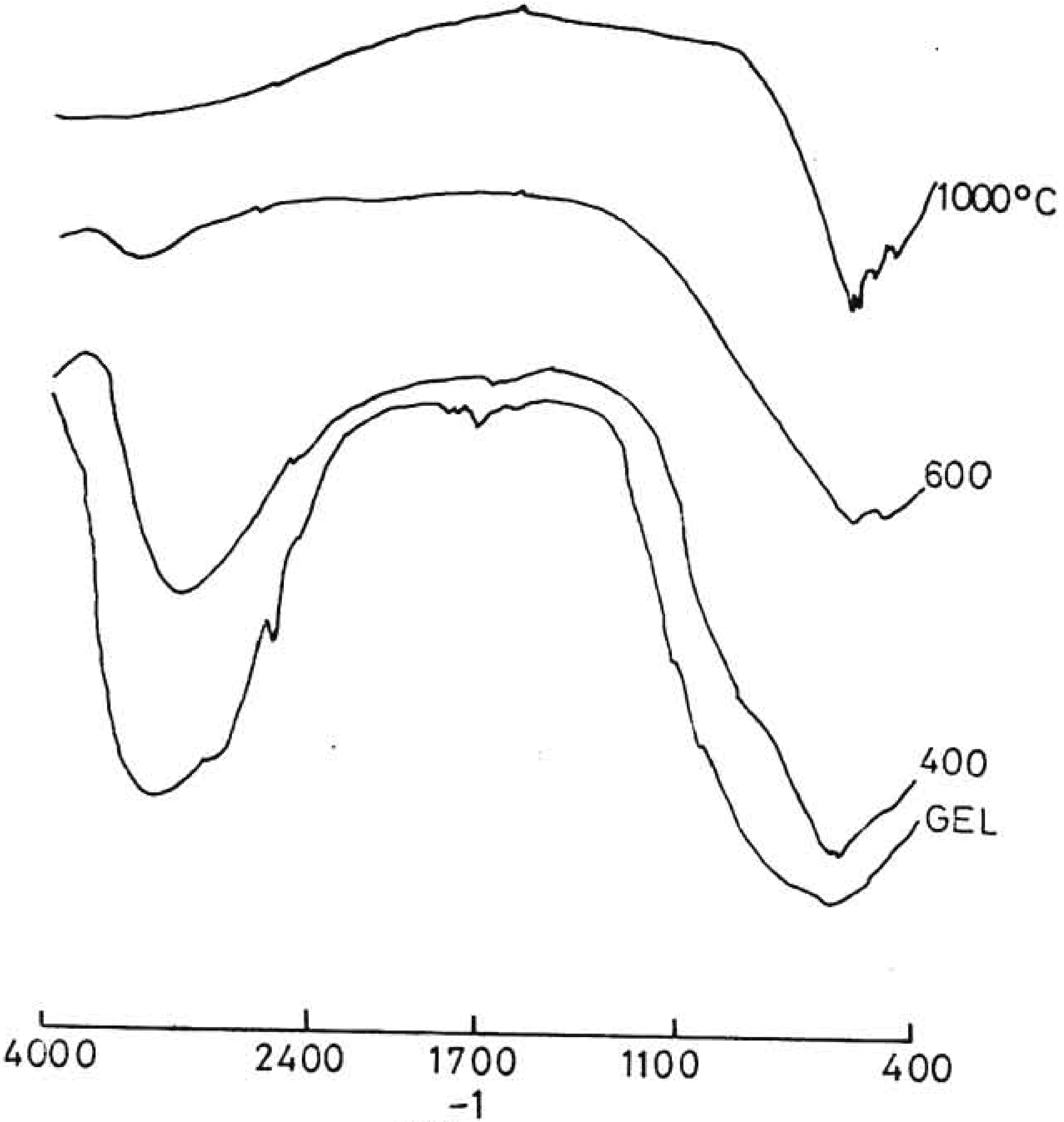
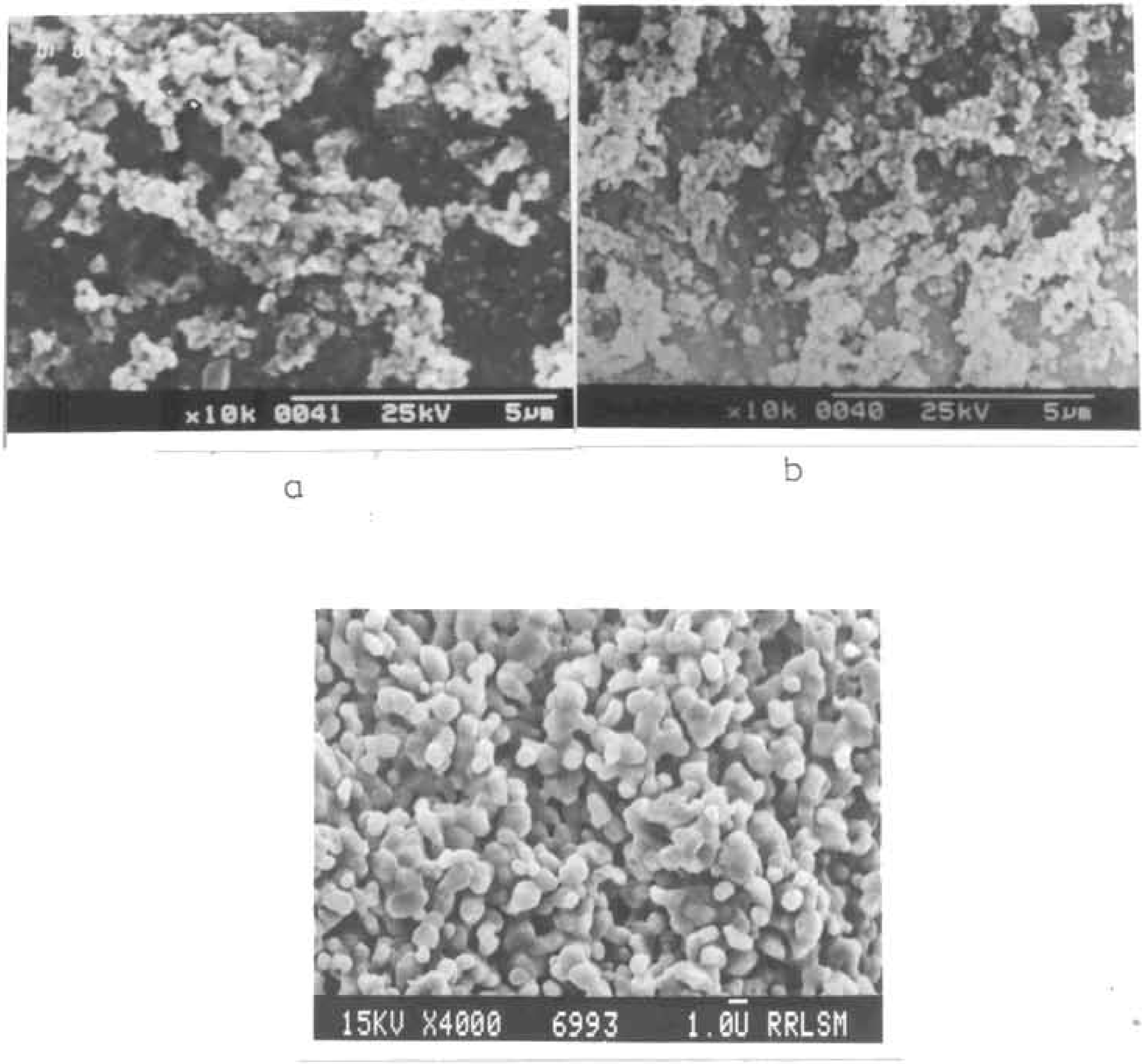


Fig.3.9 IR Spectra of isopropanol treated boehmite calcined at various temperatures

Table 3.4 Specific surface areas of solvent treated boehmite gel calcined at various temperatures

Sample	temp. calcination (°C)	Sp. Surface area (m^2/g)
Acetone washed gel	400	302
''	1000	46
Isopropanol	400	310
''	1000	65



a

b

c

Fig. 3.10 Powder morphology of alumina obtained from solvent treated gels (a) acetone & (b) isopropanol treated gels (c) powder 'b' sintered at 1250°C for 1h

Table 3.5 Density variation for solvent treated gel derived powders calcined at 1000°C (compaction pressure, 150 MPa)

Sample	Green density (kg/m^3)	Sintered density (kg/m^3)
Acetone treated gel derived	1870	3705
Isopropanol treated gel derived	1900	3810

a specific surface area of 302 m^2/g which was lowered to 46 m^2/g after heating to 1000°C.

The powder morphology shows grains of less than 1 μm in size (Fig.3.10). The grains are not spherical in shape.

Table 3.5 indicates the green density and sintered density of alumina powder obtained at 1000°C, The sintering was done at 1450°C and obviously the sintered density of the powder obtained from solvent treated gels are much higher than that those obtained from nontreated gels. At 1450°C, the isopropanol treated gel derived powder attained 96% density but only 92% was obtained for the untreated one at this temperature value. Among the treated powders, isopropanol derived one gave highest densities to that of acetone. This may be due to the effective dissolution-removal of pore water and surface hydroxyls from the powder by isopropanol thus introducing least agglomeration at high temperature processing.

3.1.3 Characterisation of spray-dried powder

The boehmite sol spray-dried powder was used for this study. The result of the surface area of the powder calcined at various temperatures are presented in Fig. 3.11. As in the earlier case the surface area is highest at 400°C and goes down to 20 m^2/g at 1200°C. A similar set of experiment were conducted in isopropanol treated spray dried boehmite powder in surface area measurement. Surface area measurements indicates that

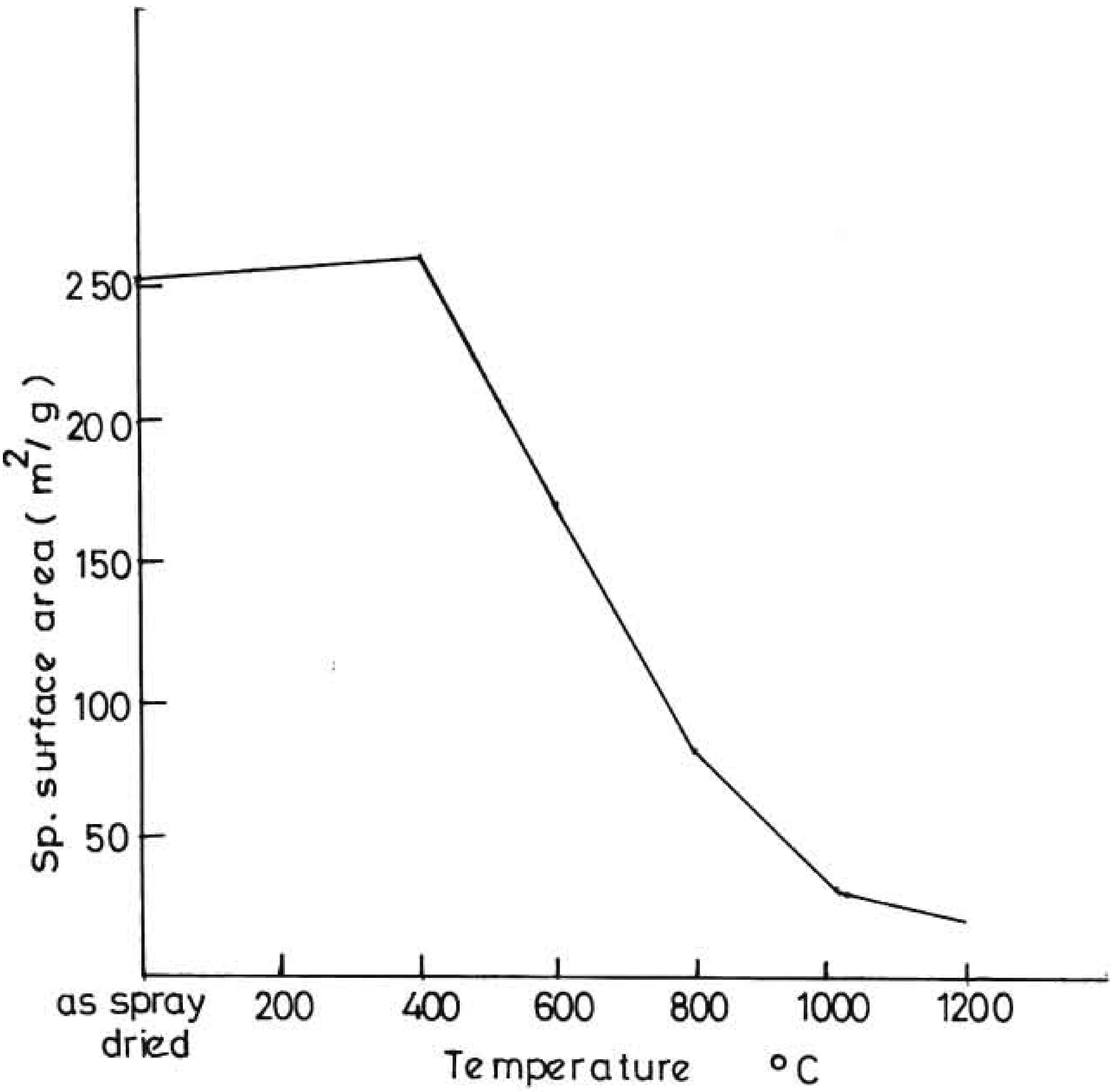
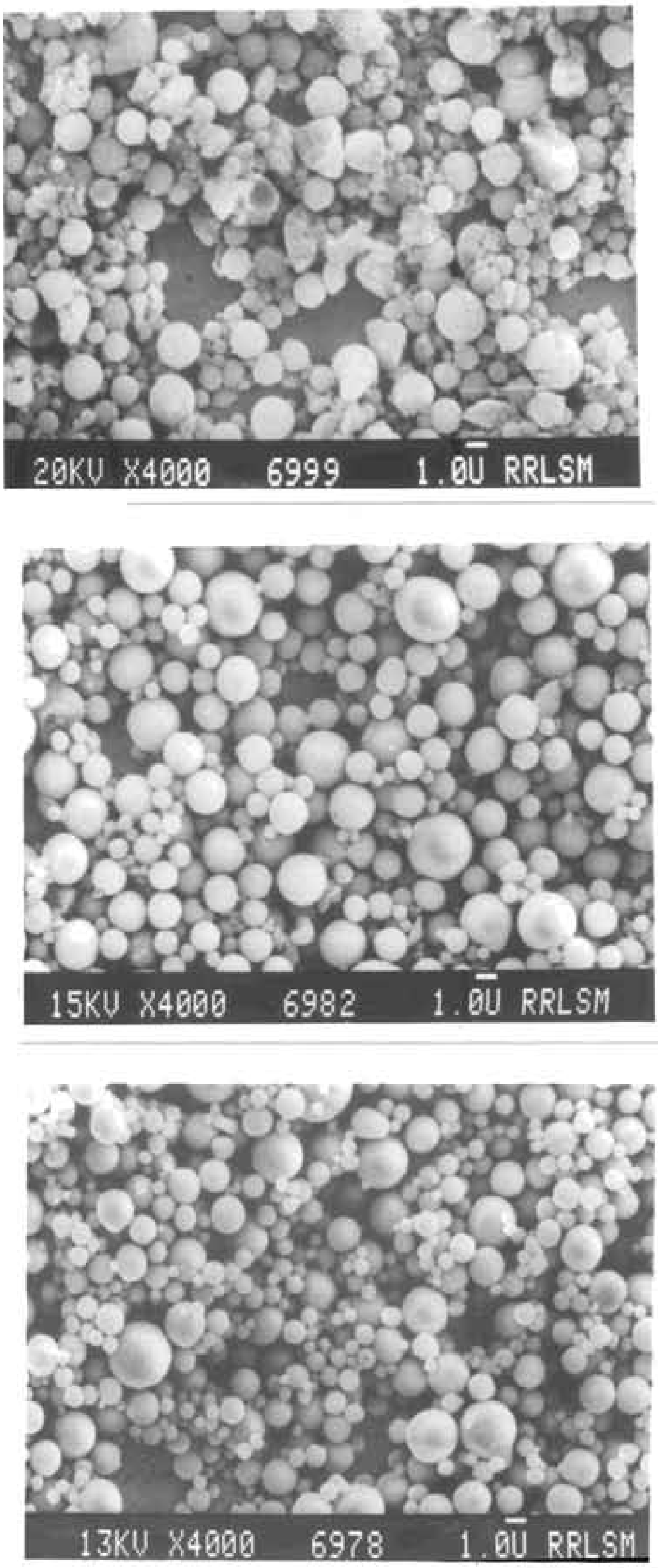


Fig. 3.11 Sp.surface area variation of spray dried powder on calcination.

spray dried powder after isopropanol treatment undergoes lowest agglomeration. This is, obviously, due to the substitution of the alkoxy groups and hence avoiding the interparticle condensation during calcination at higher temperature.

SEM study of alumina powder obtained from spray dried powder with and without alcohol treatment indicates loss of spherical morphology of spray dried boehmite powder on calcination at 1200°C while the solvent treated powder retains the same (Fig. 3.12). This figure also indicates the extend of grain growth occured in non treated powders. Spherical alumina particles with size below 0.5µm are seen in solvent treated boehmite calcined powders. Figure 3.13 also indicates the particle size distribution curve of these powders and show that the average particle size in solvent treated powder is around 1 µm.

The densification studies of spray dried powder show variation in densities with respect to the solvent treatment of the spray dried powder. Figure 3.14 indicates the packing charactristics of alumina obtained from spray dried powders with and without solvent treatment. The green density does not leave much variation but the sintered densities show a markable difference of about 5.34%.



not treated

acetone treated

isopropnol treated

Fig. 3.12 Morphology of spray dried powder after calcination at 1200°C

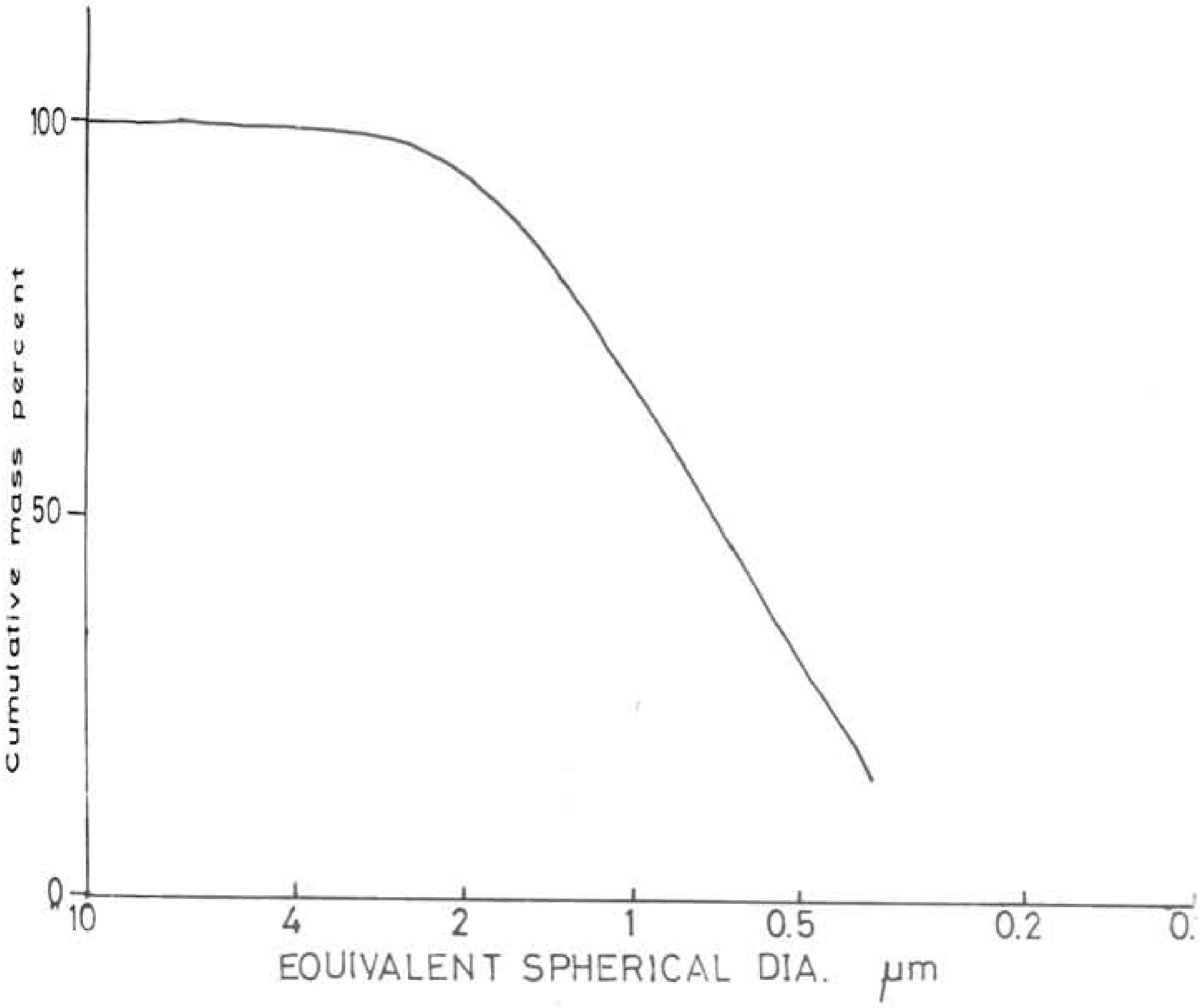


Fig.3.13 Particle size distribution of spray dried boehmite calcined at 1200°C

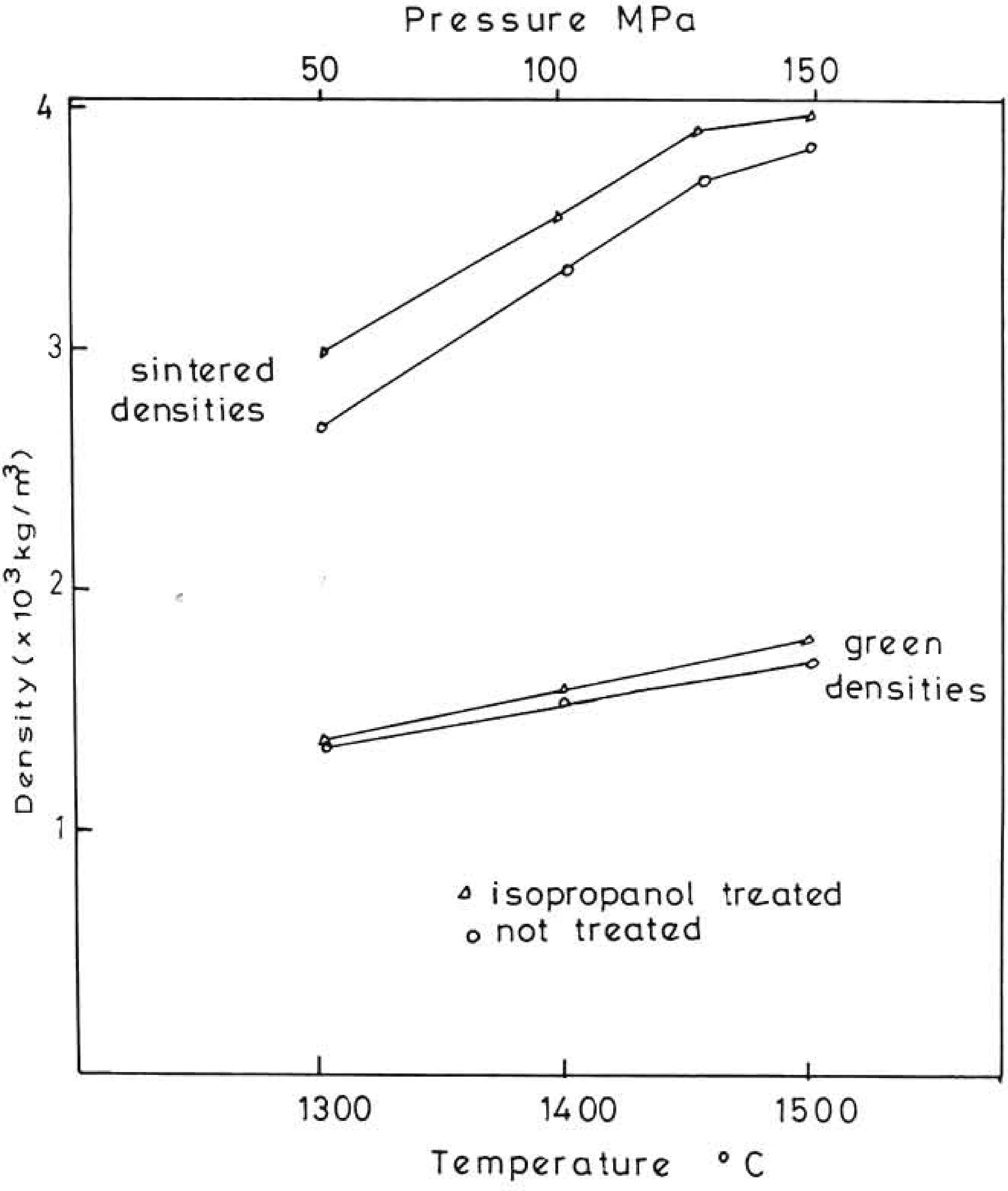


Fig. 3.14 Compaction-densification features of alumina from spray dried powders

3.3 CONCLUSION

Boehmite (AlOOH) has been synthesized from aluminium nitrate and characteristics of alumina obtained after calcination at various higher temperatures were analysed. Calcination of boehmite at 1000°C resulted in a powder containing $\gamma, \delta, \theta, \alpha$ alumina phases. The same powder on sintering at 1600°C obtained maximum density than other samples. The boehmite gel on calcination at 400°C resulted a maximum surface area of 274 m^2/g and that on treatment with acetone and isopropanol and further calcination at 1000°C obtained powders which sinters to very high densities at low temperature of 1450°C. Solvent treated boehmite gel heated to 400°C resulted in very high surface area of 310 m^2/g due to the low extent of agglomeration. Spray drying of boehmite and further calcination resulted in fine spherical alumina which also showed enhanced sinterability features.

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CHAPTER IV

STUDIES ON THE SOL-GEL DERIVED ALUMINIUM TITANATE

4.1 CHARACTERISATION OF PRECURSOR GEL AND ALUMINIUM TITANATE POWDER

(a) Characterisation of the gel:

The transparent gel prepared as discussed in Chapter II(b) was subjected to thermogravimetric and differential thermal analyses. Calcination of the gel was done at various temperatures ranging from 200 to 1400°C. The heating was done in an electric muffle furnace with a heating rate of 600°C/h and held for 4 h at each temperature set point. The powders were characterised by powder X-ray diffraction technique. The calcined gel was analysed for the removal of hydroxyl groups using *IR Spectrometer (Perkin Elmer). Samples for IR spectral* data were made by mixing a 0.5 gm dried KBr with 0.01 gm of sample and converting to thin transparent discs.

(b) Characterisation of Aluminium Titanate powder:

The powder calcined at 1400°C contain only aluminium titanate and this was ground in a mechanical grinder (Retsch, Germany) and the powder characteristics such as specific surface area, particle size distribution, packing characteristics, morphological features and sinterability were studied.

(c) Study on the gelation characteristics of aluminium titanate precursor gel:

A separate set of experiment was conducted to study the nature of gelation of the aluminium titanate precursor sol in various media. Titanium isopropoxide-acetic acid mixtures were made by mixing 38.375 g Ti alkoxide and 81 g of glacial acetic acid (16 N) under cold conditions ($T < 10°C$) in an ice bath. The alkoxide-acid molar ratio was kept at 1:10. Standard boehmite sol was mixed with alkoxide acid mixture. The total mixed sol was divided into three and each were made upto 1 litre with water, isopropanol and dioxan separately. In all the cases the aluminium titanate concentration was kept at 0.045 M.

Small amount of the mixed sol was withdrawn after different time intervals using pipette without disturbing the bulk. The turbidity was measured in a Nephelometer which was already standardised using double distilled water. As the gelation proceeds, the turbidity also increases. Suitable extent of dilution was done to get the Nephelometric reading within the measurable range. A graph was plotted with residence time vs turbidity of the three systems.

(d) Solvent treatment of aluminium titanate precursor gel:

The aluminium titanate precursor gel made as described above in water system was dispersed ultrasonically in isopropanol and acetone in separate batches. These slurries were vacuum filtered and repeatedly washed for 4 times. The solid content of the slurry was adjusted to 3 wt% during washing. The gel after washing was subjected to thermal analysis (DTA and TGA) and the aluminium titanate powder prepared was used for further study.

(e) Microwave drying of the aluminium titanate precursor gel:

The transparent aluminium titanate precursor xerogel was dried in a microwave oven of 2.45 GHz frequency and 600 W power for 10 min. This gel was further characterised by thermal analysis and the aluminium titanate powder thus obtained was used for further studies.

4.2 RESULTS AND DISCUSSION

The starting boehmite sol and titanium isopropoxide were standardised to arrive at 1:1 molar ratio of Al_2O_3 and TiO_2 in the composite gel. The boehmite sol was prepared earlier and aged for 48 h before use. The titanium isopropoxide was handled under glove box conditions taking care not to expose to atmosphere and thus to avoid any premature hydrolysis.

(a) Gelation characteristics of Aluminium Titanate Precursor Sol:

The processes of gelation of aluminium titanate precursor sols in various solvent systems have been studied by nephelometer and the results are represented in Fig.4.1. The increase of turbidity during gel formation was followed by the nephelometer. This figure shows that turbidity increases with time but the rate of increase of turbidity is not the same in all three systems. The curve 'A' which represents the gelation in water medium reaches the plateau after about 30 h but the other two, 'B' and 'C' reach the maximum turbidity range within 8 and 5 h respectively. This indicates that the medium in which sol is prepared has an influence on the gelation time. This, of course, should lead to structural changes and properties of the aluminium titanate formed which was not investigated during this study.

(b) Preparation of transparent aluminium titanate precursor gel:

Table 4.1 shows the effect of temperature of drying and pH conditions on the transparency of the aluminium titanate precursor gel. The molar ratio of alkoxide to acetic acid should not exceed 0.16 in order to get a transparent gel. Figure 4.2 indicates the flow diagram of the total process. Another feature which decides the transparency of the gel is the temperature of mixing of the reactants. The alkoxide undergoes fast hydrolysis at higher temperature. Thus all the reactants were mixed in ice bath keeping the reactant temperature below 10°C. The transparent gel pieces are displayed in Fig.4.3. On

Table 4.1 Drying conditions and physical appearance of the gel

Alkoxide / Acetic acid ratio	Temp. conditions (°C)		pH	Time of gelation (h)	Physical appearance
	Mixing	drying			
0.4	10	25			White precipitate on addition of boehmite sol
0.25	10	25	3.8	8	Clear solution after mixing and turn opaque gel
0.16	10	25	1.8	120	Clear solution turn to translucent gel after 48h and converted to transparent hard gel after 5 days. Cracks were observed on further drying
0.16	40	-	-	-	Gelation wihtin 10 min. leading to opaque gel.

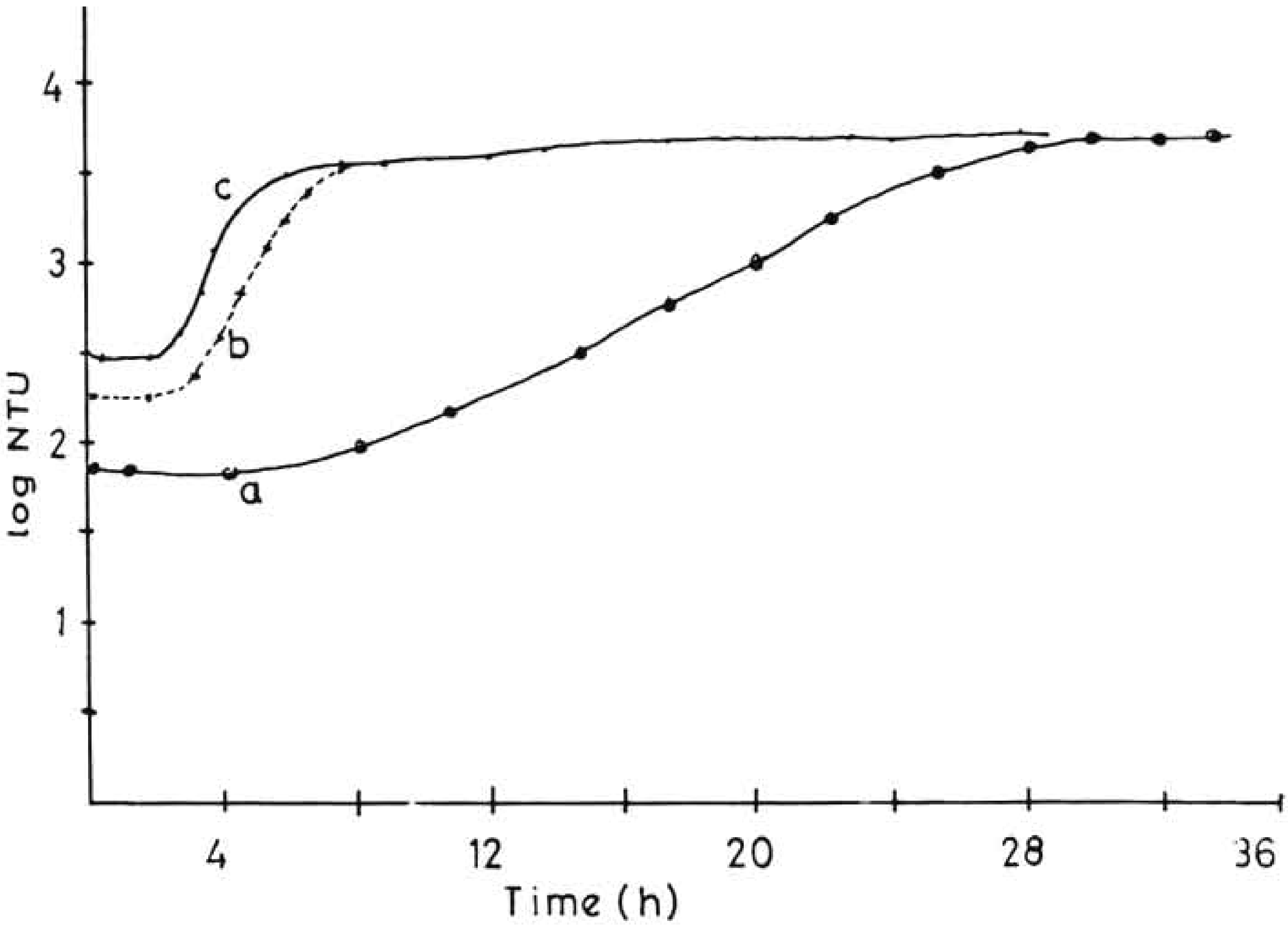


Fig. 4.1 Increase of turbidity with time during gelation

(a) water (b) water - dioxane

(c) water-isopropanol media

Fig. 4.2 Flow diagram for transparent Al_2TiO_5 precursor gel

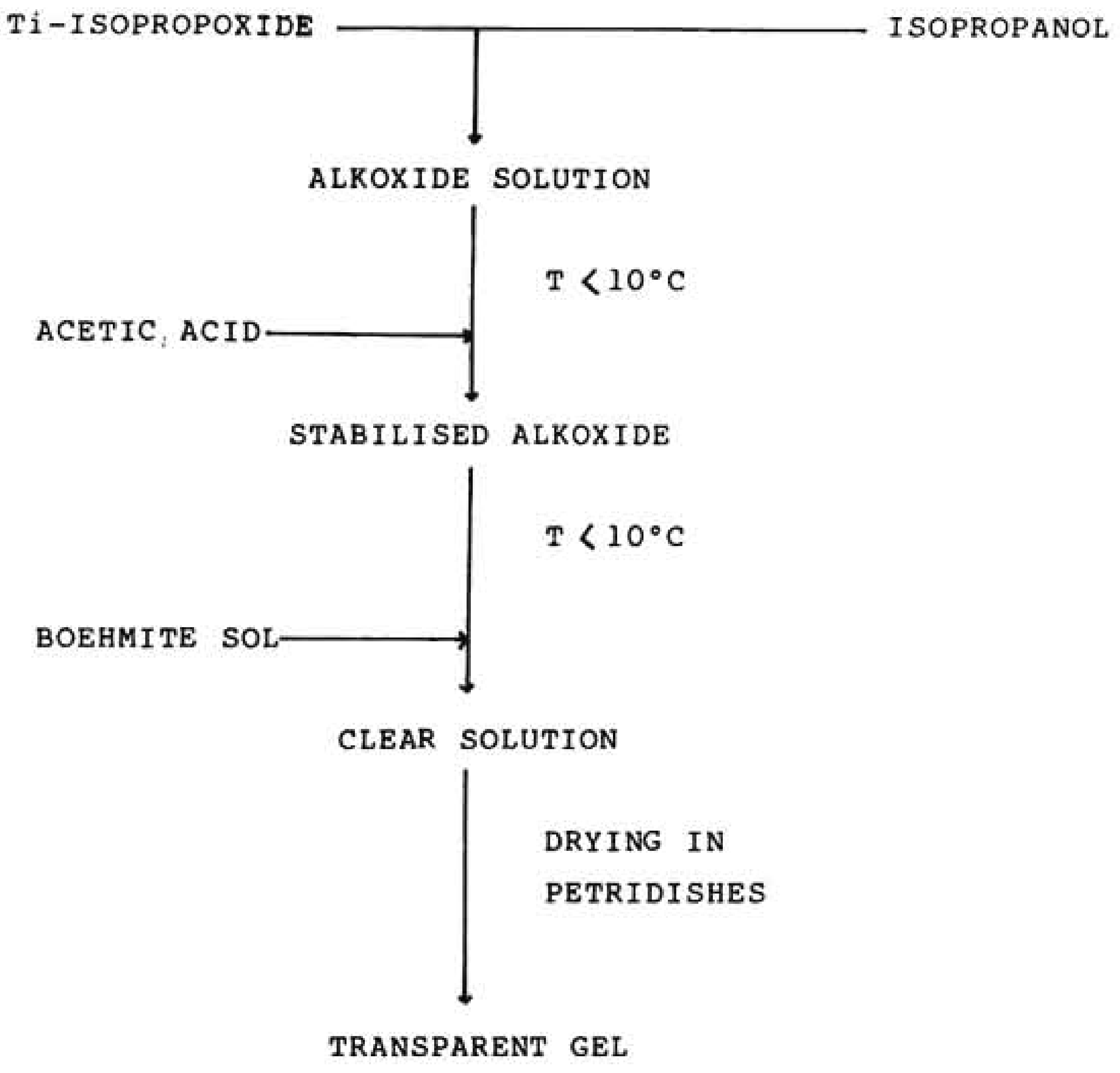


Fig. 4.3 Photograph of transparent gel

further heating, it undergoes cracking and becomes opaque above 300°C indicating the crystallisation of oxide phases.

The transparent aluminium titanate precursor gel was characterised by thermal analysis. Figure 4.4 shows the trace of TGA curves of precursor gels of aluminium titanate, alumina and titania (Figs.4.4a,b&c). While the titania gel has got the maximum loss as early as 350°C, the boehmite requires a temperature of 600°C. However, the weight loss characteristics of the aluminium titanate precursor gel extends over a temperature beyond 800°C. Infrared Spectra (Fig.4.5) shows the characteristic absorption of OH group in the gel between 3200 and 3600 cm^{-1} which get progressively removed with increasing temperature and get fully dehydrated only above 1000°C.

The DTA (Fig.4.6) of transparent gel shows various endothermic reaction upto 300°C, covers the removal of gel water and volatiles. But a sharp exothermic peak at 305°C may indicate the decomposition of acetate radicals present in the gel. This large exothermic process is the cumulative effect of crystallisation of γ-Al_2O_3 and anatase from the amorphous gel structure. A small exothermic peak at 1070°C shows the crystallisation of α-Al_2O_3. It is obvious that the presence of titania decreases the α-Al_2O_3 transformation temperature(1). The endothermic peak obtained around 1370°C indicates the formation of aluminium titanate phase from α-Al_2O_3 and rutile. The calcination temperature for phase analysis was fixed based on this DTA pattern.

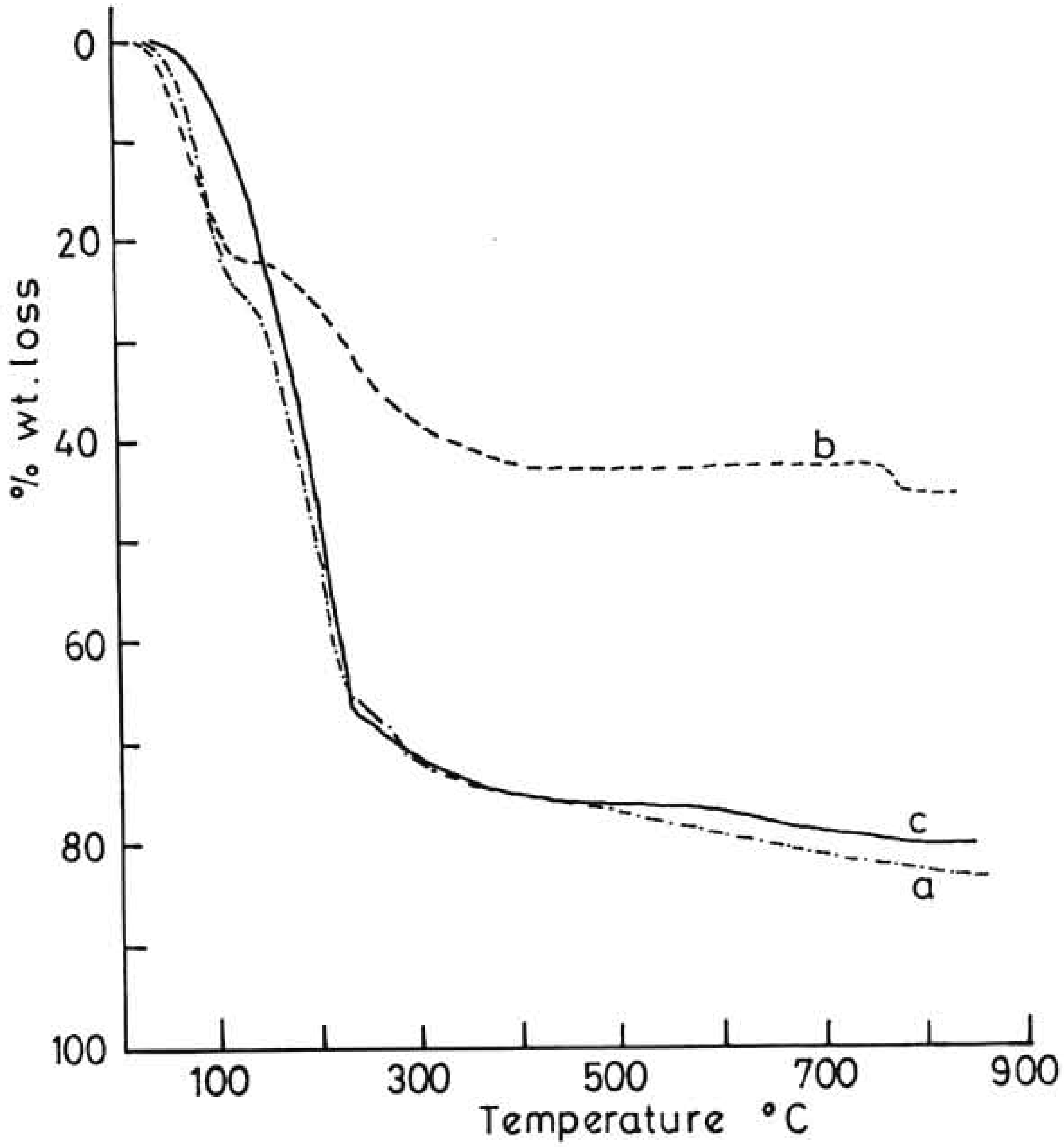


FIG. 4.4 TGA Curves of (a) AT precursor gel (b) hydrous titania (c) boehmite

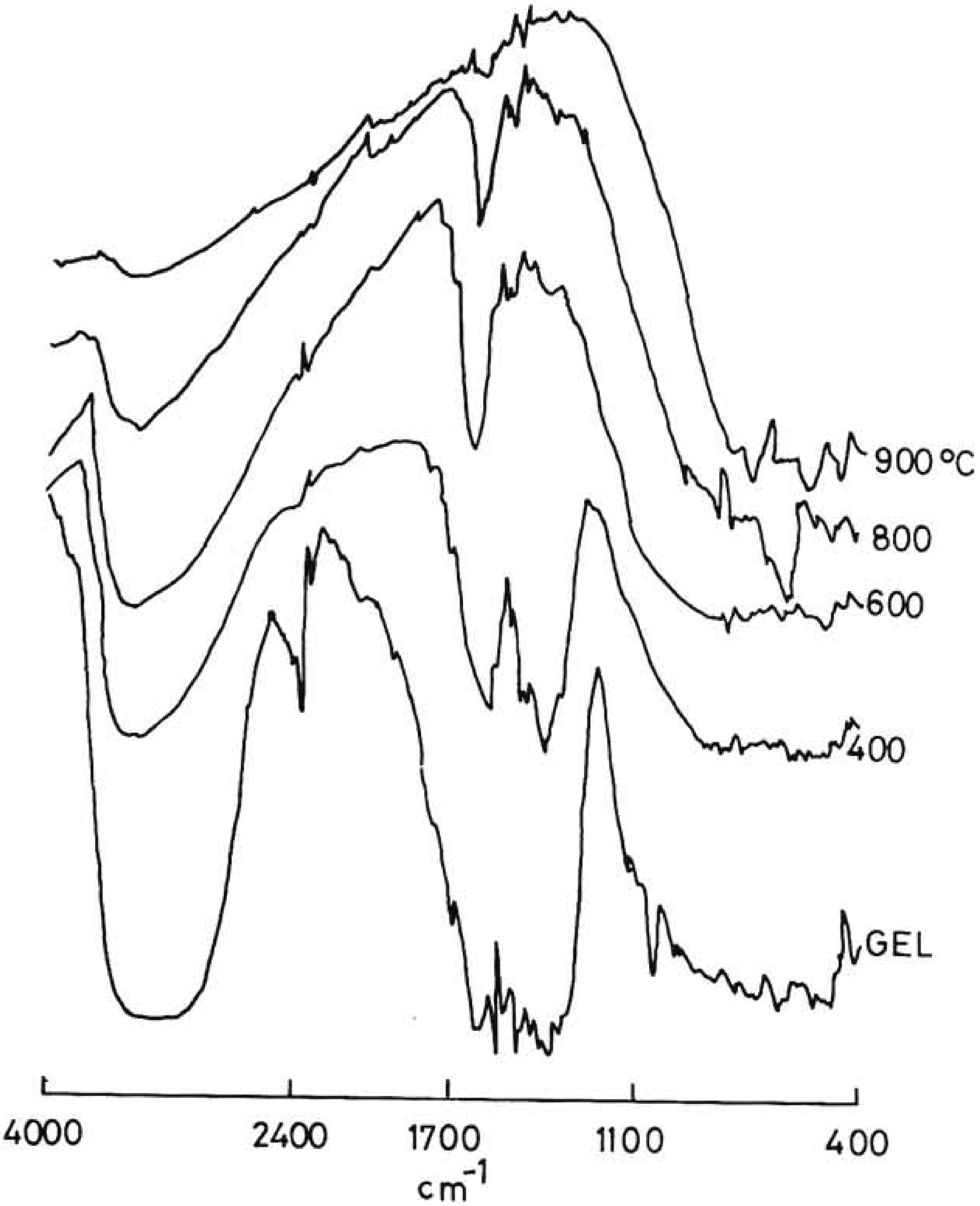


Fig. 4.5 IR Spectra of AT precursor gel heated various temperatures.

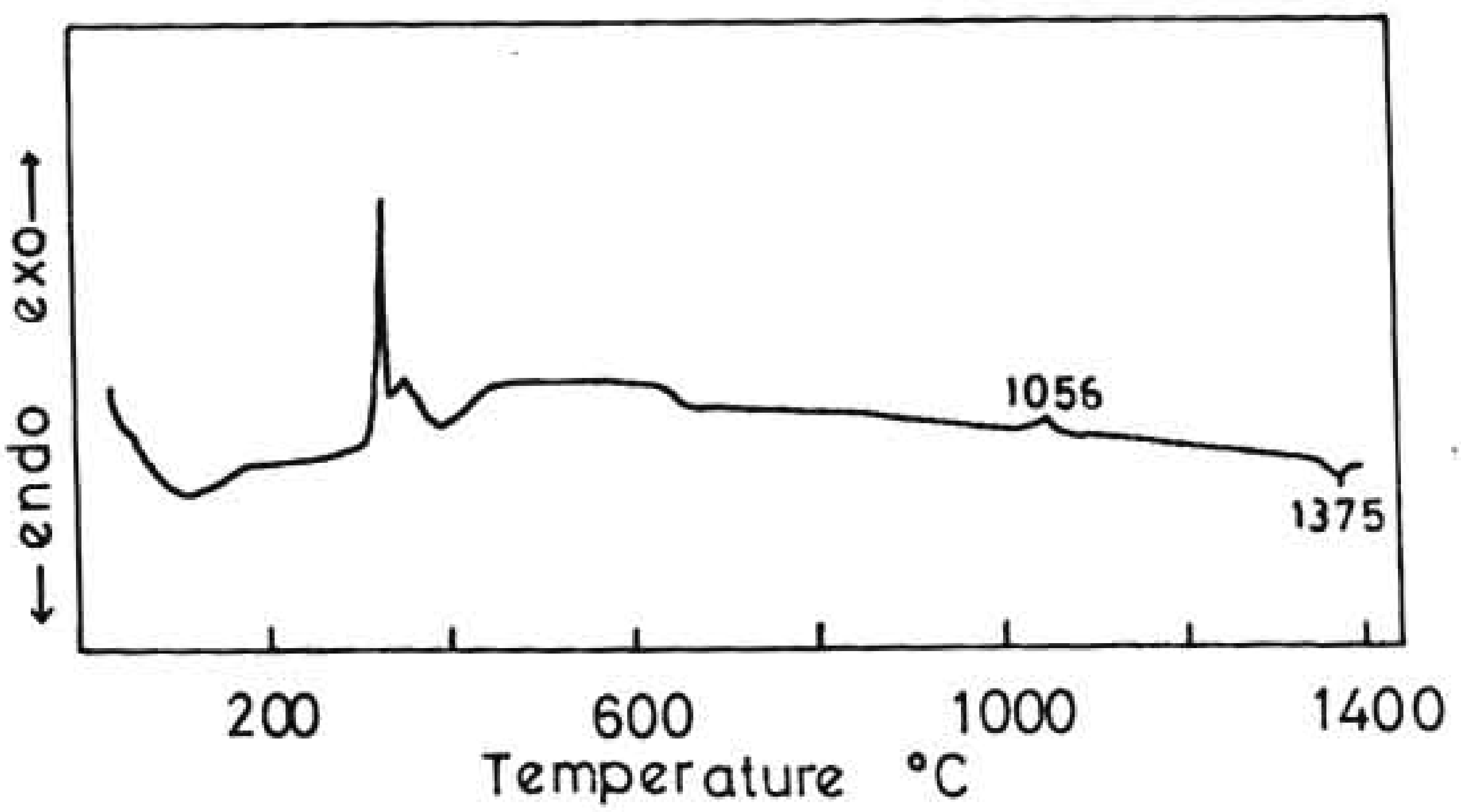


Fig. 4.6 DTA Curve of AT precursor gel

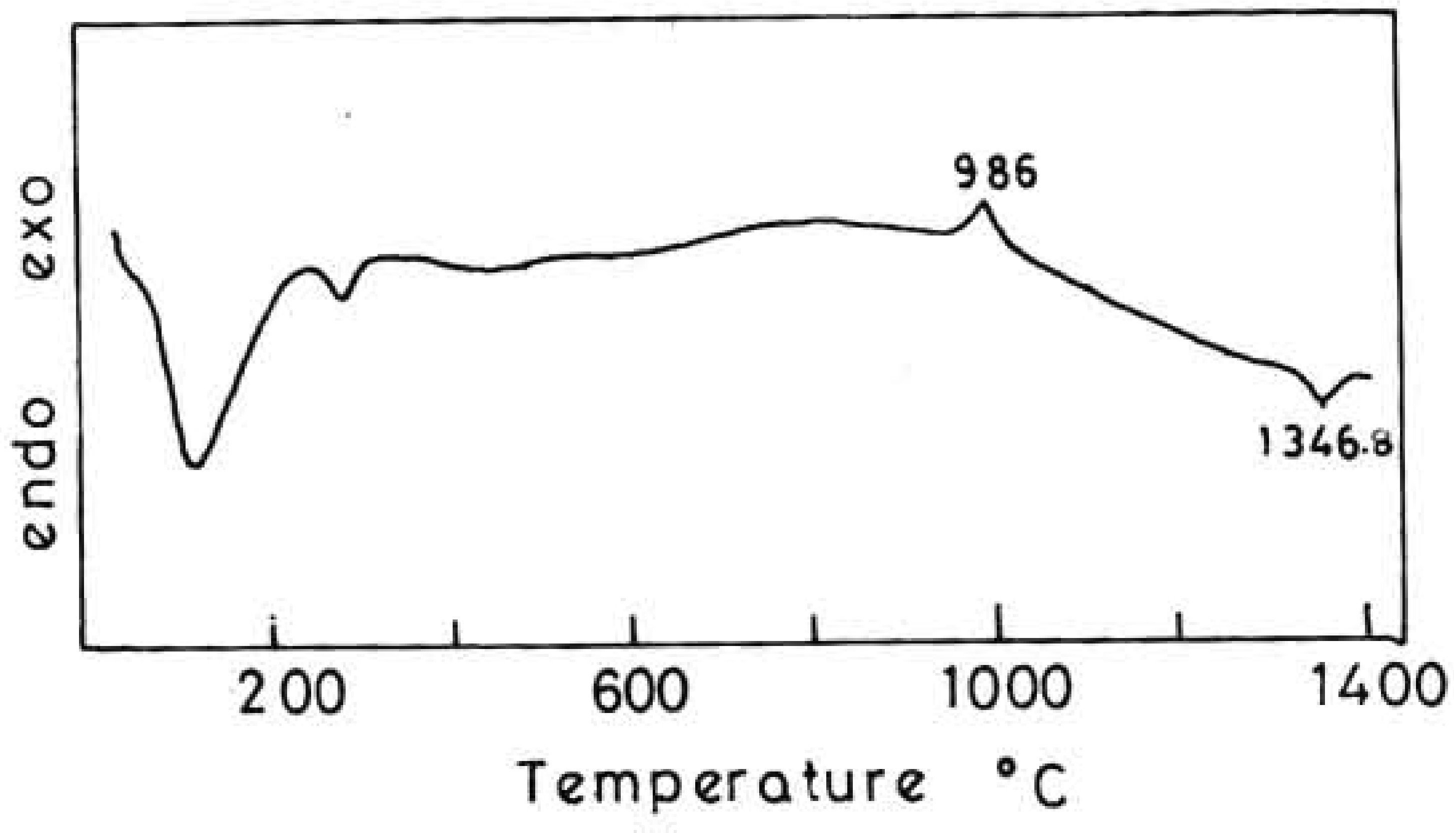


Fig. 4.7 DTA curve of AT precursor gel after thorough washing

(c) Modification of Aluminium Titanate Precursor gel:

The precursor gel modification was based on three objectives. They are, (i) removal of residual anions through washing, (ii) treatment and washing of the gel with organic solvents and (iii) microwave drying of the gel.

(i) Effect of removal of anions on aluminium titanate phase formation:

The gel system was thoroughly washed to remove maximum amount of acetate and nitrate radicals. The Fig.4.7 shows the DTA of this gel after drying at 100°C which indicates the absence of the exothermic peaks at lower temperature ranges of 250-300°C indicating the complete removal of anions. Further, the α-Al_2O_3 formation is indicated by an exothermic peak at 986°C which is around 10°C higher than in the case of unwashed gel. But surprisingly, the aluminium titanate formation temperature was sharply reduced to 1346.8°C indicating the influence of precursor gel structure and its constituent on the aluminium titanate formation at higher temperature.

(ii) Effect of solvent treatment:

Figure 4.8 indicates the DTA of aluminium titanate precursor gel washed with acetone and isopropanol. The temperature of formation of alumina was shifted to lower

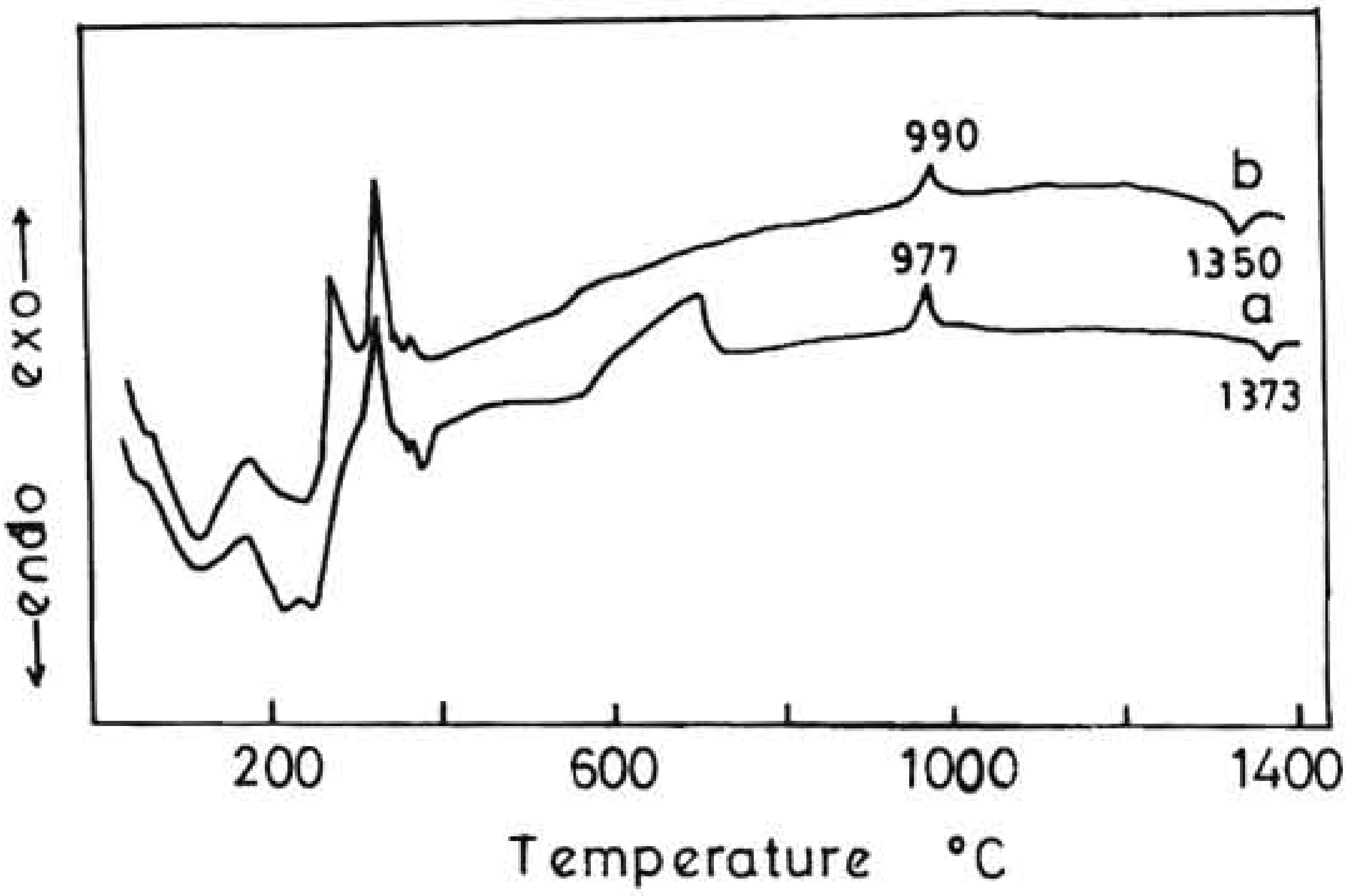


Fig. 4.8 DTA curves of treated gels
(a) acetone (b) isopropanol

temperature in acetone washed gel but the formation of aluminium titanate is shifted to lower temperature in isopropanol washed gels. The anatase formation was clearly indicated in acetone washed gels by the exothermic peak around 600°C but no such peak is observed in isopropanol washed one. Thus it could be reasonably indicated that the solvent influences the crystallization of the alumina and titania and also the aluminium titanate phase.

(iii) Effect of microwave drying:

When microwave energy was used to dry the thoroughly washed gels, the endothermic peak at 274°C was absent but a new exothermic broad peak at around 472°C is indicated Fig.4.9a. The γ-Al_2O_3 conversion is not generally a sharp process as shown by a broad exothermic region in microwave dried samples. The formation of aluminium titanate was taken to higher temperature of 1363°C in the microwave dried samples. Thus these results lead to the fact that the gel structure, its composition, presence of anions, drying procedures etc. affect the formation of aluminium titanate at higher temperature. Even simple solvent treatment of the washed gel shows a variation in the aluminium titanate formation. Figure 4.9b shows the DTA of aluminium titanate precursor gel treated with acetone and microwave drying after thoroughly washing it with water. The aluminium titanate formation peak was shifted to 1375°C. Any disturbance of the gel structure, influences the

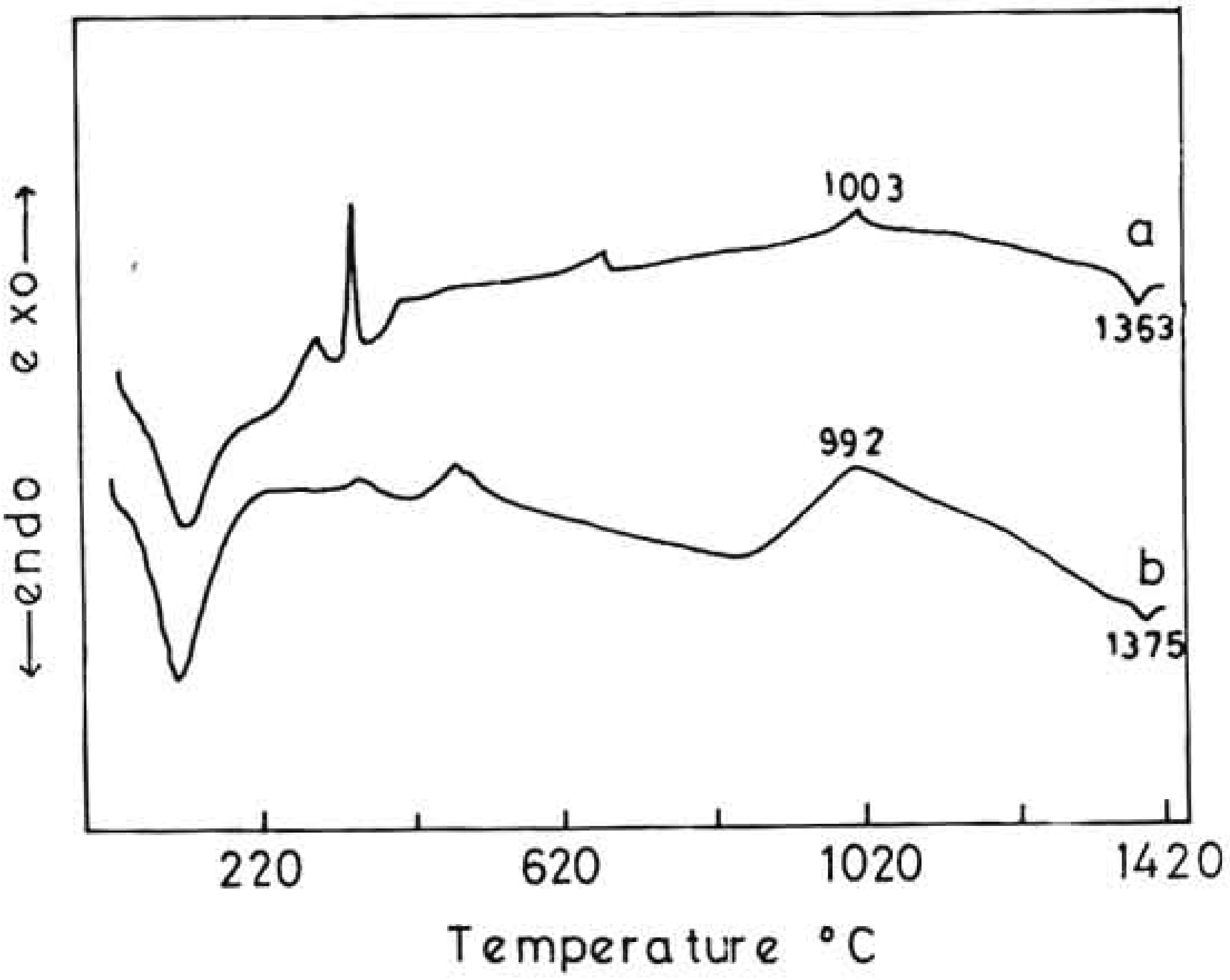


Fig. 4.9 DTA curves of AT precursor gel (a) MW dried (b) acetone treated washed gel

crystallisation of oxide phase and its transformation to other polymorphic states, the surface activity of the oxide particles which may increase or decrease the final reactivty.

(d) XRD studies:

Figure 4.10 indicates the XRD pattern of aluminium titanate precursor gel and gel heated to various temperature upto 1400°C. XRD pattern of gel shows an amorphous nature but during heating to 600°C, peaks corresponding to anatase are observed. The gel calcined at 800°C shows presence of rutile and that heated at 1000°C shows both alumina and rutile. This is a complementary result of DTA which indicate the early formation of α-Al_2O_3 by the exothermic peaks. The powder obtained after calcination at 1400°C indicates presence of aluminium titanate only. The 'd' values and I/Io values of aluminium titanate observed from JCPDS file were compared for confirmation.

(e) Characteristics of aluminium titanate powder:

(i) Density:

Density of aluminium titanate powder determined by pychnometric method is 3680 kg/m^3. Theoretical density of aluminium titanate is 3700 kg/m^3.

ii) Surface area of aluminium titanate powders:

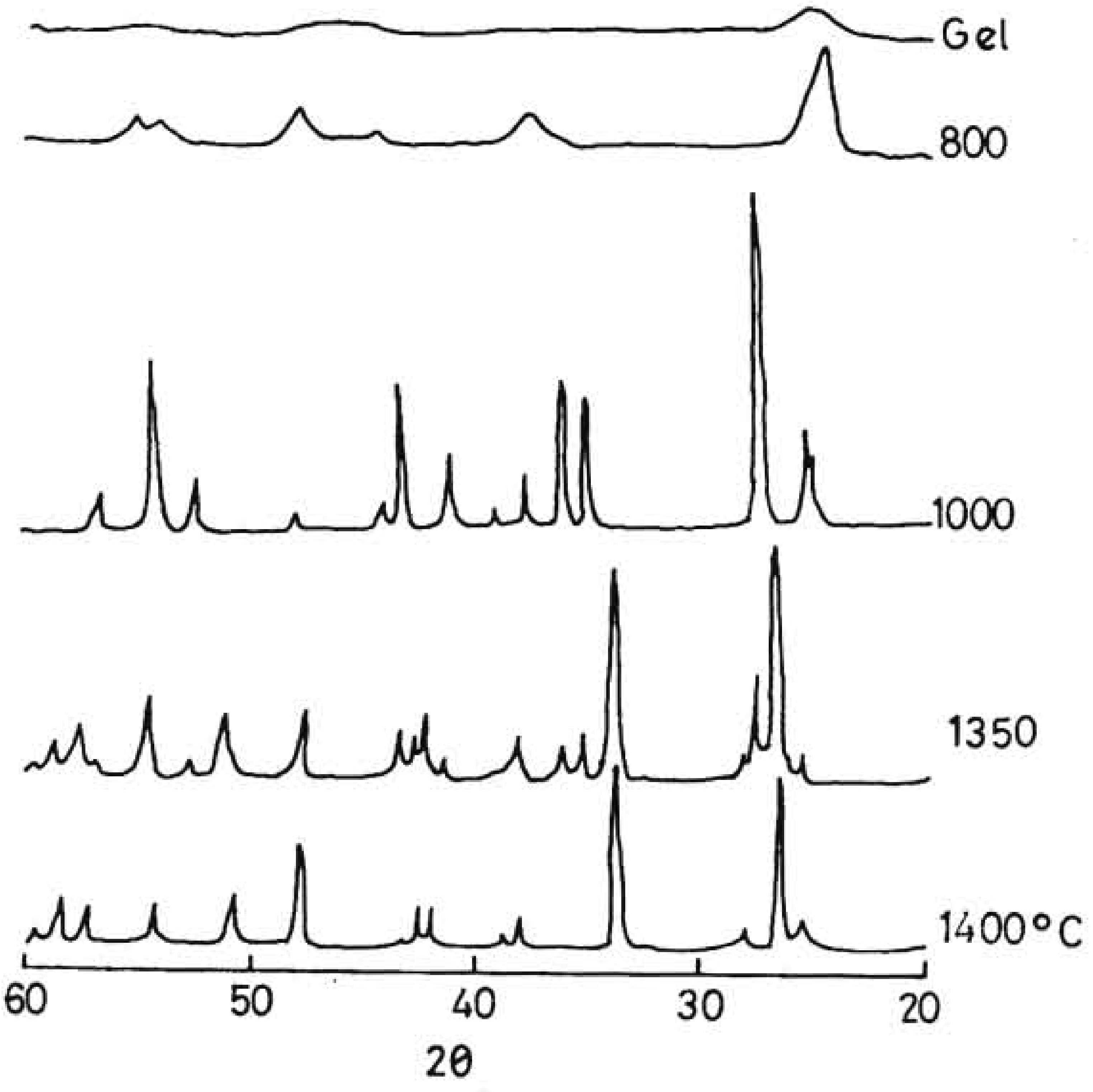


Fig. 4.10 XRD pattern of AT precursor gel heated to various temperatures

Table 4.2 indicates the specific surface area of aluminium titanate obtained from gel treated in various ways. The table indicates a drastic decrease of surface areas as a result of high temperature calcination. It is obvious that this decrease is due to aggregation and grain growth occuring at high temperatures. But the lowest value of 0.5 m^2/g at 1400°C also indicates the reaction between Al_2O_3 and TiO_2 and followed grain growth of aluminium titanate grains.

(iii) Particle size distribution:

Figure 4.11 represents the particle size distribution of aluminium titanate powder obtained from transparent gel and gel after repeated washing. The average particle size is around 2.5 micrometers. This average particle size is around the critical grain size required by aluminium titanate as calculated by Parker et.al(2). Thus the sol-gel method preparation of aluminium titanate powder to attain sufficiently smaller sized particles.

(iv) Morphological features of aluminium titanate powders:

Figure 4.12 indicates the powder morphologies of aluminium titanate prepared from gels with and without treatments. The average particle size ranges about 2-2.5 µm and has an almost uniform size distribution. The surface porosities are not evident which also contribute for the lower specific surface area values of aluminium titanate powders. The lowest

Table 4.2 Variation in sp. surface areas of Al_2TiO_5 precursor powders

Temperature of calcination (°C)	Surface area (m^2/g)
600	63
1000	26
1200	10
1400	0.5

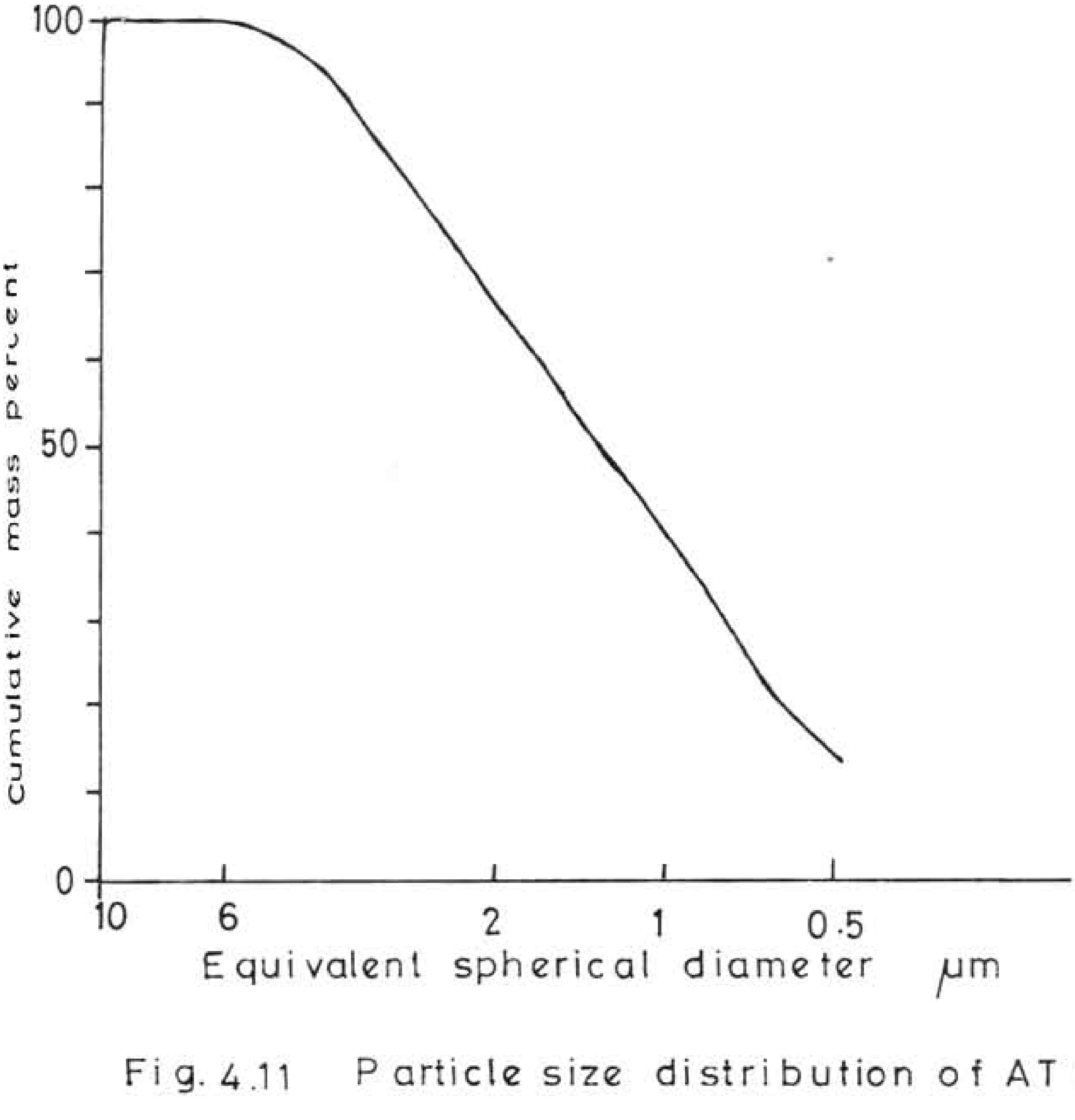
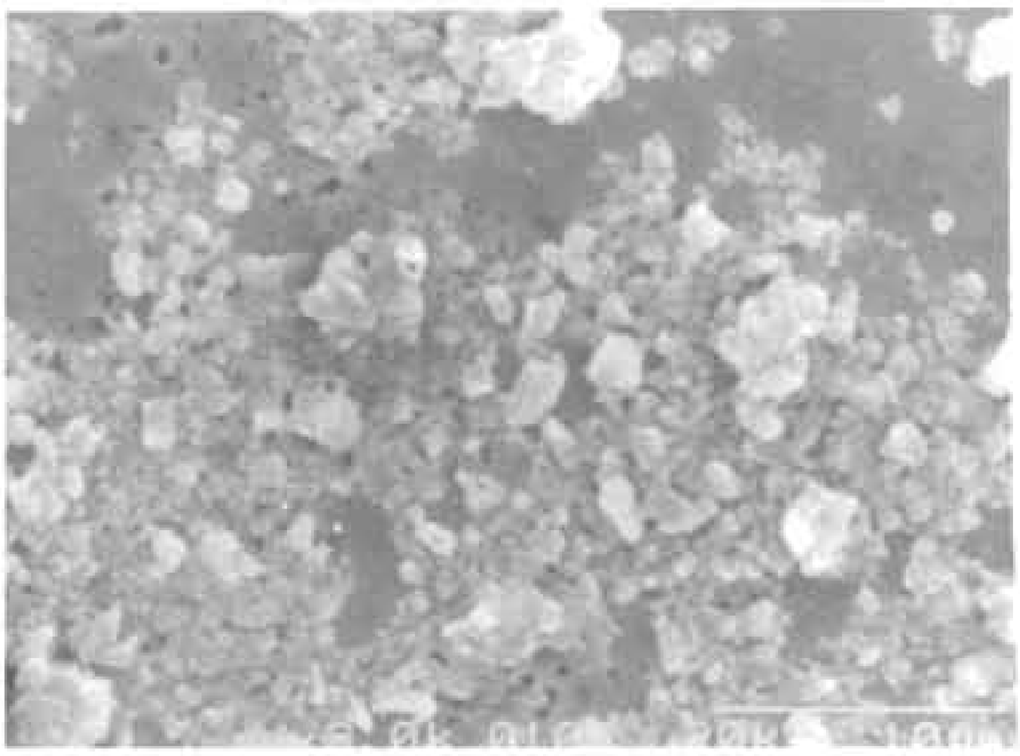
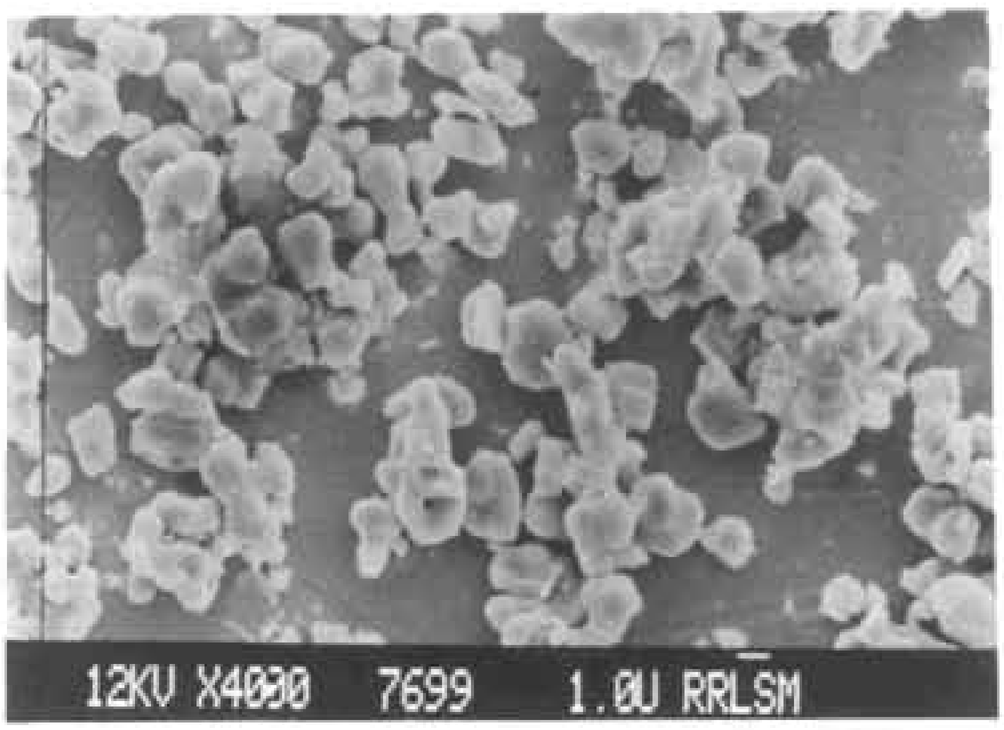


Fig. 4.11 Particle size distribution of AT powder



from isopropanol treated gel



from not treated gel

Fig. 4.12 SEM morphology of aluminium titanate powders grain sizes are observed in isopropanol washed gel derived aluminium titanate system indicating the low aggregate level.

(v) Compaction-densification of aluminium titanate powder:

Table 4.3 indicates the green and sintered density of aluminium titanate powder obtained by decomposition of transparent gel. The sintered densities are measured on samples sintered at 1500°C. The density of compacted discs after heating at still higher temperature is also mentioned in Table 4.3 and the trend is pictoriously represented in Fig.4.13. The aluminiom titanate powder obtained from transparent gel shows a highest sintered density of about 96% of theoretical at 1500°C. But heat treatment at still higher temperature makes the compact devoid of strength, i.e., an 'anti sintering' phenomenon occurs. This is, of course, due to the presence of large cracks due to exaggerated grain growth at higher temperature. But the powder obtained from solvent treated aluminium titanate precursor gel shows a lower sintered density of around 92% at 1500°C. The DTA results show that precursor gel treated with isopropanol form aluminium titanate at lowest temperature but this sinters to relatively low density. But the transparent gel forms aluminium titanate phase at higher temperature and the powder shows better sintering behaviour. Thus a direct relationship of the phase formation temperature and sinterability is not possible.

Table 4.3 shows how the density of aluminium titanate

Table 4.3 Sintered densities of Al_2TiO_5 powders at 1500°C

Al_2TiO_5 powder from	Green density (kg/m^3)	Sintered density (kg/m^3)
Transparent gel	2040	3550
IsoproH washed gel	2030	3415
Acetone washed gel	2041	3410
Thoroughly washed gel	2018	3510

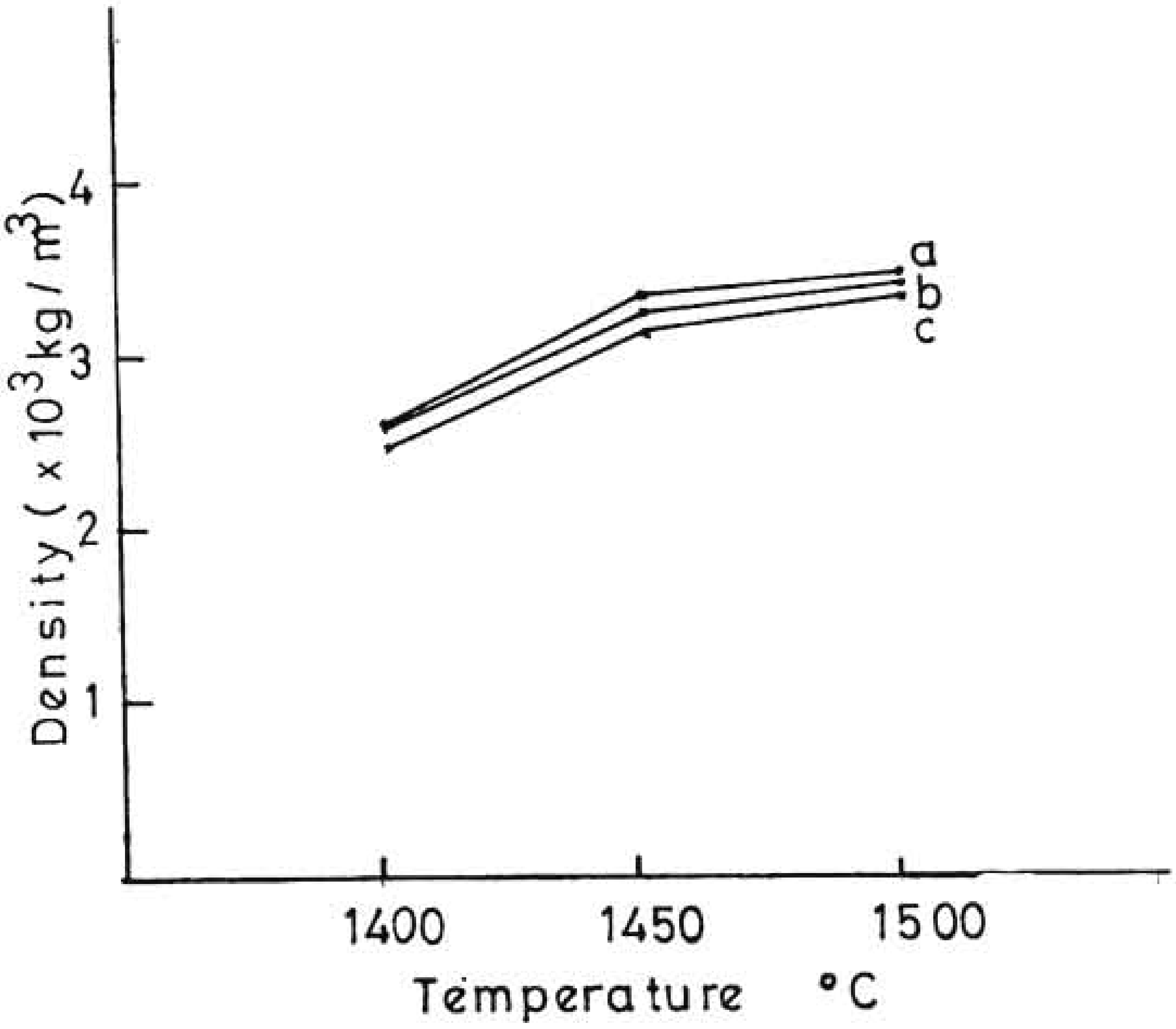
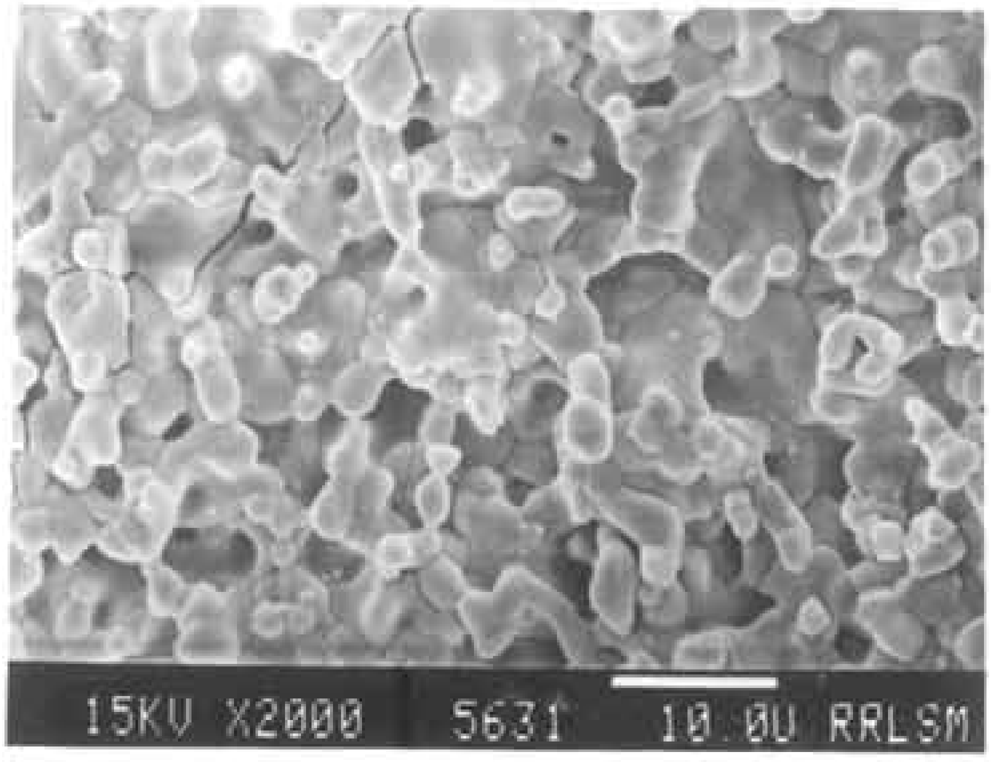
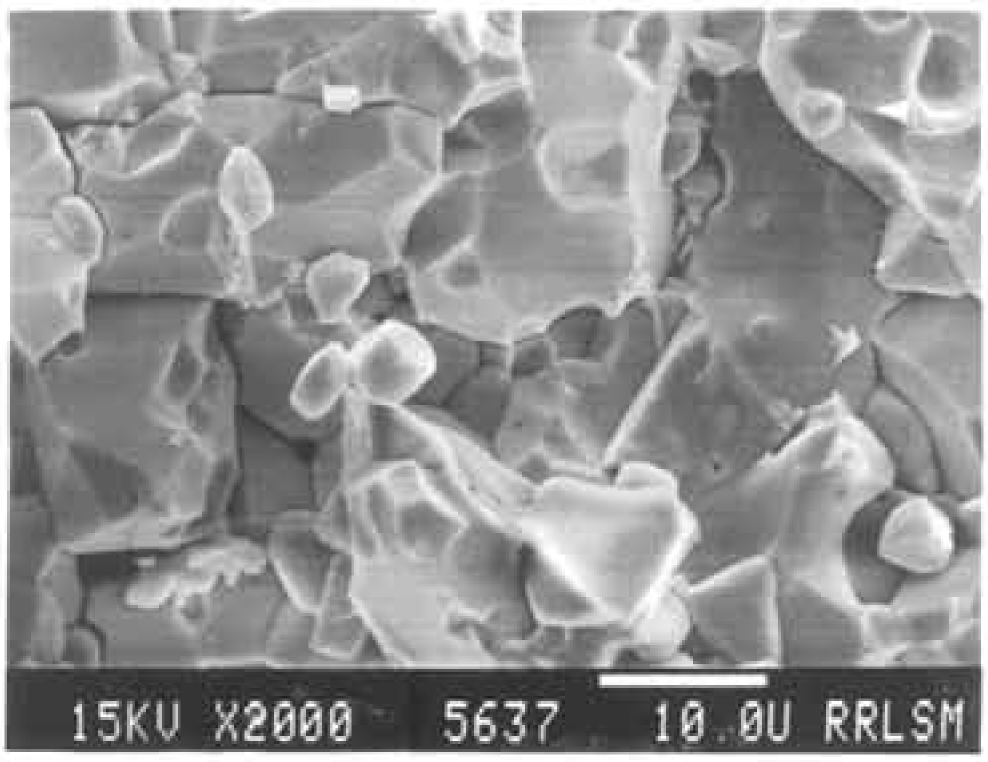


Fig. 4.13 Sintered densities of different AT powders from
(a) transpaent gel
(b) thoroughly washed gel
(c) isopropanol treated gel



from ispropanol treated gel



from not treated gel

Fig. 4.14 SEM fractographs of aluminium titanate from various powders obtained from gels washed free of anions and that dried in a microwave oven varies. Both of these powders show almost similar behaviour in sinterability attaining about 96.5% theoretical density at 1500°C. The high value has been obtained without any additives.

Figure 4.14 shows the fractographs of sintered aluminium titanate sample indicating the presence of microcracks. The microcracks are present at the intergranular region. Minimum microcracks are observed in aluminium titanate samples obtained from isopropanol treated gels.

4.3 CONCLUSION

The aluminium titanate precursor gel can be made in a transparent form by controlling the preparative conditions such as mixing, temperature, pH, concentration of alkoxide, water solvents, drying humidity etc. The gelation time of aluminium titanate precursor sol varies depending on the medium. The transparent gel undergoes decomposition to very fine constituent alumina and titania during calcination at higher temperature. These oxides react to form aluminium titanate phase at around 1370°C. The pre-treatment of the gel changes the gel structure which eventually shows variation in phase evolving processes. The anionic impurities cause delay in aluminium titanate formation as shown by DTA results and their removal by thorough washing registered a lowest aluminium titanate formation temperature of 1347°C. Preferential washing of the gels with solvents like isopropanol and acetone influences to lower the aluminium titanate phase formation temperature while increasing the sintering temperature. All these treatments affect the powder characteristics, especially its densification. Aluminium titanate compacts on heating at 1600°C for 30 min undergo catastrophic cracking due to the exaggerated grain growth.

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PART II

CHAPTER V

STUDIES ON THE SOL-GEL PREPARATION OF Bi-BASED SUPERCONDUCTOR PARTICULATES AND THEIR PROCESSING

ABSTRACT

Two routes were attempted for preparing precursor powder for Bi-Pb-Sr-Ca-Cu-O based high-Tc superconductor particulates. One is based on the use of acrylic acid and constituent metal nitrates, converting to a gel and decomposing it to black precursor powders. Second method is based on the use of microwave decomposition of constituent metal nitrates with and without an activator, starch, during which the nitrate directly decomposed to the highly reactive precursor powders. These powders were heat treated at various conditions of temperature and time to arrive at a time-temperature-transformation relationship. Acrylic acid system resulted in 95% 2223 within 35h but microwave derived one required only 30h to reach the same composition. Characterisation by XRD of the various intermediates show that calcination around 800-820°C is required to facilitate the 2223 phase formation. The Tc measurements show a transition at 107K indicating the presence of 2223 phase as major component. Particle size measurement shows that an average agglomerate size around 2 um in acrylate

derived gel and 3 μm in microwave decomposed samples. The SEM analysis of the powder reveals that the grains are flaky in morphology. The acrylate derived powders achieve higher green density (52% TD) to the microwave derived powder (48% TD). The acrylate derived powder also achieve higher sintered densities to ≈96% compared to microwave derived one (≈92%) after 12 h sintering at 845°.

The BPSCCO powder obtained by acrylate gel decomposition was used for further processing to get grain aligned bulk compacts. Different methodologies adopted are slurry processing as a presintering processing (PSP) and zone melting refining as postsintering treatment (PST). These techniques independently lead to considerable texturing of the grains, an integration of PSP and PST were also tried which resulted in highly grain oriented microstructures.

5.1 ACRYLATE GEL PRECURSOR FOR PARTICULATE BPSCCO SUPERCONDUCTOR

(a) Calcination of gel:

The precursor gel made as described in Chapter II(c) on further heating at around 350°C for 3 h undergoes decomposition resulting in black fluffy powder which was calcined at 790°C for 10 h and was further heated at different temperatures ranging from 810 to 845°C. XRD patterns of various heat treated samples were taken in an X-ray Diffractometer (Rigaku, Japan).

Changes in the morphological features of the powder after different stages of heat treatment were studied by SEM (SEM, JEOL 35C, Japan). The TGA of the gel in air was also done in Schimadzu TGA unit with a heating rate of 10°C/min.

(b) Powder compaction and sintering:

BPSCCO powder was ball milled in isopropanol for 12 h using stabilized zirconia grinding medium. It was dried at 90°C in an air oven for 4 h and compacted uniaxially to discs of size 10 mm diameter and 2 mm thickness and sintered at 845°C for 12 h. Tc of these sintered compacts were measured. The fracture surface was observed in SEM to study the morphological features. The sintered density was measured by Archemedies principle.

(c) Tc measurement:

The powder obtained after calcination at 820 and 845°C were sintered after compacting into small pellets and Tc measurements were carried out using standard four probe method. Liquid nitrogen is used as the coolant. The resistance measured at various temperatures during cooling were plotted.

5.1.1 Results and Discussion

(a) Gel formation:

Polyacrylic acid possesses many reaction sites for linking up with metal ions and hence there is immense possibility of the same molecule bearing all the constituent metal ions of the precursor complex(1). Further, the acrylic acid complex is sufficiently stable in aqueous medium and hence elements such as bismuth can be prevented from being precipitated from aqueous medium. The acrylate radical undergoes polymerisation simultaneously forming gel network. This enables the formation of highly homogeneous system of holding all the metal ions.

(b) Thermal analysis of gel:

Thermogravimetric analysis (Fig. 5.1) of the gel reveals that the decomposition is complete well before 350°C and is almost a single stage process. This indicates that in the present case, the gel contains acrylic acid derivatives of constituent cations and not as separate nitrates. Further, the observation regarding the evolution of oxides of nitrogen prior to gelation of the mixture indicates the decomposition of nitrates to form acrylates.

(c) Effect of heat treatment on phase formation:

Figure 5.2 represents the X-ray diffraction pattern of precursor gel heated to various temperatures for various time intervals. The gel calcined at 350°C (Fig. 5.2a) shows the formation of precursor phases and not independent oxides except a small amount of CuO. Usually the formation of BPSCCO superconductor is associated with 2201 phase around 600°C and

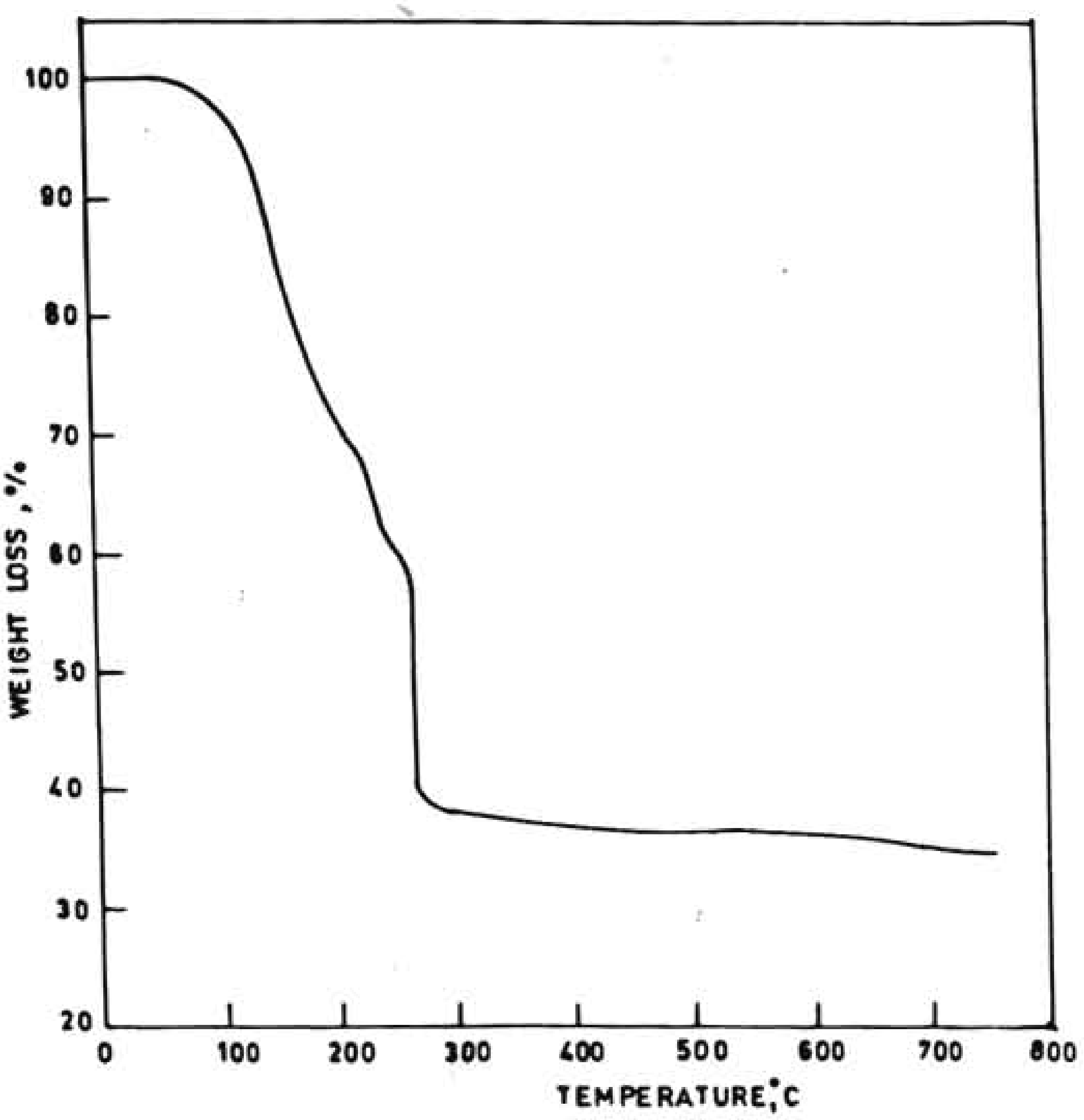


Fig. 5.1 TGA of acrylate gel

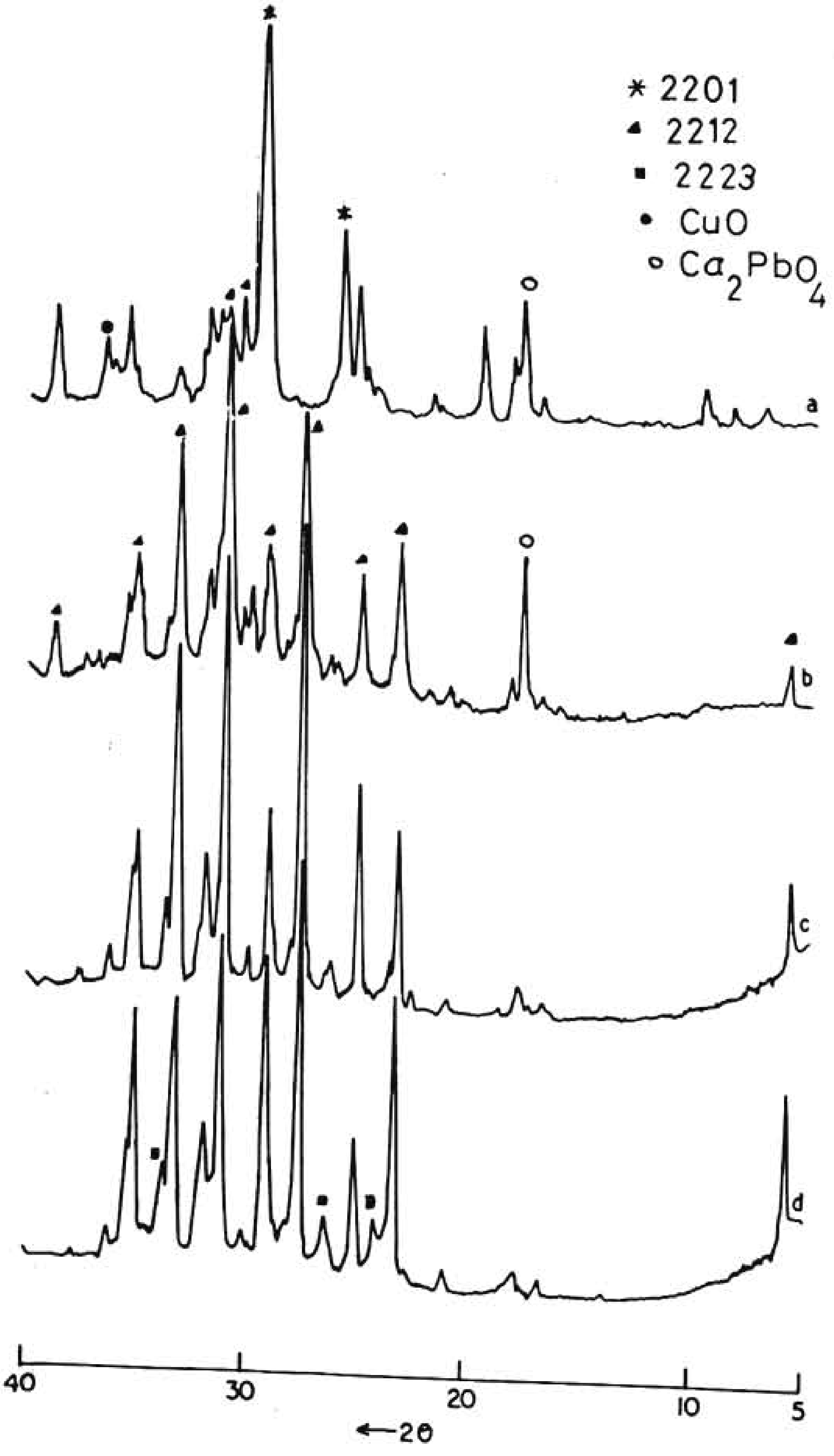


Fig. 5.2 XRD of precursor gel heated to (a) 350°C (b) 790°C (c) 800 and (d) 820°C

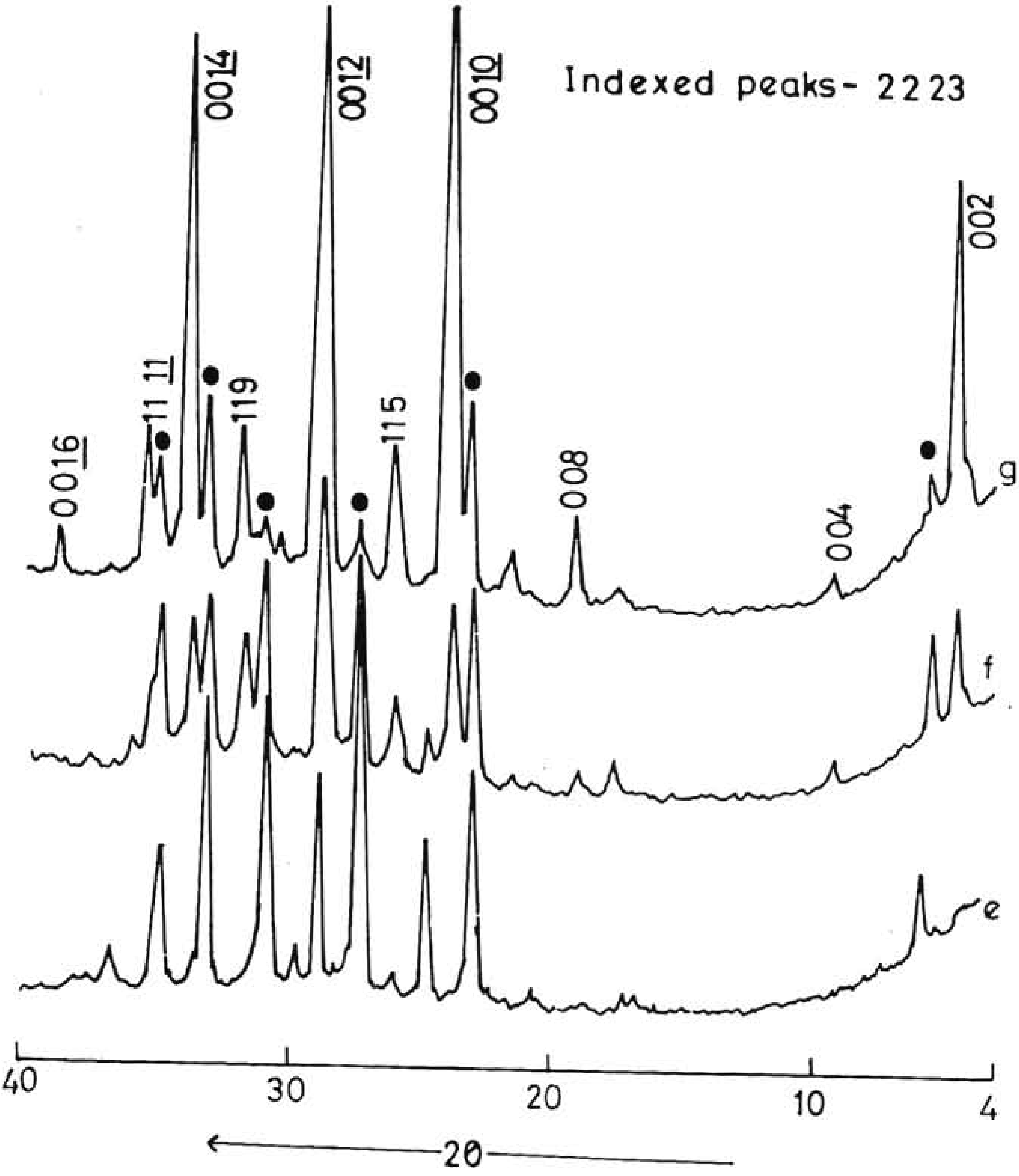


Fig.5.2.XRD Indicating formation of 2212-2223 phases

e. Precursor powder heated at 820°C for 10hrs.

f. powder(a) heated at 845°C for 10hrs. and(g) for 30 hrs. with grinding after each 10hrs. heating.

2212 phase above 800°C(2,3). Almost all peaks in the Fig.5.2a are characteristic of 2201 and other binaries like Ca_2PbO_4. On calcination at 790°C all peaks related to 2201 get converted into those corresponding to 2212 within an interval of 5 h (Fig.5.2b). Since the large polymer molecule possibly holds the constituent metal ion, the inhomogeneity in phases are minimized. Figures 5.2c and d correspond to the XRD peaks of the powder heated to 800°C and 820°C respectively after calcination at 790°C for 5 h. The effect of calcination can be seen from the comparison of XRD peaks of that not calcined at 790°C (Fig.5.2d). The 2212 formation was facilitated in the calcined one at higher temperatures. Figures 5.2c and d reveal the possible advantage over processing time at higher temperature. It has been reported that the heat treatment at higher temperature introduce loss of lead but calcination at lower temperature and further processing at higher temperature for lower time could help in reducing the lead loss. Figures 5.2 e-f reveal the extent of formation of 2223-2212 phase by heating at 845°C over various time intervals. Further, the XRD of precursor heated to 845°C for 35 h with and without prior calcination are presented in Figs.5.3a and b. Thus it can be understood that even at 845°C, 2223 phase is formed through intermediates. So, the formation of 2212 phase at lower temperature facilitates the formation of 2223 phase at 845°C. If the processing is done at 845°C, the inevitable steps of formation of intermediates also have to occur at this

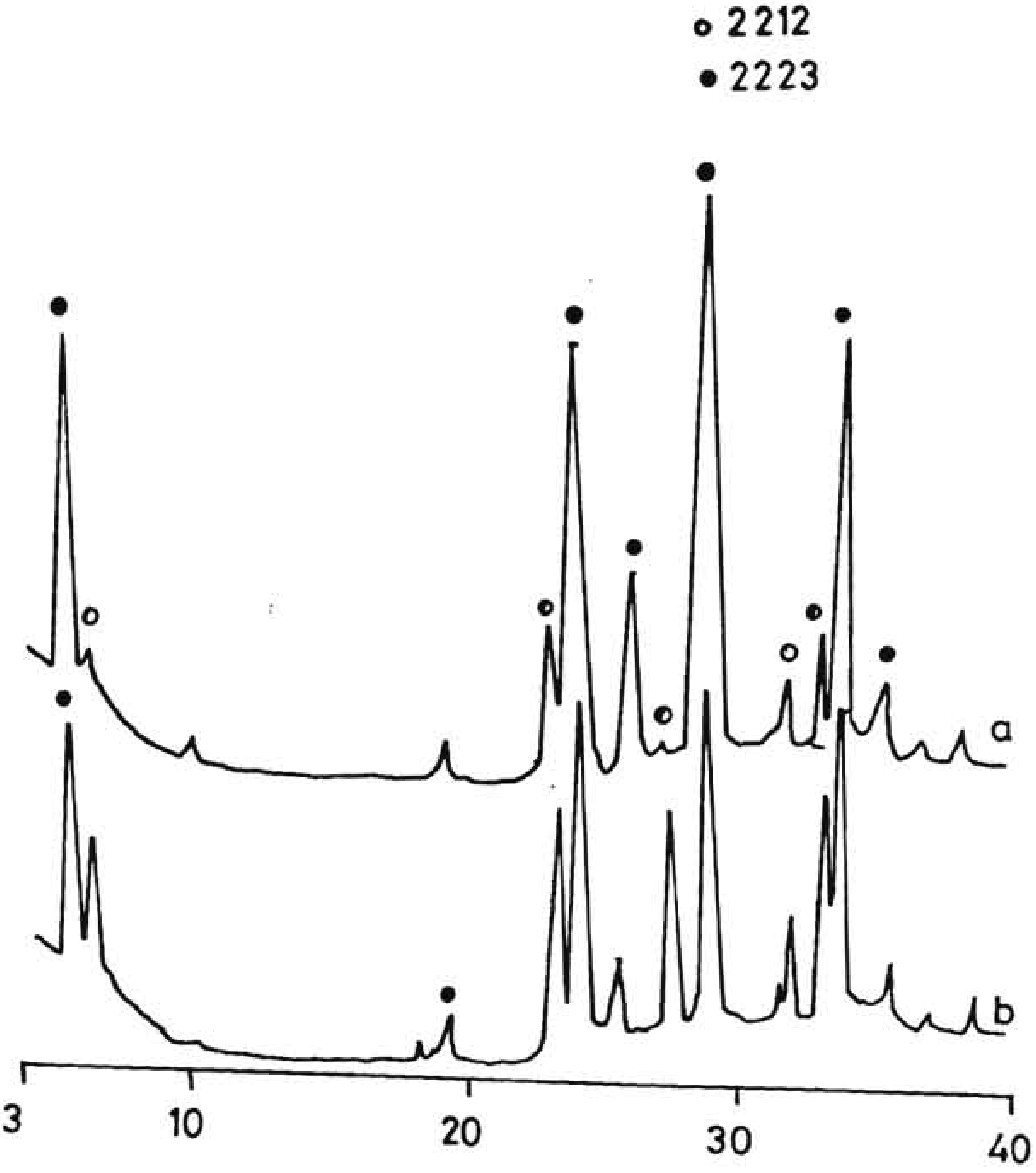


Fig.5.3 XRD of gel heated to 845 °C
(a) with and (b) without prior calcination

temperature. Hence the desirable heat treatment would be the phase formation at 845°C after a prior calcination at lower temperature to allow the formation of low Tc phase intermediates. This procedure introduces low lead loss also.

(d) Tc measurement:

The transition temperature of the pellets sintered at 820°C and 845°C were found out using four probe method and it was observed that transitions at 80K and 107K respectively and Fig.5.4 represents the variation of resistance with temperature.

(e) Morphological features:

Figure 5.5(a-d) indicates the morphological feature of BPSCCO phases obtained from the acrylate gel calcination. First of all the gel undergoes transition to spherical particles and then on further heating at 845°C these particles change to flaky structures. Figure 5.5d shows distinct powder grains in distinct flakes form with average grain size of 6-8μm

5.2 ACTIVATOR INDUCED MICROWAVE PROCESSING OF BPSCCO SUPERCONDUCTOR

5.2.1 Results and Discussion

Generally copper nitrate is very much microwave active and hence easily get decomposed to oxide. The temperature rises

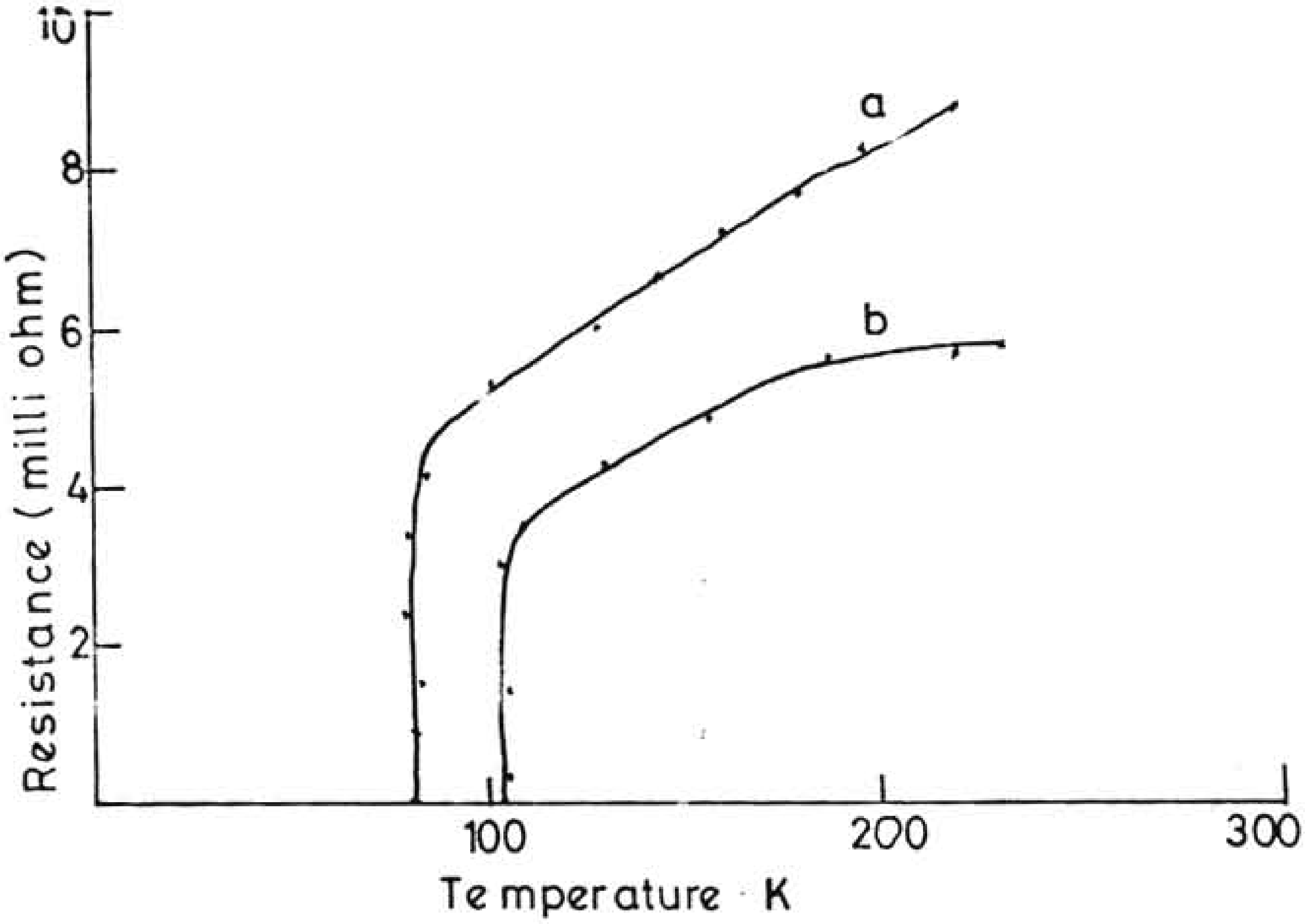
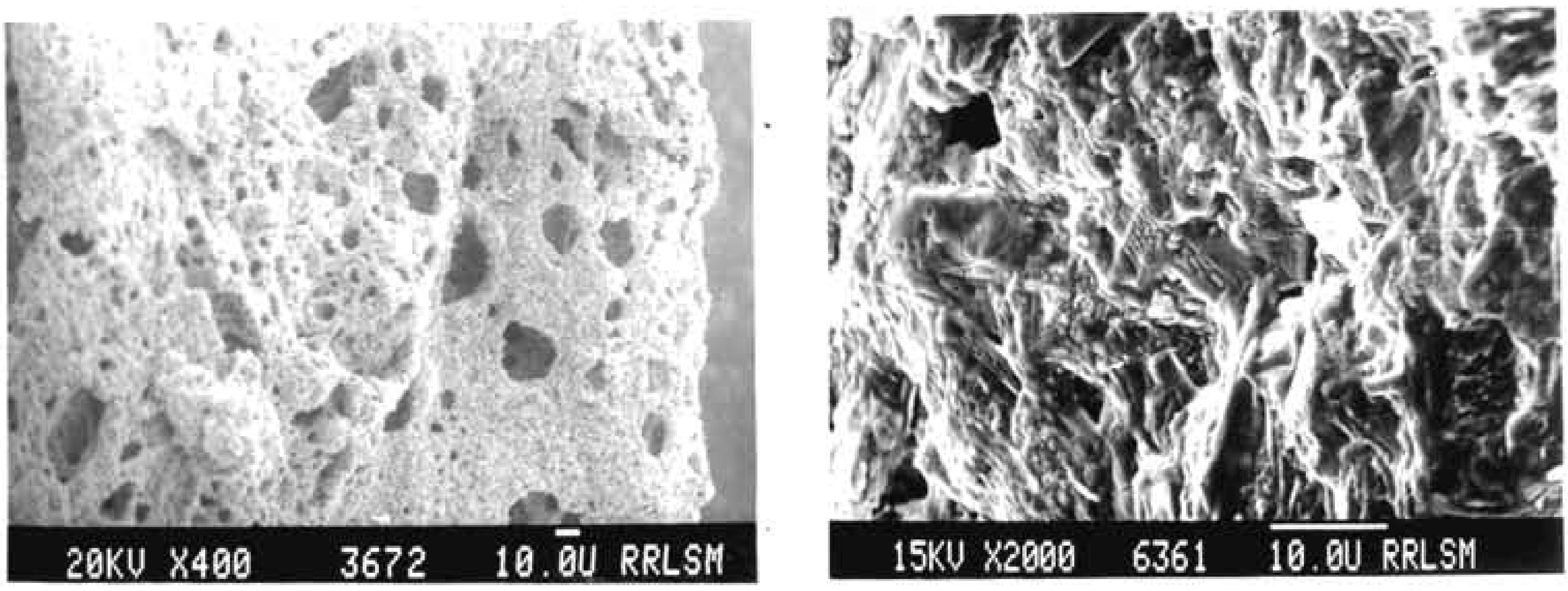
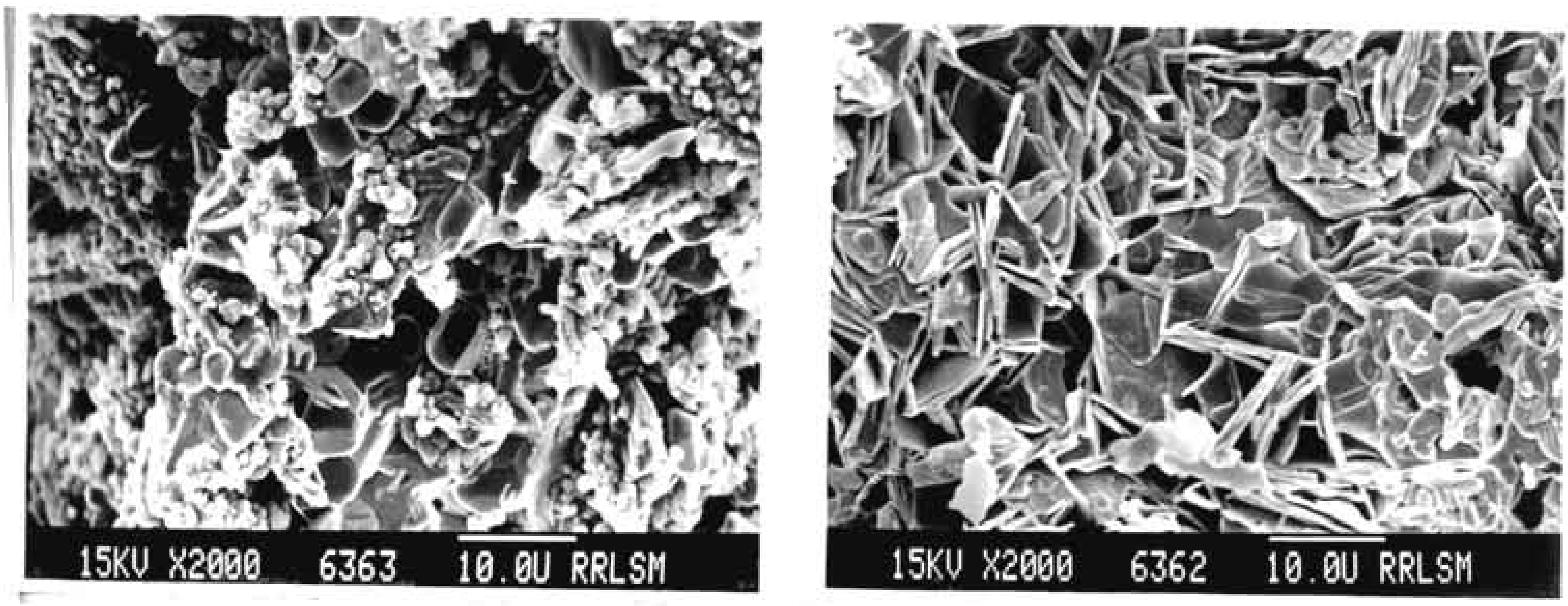


Fig. 5.4 Transition temperature plot of (a) 2212 (b) 2223



a. gel decomposed at 300° C (5 h)

b. 600°C (5h)



c. 700°C (5h)

845°C (5h)

Fig. 5.5 Variation in morphology during superconducting phase formation from acrylic gel above 900°C(4) within about 120 sec. Recent reports suggest extremely fast decomposition of nitrates in the YBCO composition which contain higher copper content(5). However, the mixture of nitrates in BPSCCO composition has other constituents in addition to copper which are not as active as copper nitrate. Table 5.1 indicates microwave response of the constituents in BPSCCO over a period of five minutes of exposure. Copper and bismuth nitrates readily decompose to form the corresponding oxides. But calcium nitrate losses essentially the water of hydration only and the product thus obtained is still soluble in water. Strontium and lead nitrates show no appreciable weight loss and may be the least active components in BPSCCO nitrate mixture. Hence the decomposition is incomplete and highly inhomogeneous. A microwave sensitive activator having no interference with the constituent cations would be an essential additive in this situation. Starch was found to form a gel during microwave exposure with adequate amount of water and to undergo easy decomposition in presence of nitrate ions. This property of starch has been made use of in BPSCCO composition containing nitrate ions and water molecule. Figure 5.6 indicates the sequence of formation of gel and black precursor powder under microwave. Hence the reaction consists of decomposition of nitrates accompanied by gelation in the microwave oven ensuring adequate distribution of constituents during precursor formation. In the absence of starch, no such processes take place as is further clear from

Table 5.1 Behaviour of individual nitrates during microwave exposure

Compounds	Appearance and wt. taken (gm)	Appearance and wt. after microwave exposure (gm)	% wt. loss	wt. loss corresponding to
Bi-nitrate $Bi(NO_3)_3.5H_2O$	White, crystals 1	Yellow, powder 0.5	50	Decomposed to Bi_2O_3
Pb-nitrate $Pb(NO_3)_2$	White, crystal 1	White, crystal 1	-	No loss
Sr-nitrate $Sr(NO_3)_2$	White, crystal 1	White crystal 1	-	No loss
Ca-nitrate $Ca(NO_3)_2.4H_2O$	White, crystals 1	White foamed 0.68	32	Loss of water of hydration
Cu-nitrate $Cu(NO_3)_2.3H_2O$	Blue, crystals 1	Black, powder 0.3223	67.7	Decomposed to CuO

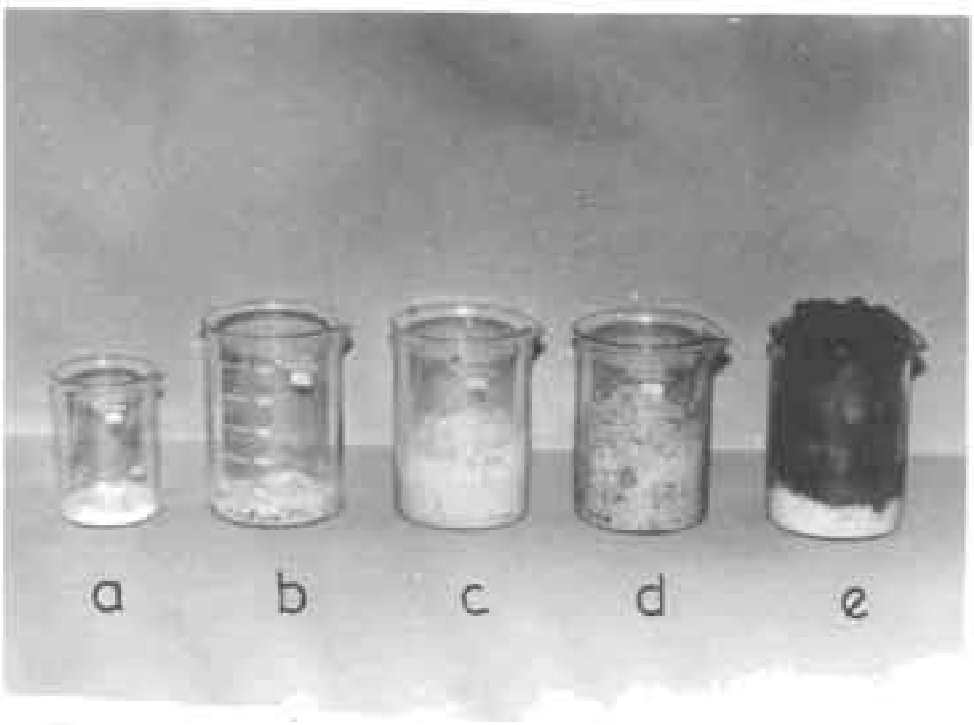


Fig. 5.6 Sequence of gel formation during microwave exposure of nitrates mixed with activator (a) as such, (b, c, d and e) after two, three and four minutes of microwave exposure

Fig.5.6a The XRD pattern of the decomposed nitrate in presence of starch after 240 sec. is presented in Fig.5.7 shows the evidence of Bi_2O_3 and CuO alongwith formation of Ca_2PbO_4 and $Bi_2Sr_2CuO_6$ phases (Fig.5.7a). The formation of these binaries and ternaries again indicates the extent of uniform reactivity as a result of gel formation and exothermic conditions prevailed during microwave decomposition of nitrate-starch mixture. However, on further exposure to 360 sec., continued to 480 and 600 sec., there is a progressive formation of 2212 accompanied by gradual reduction in 2201. Less prominent CuO and Bi_2O_3 peaks are observed in XRD corresponding to these samples (Figs. 5.7b, c and d). In fact, the sample exposed to 600 sec. was having maximum 2212 phase and minimum of other phases and hence considered as the best precursor. When exposure to microwave was extended to 1200 sec., decomposition of Ca_2PbO_4 resulted while 2201 phase was retained as seen in Fig.5.7e.

The precursor prepared by exposure for 600 sec. in microwave was further heat treated at 820°C over a period of 10 h in air resulting in fully 2212 phase (Fig.5.7f). As is already known, the formation of 2212 phase requires much longer heat treatment time. Further, considerable conversion to 2223 phase also occured (Fig.5.7g) which by other methods is seldom possible. On heating for 30 h at 845°C with three intermediate grinding steps, the powder showed a Tc of 107K. Phase purities were calculated from XRD (Fig. 5.7h) intensity of (002) peaks

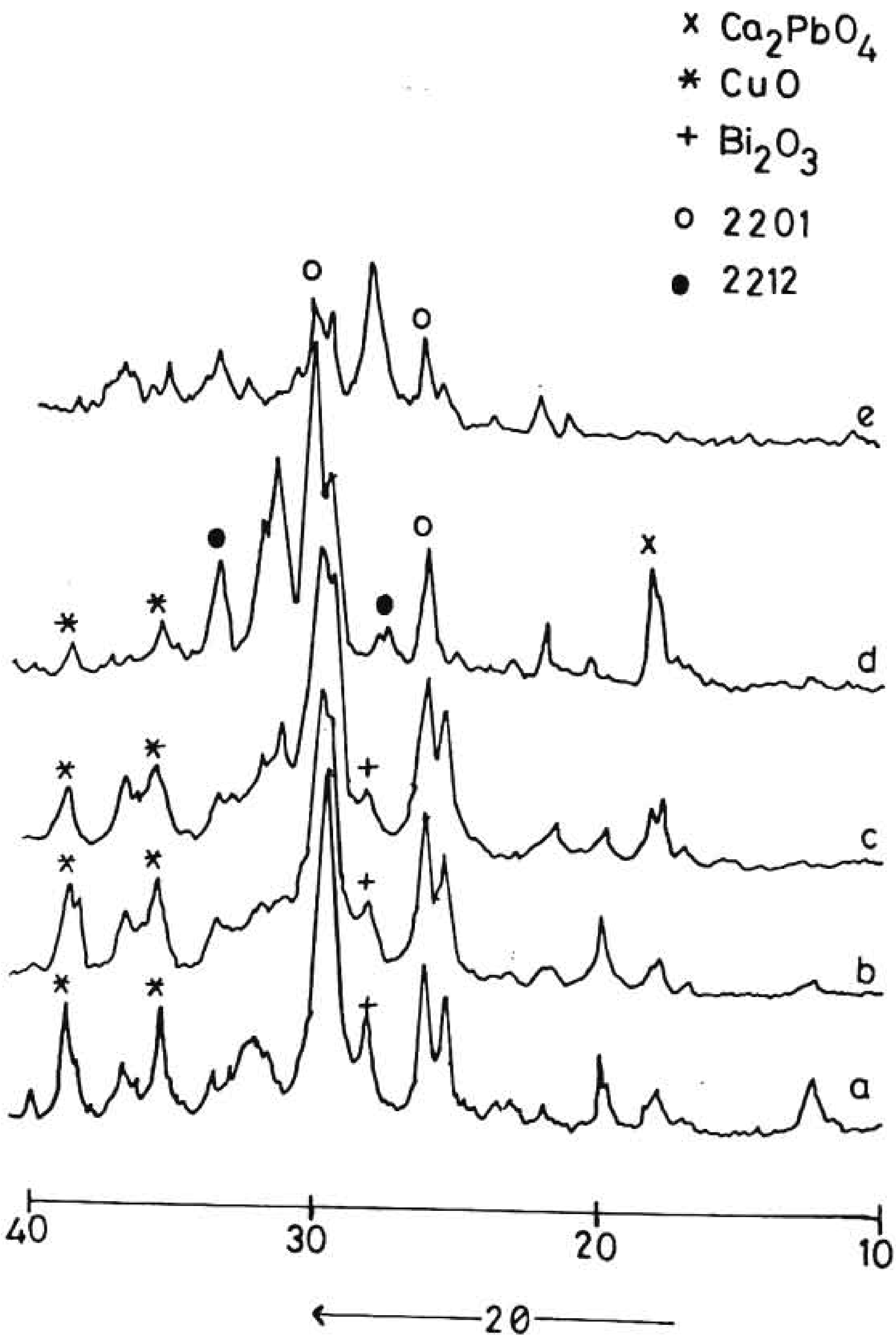


Fig. 5.7 XRD Pattern showing change in composition with microwave exposure time

a. 240 sec b. 360 sec c. 480 sec
d. 600 sec e. 1200 sec

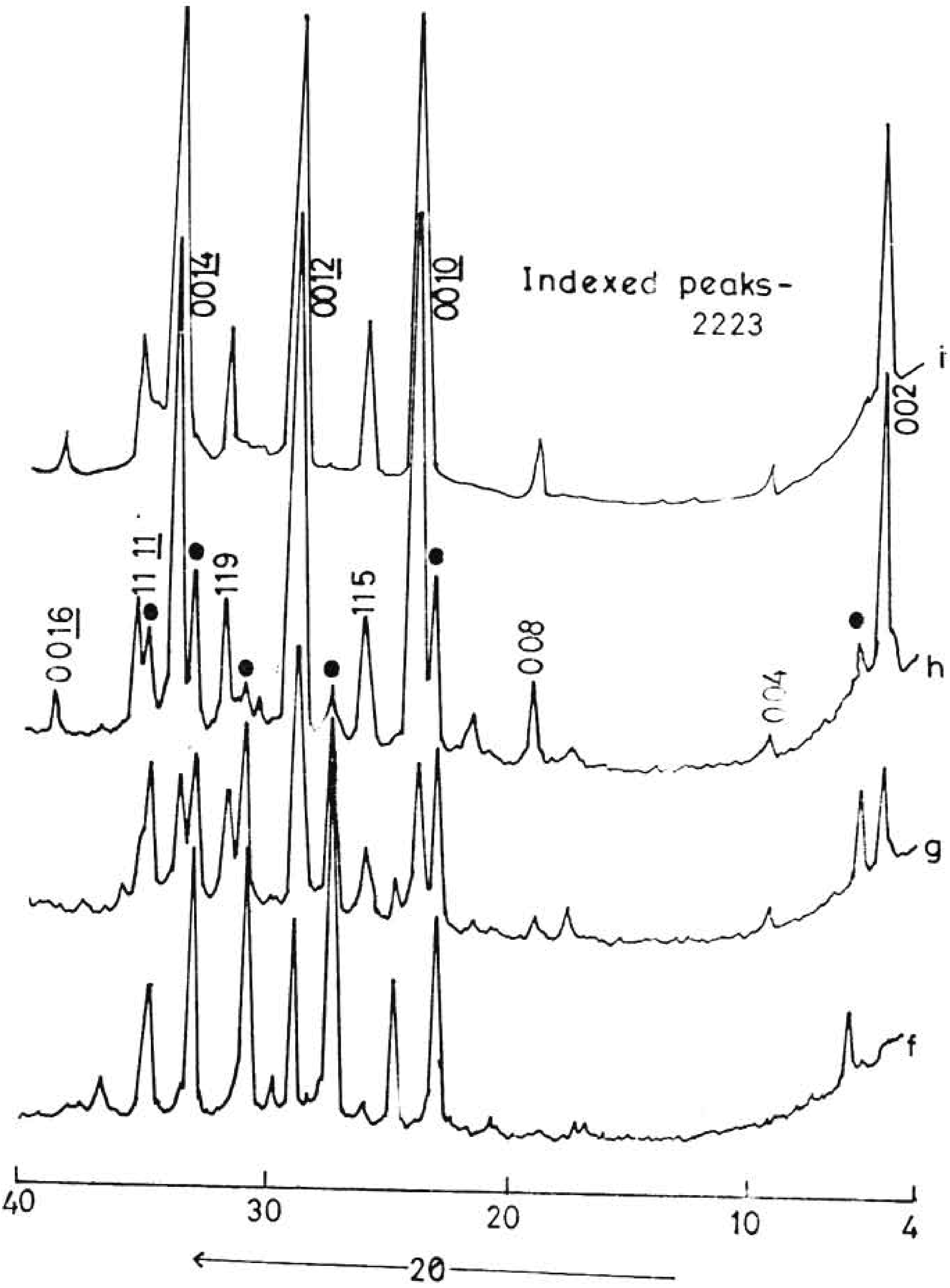


Fig. 5.7. XRD Indicating formation of 2212-2223 phases.

f. Precursor powder heated at 820°C for 10hrs.

g. powder (a) heated at 845°C for 10hrs. (h) & (i) 30 & 40h heating with grinding after each 10hrs. heating.

of 2223 and 2212 phases as

$$\% \ 2223 \text{ phase} = \frac{I_{4.7}}{I_{4.7} + I_{5.7}} \times 100$$

where $I_{4.7}$ and $I_{5.7}$ are the intensities of 002 peaks of 2223 and 2212 peaks respectively.

On heating to a total of 40 h, the 2223 phase formation is complete in the present case. Thermogravimetric analysis of the microwave exposed sample showed further weight loss less than 2% which indicated near complete decomposition in the oven (Fig.5.8).

The microwave precursor as well as the 2212 and 2223 phases distinctly show different densities as seen in Table 5.2. The bulk densities show a regular increase from precursor powder to those containing high Tc phases. Morphologically, the 2223 powder appeared as flakes with regular shapes and rounded edges as shown in Fig.5.9. The total steps involved in BPSCCO powder preparation are shown in Fig.5.10.

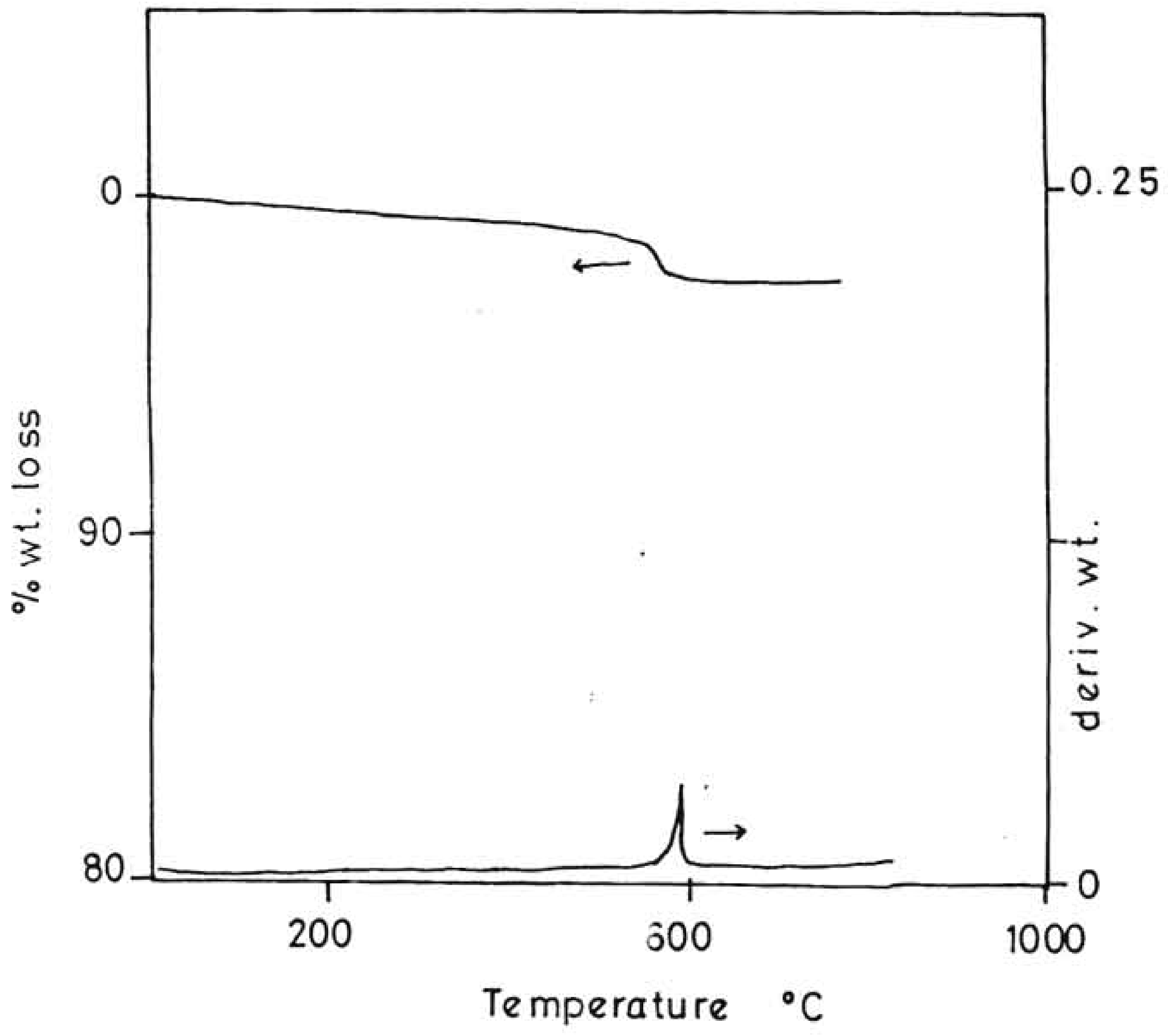


Fig. 5.8 TGA of MW exposed samples

Table 5.2 Comparison of powders

	Precursor (Cal. 700°C)	2212 rich	2223 rich
Specific gravity (kg/m^3)	4610	5760	6500
Bulk density (tap density) (kg/m^3)	1142	2000	2030

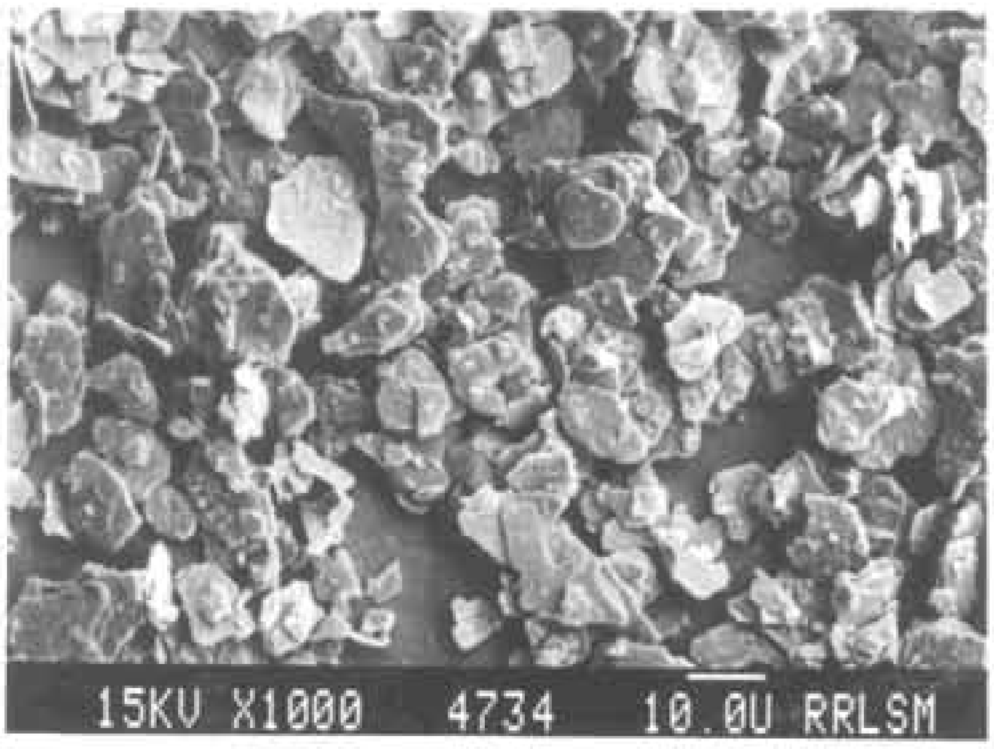


Fig. 5.9 Powder morphology of 2223 superconductor from microwave derived precursor

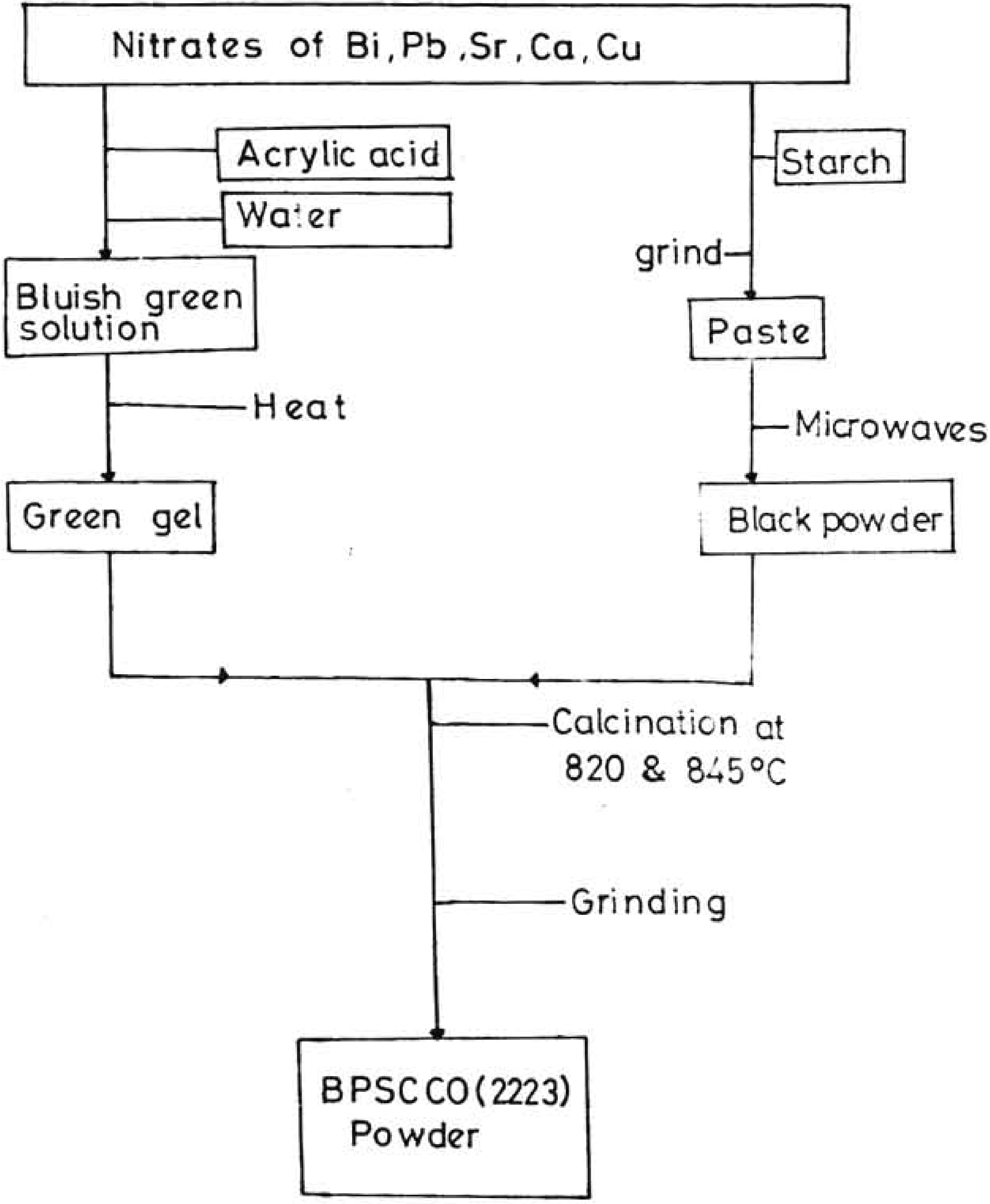


Fig. 5.10 Flow sheet for BPSCCO powder

5.3 BPSCCO SUPERCONDUCTOR BULK WITH ORIENTED MICROSTRUCTURE

Many methods have been reported to derive a microstructure with a-b plane (c-axis) oriented grains(6-7). Earlier work is related to thin films and Ag-sheathed wires. The processes were based on long heat treatment schedules and also introduction of certain second phases and were rather restricted to very small samples. Earlier work on YBCO superconductor had shown the possibility of a melt processing technique to introduce texturing(8). However, in the case of BPSCCO, other approaches such as melt processing of sintered compacts at partial melting conditions and controlled solidification procedure were adopted. Similarly, BPSCCO superconductor compact in a zone melting furnace melt partially and align the grains using the thermal drag. This is regarded as post sintering treatment (PST) since the zone melting was conducted on a sintered compact. If the green compact can be designed to have an oriented particle packing by adopting to slurry consolidation technique(9) before sintering, the ultimate texture would be considerably enhanced after zone melting operation. The pre-alignment of BPSCCO particulate in a green compact is termed as presintering processing (PSP). On the other hand, zone melting of compacts prepared under PSP conditions would be the most ideal since it would be an integrated approach to texture development. The following part of the discussion deals with the experiments conducted, the results obtained and possible explanations for the results.

5.3.1 Presintering Processing (PSP) of Bi-based bulk superconductor through viscous processing

(a) Experiments conducted:

The superconductor powder rich in 2223 phase prepared by sol-gel method was ball milled separately in double distilled water and isopropanol using zirconia grinding media for 10h. The viscous slurry was filter pressed under pressure upto 10 MPa at a rate of 5 mm/min in a specially designed die following the procedure as reported(9). For a typical experiment, 6 gm of powder and 4 gm of solvent were used. One set of compacts were made by conventional uniaxial pressing of dry powder. All these samples were sintered at 845°C for a period of 10h. The density of green and sintered samples were calculated by dimensional measurements. Microstructure was observed under SEM (JEOL 35C, Japan) and the XRD pattern was also studied. Another set of sample was prepared by allowing the slurry in isopropanol to settle undergravity and the features were compared.

(b) Results and discussion:

The general flow sheet adopted for PSP is provided in Fig.5.11. The die set up for viscous processing consisted of cavity of 10 mm diameter (Fig.5.12). The bottom die cavity is closed with Whatmann No.1 filter paper on a carrier with filtrate collection facilites. The mode of pressure application is shown in Fig.5.13 where the total pressing

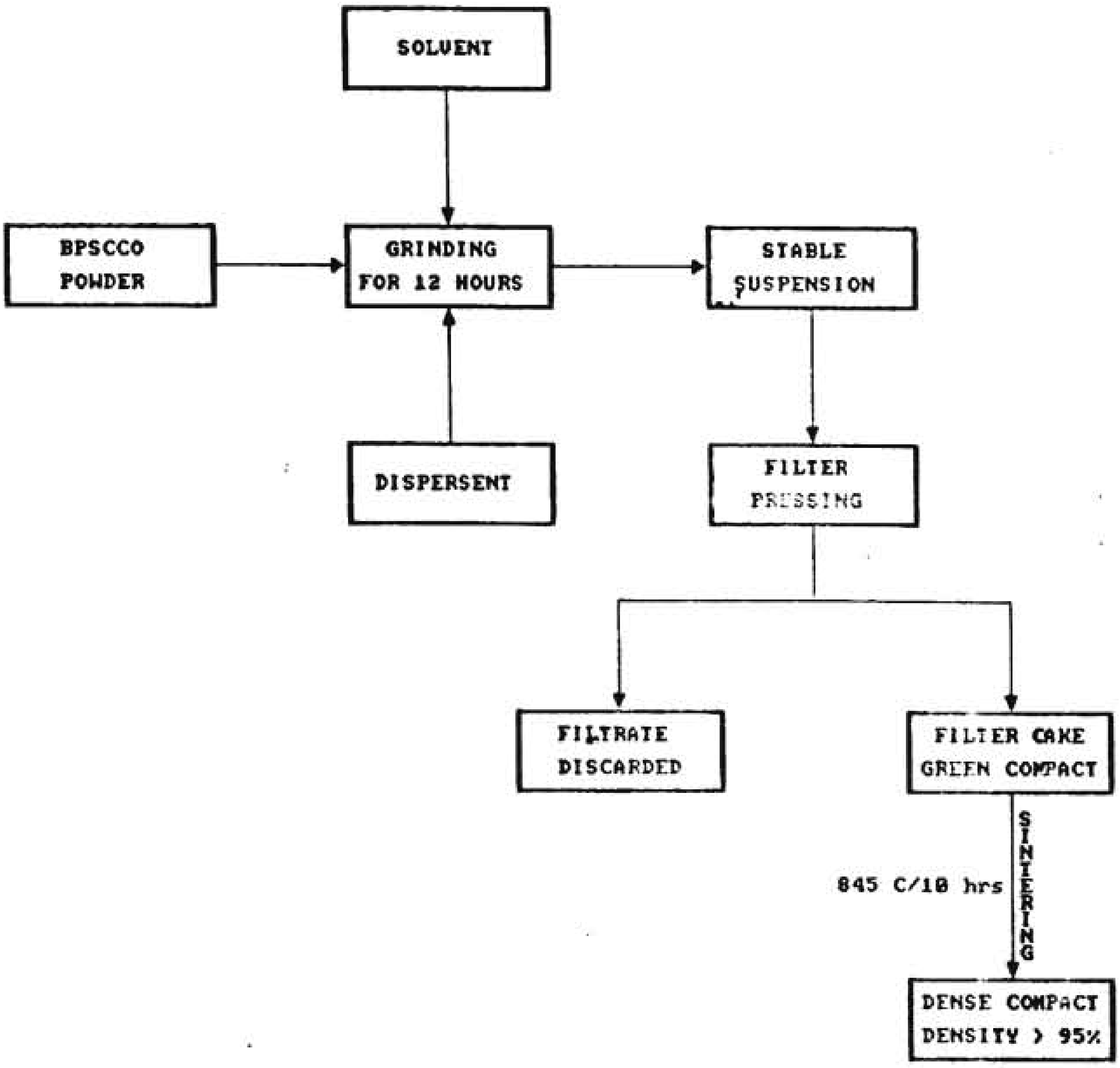


Fig. 5.11 Flow sheet for PSP

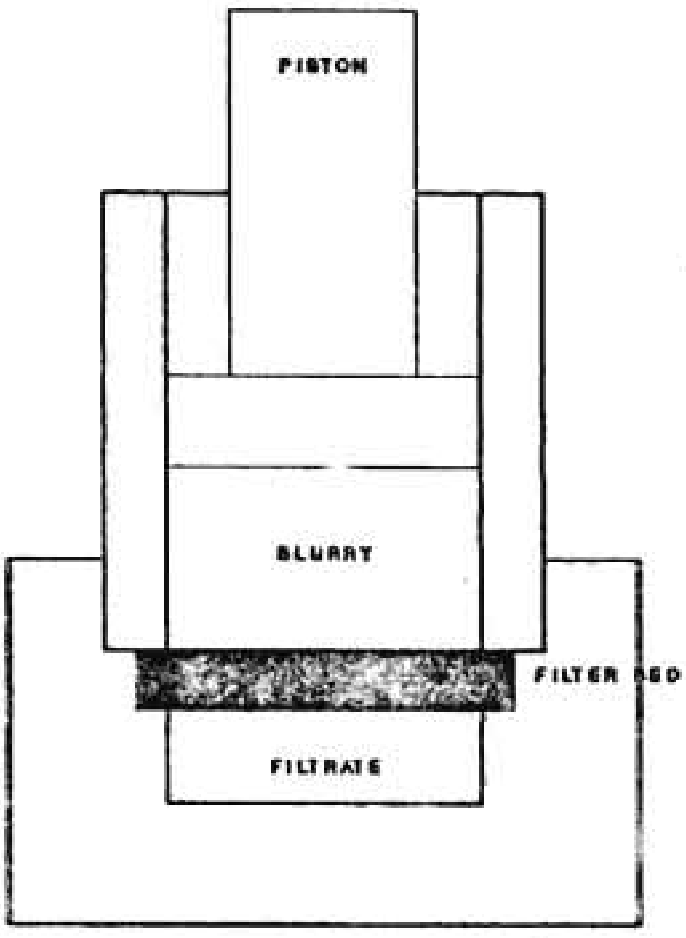


Fig.5.12 Filter pressing die set-up

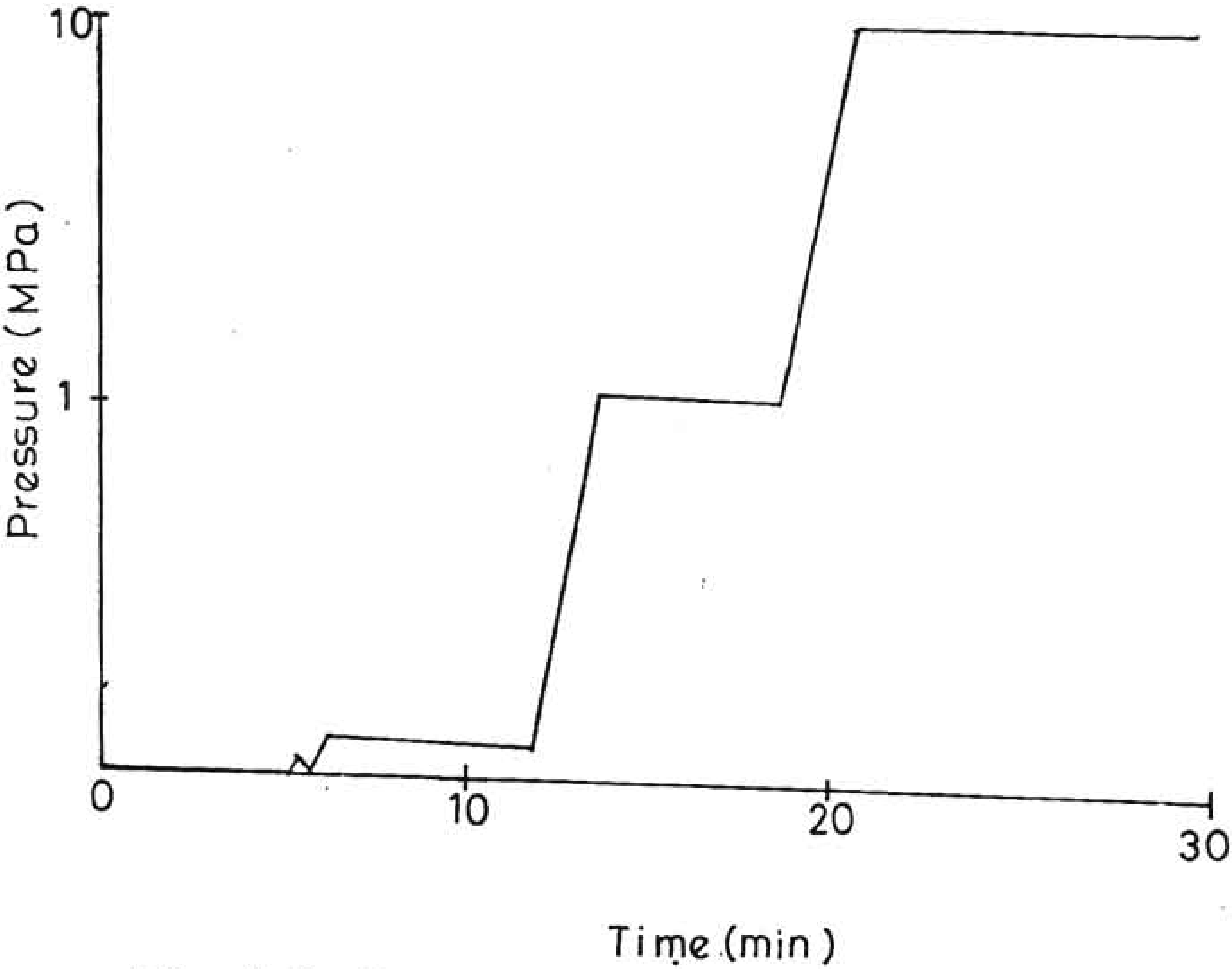


Fig. 5.13 Pressure application diagram

procedure are divided into three stages. At first stage, no pressure was developed with applied load due to the filtering out of liquid. Second stage indicates the time dependent relaxation of pressure due to the alignment of grains and draining out of the residual liquid. At third stage, pressure is applied to higher values of 10 MPa to get higher compaction. Application of pressure at higher rates may result in non-uniform packing and orientation of particles possibly with microcracks. The green compacts were dried in air oven at 80°C for 2h and were sintered according to the heating schedule as given in Fig.5.14. The compacts were heated at 300°C for 3h, removed all volatiles and further heat treatments at 800°C followed by sintering at 845°C resulted in high density BPSCCO body.

The pellets obtained were broken along the direction of pressure application direction and the microstructure of fractured surface are presented in Fig.5.15. The particle packing pattern in the various samples appeared to be distinctly different. This is due to the change in rheological characteristics of slurry, permeation properties of solvent through the cake and to the dispersibility of the powders in liquid media. The mode of application of pressure also influences the microstructure.

The SEM fractograph of the above samples after sintering are given in Fig.5.16. Usually sintering and directional grain growth are related to the initial particle packing and this has

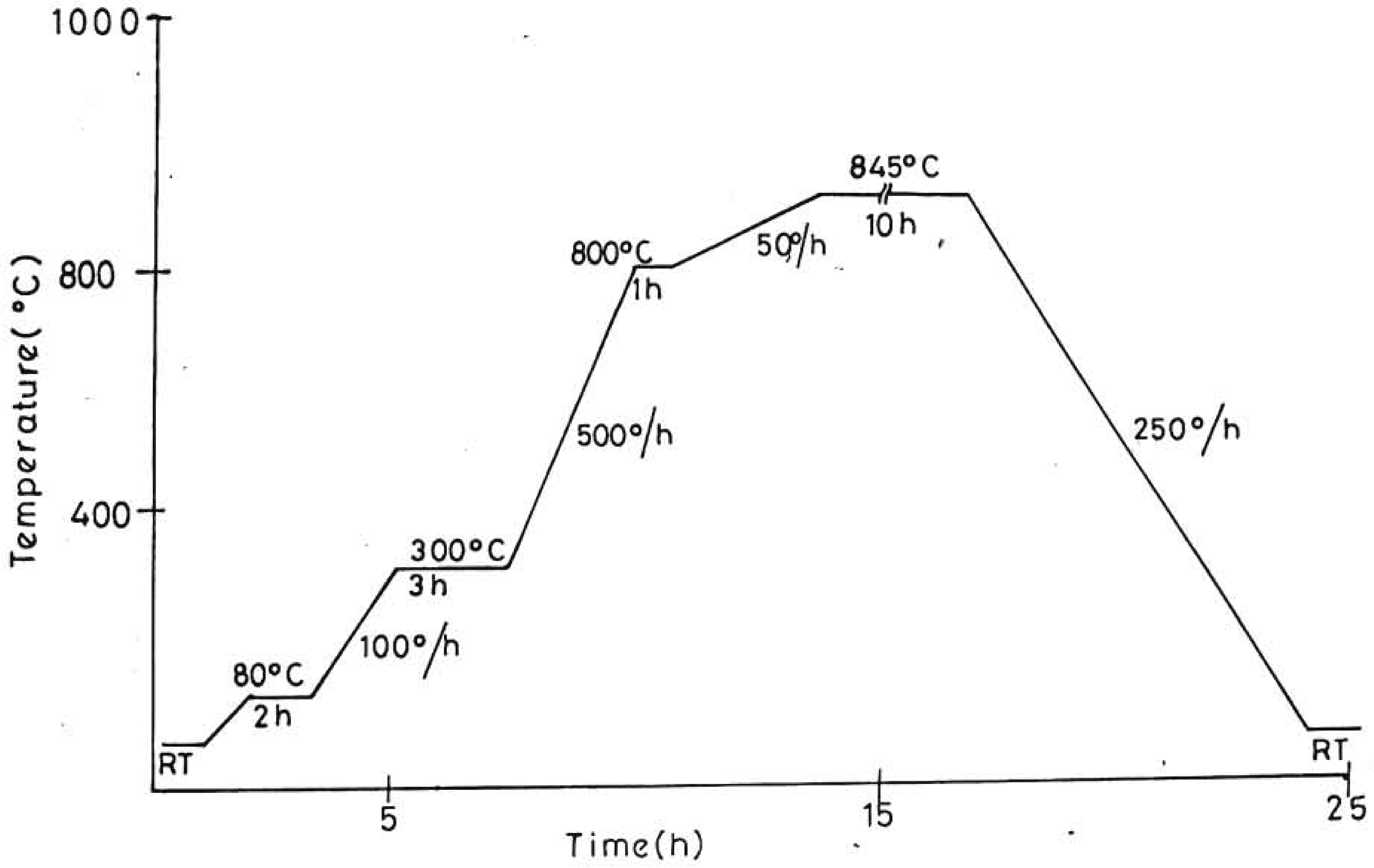
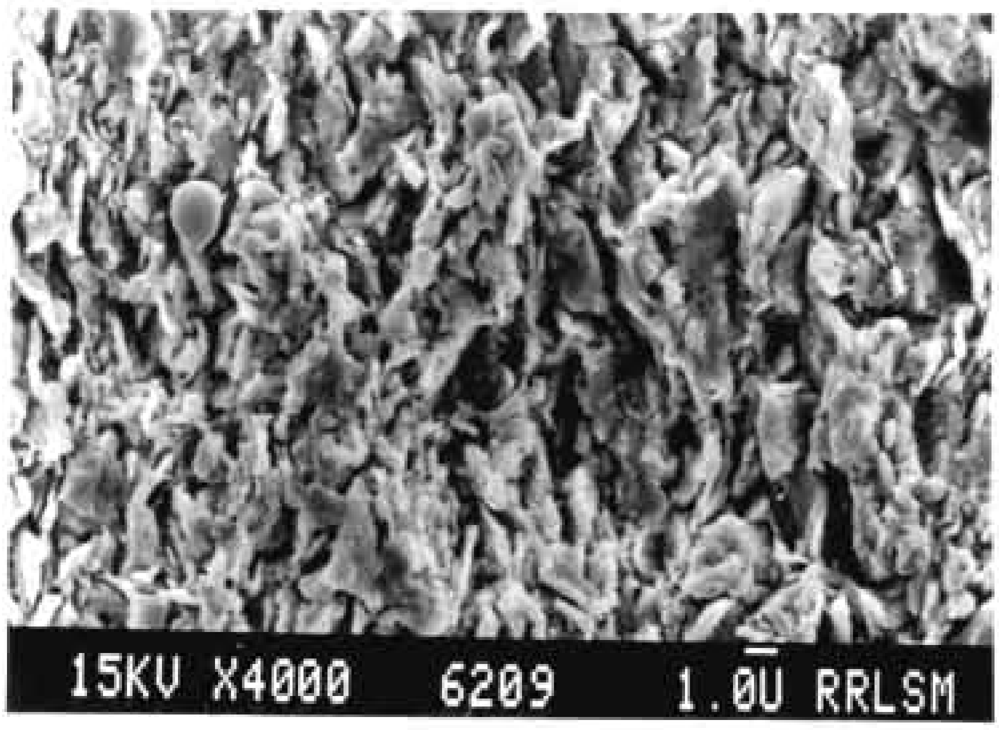
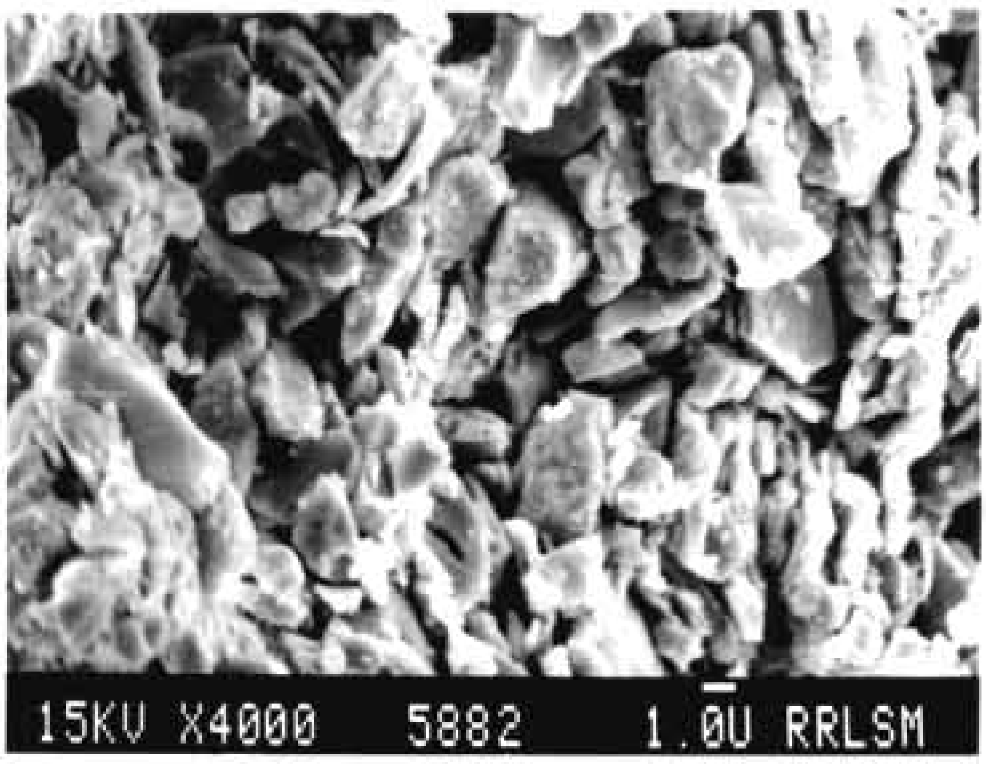


Fig.5.14 Heating schedule for sintering

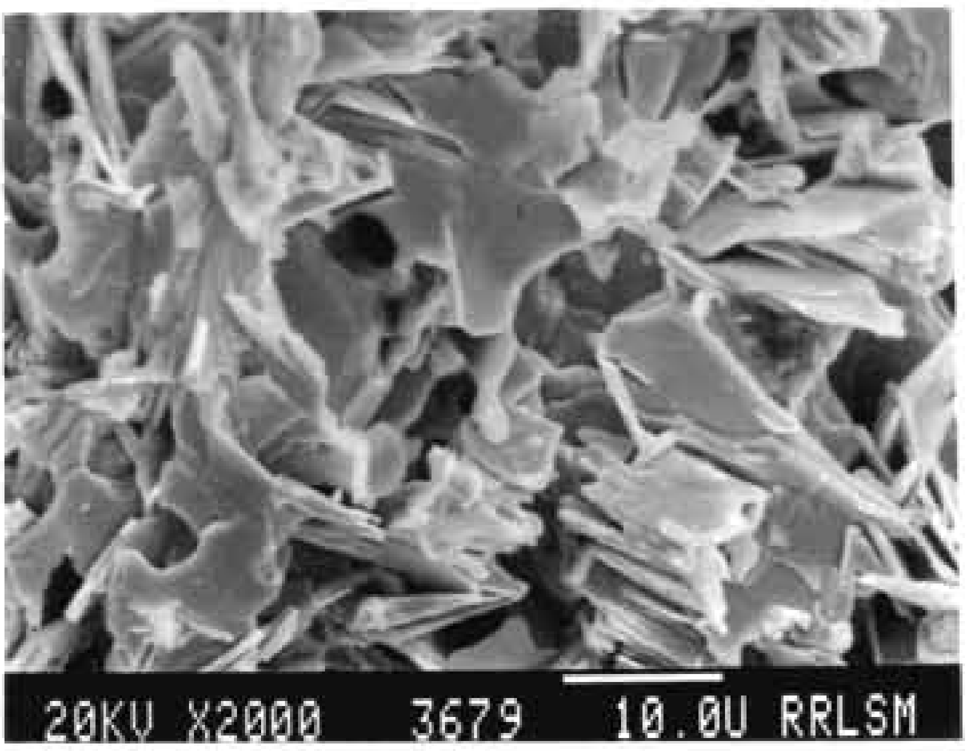


from isopropanol medium

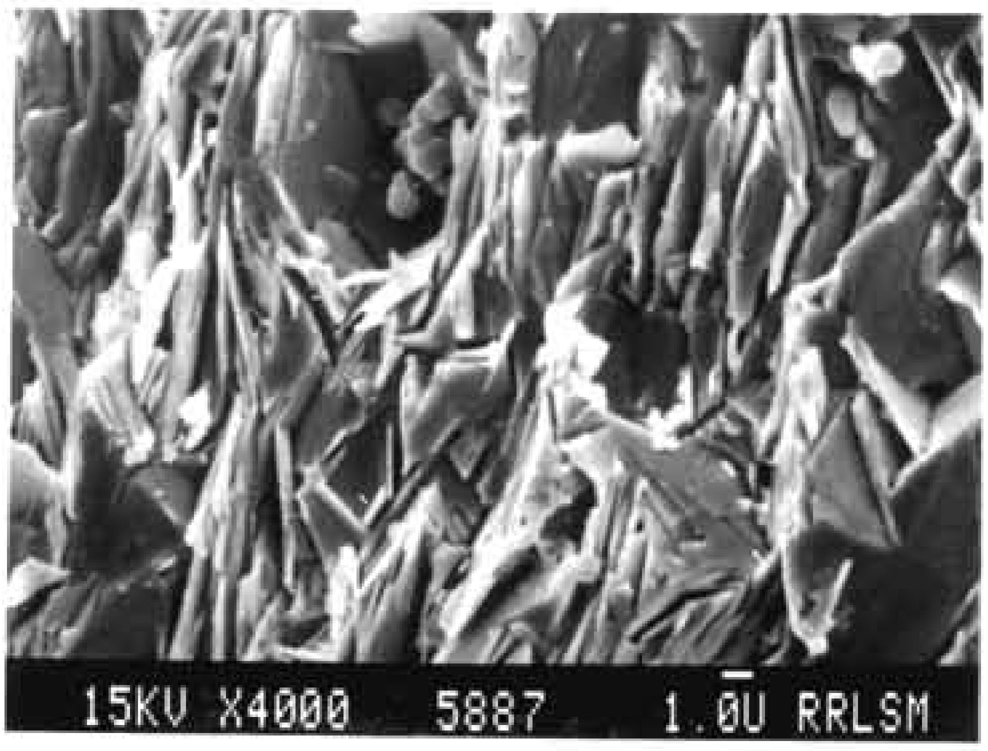


from water medium

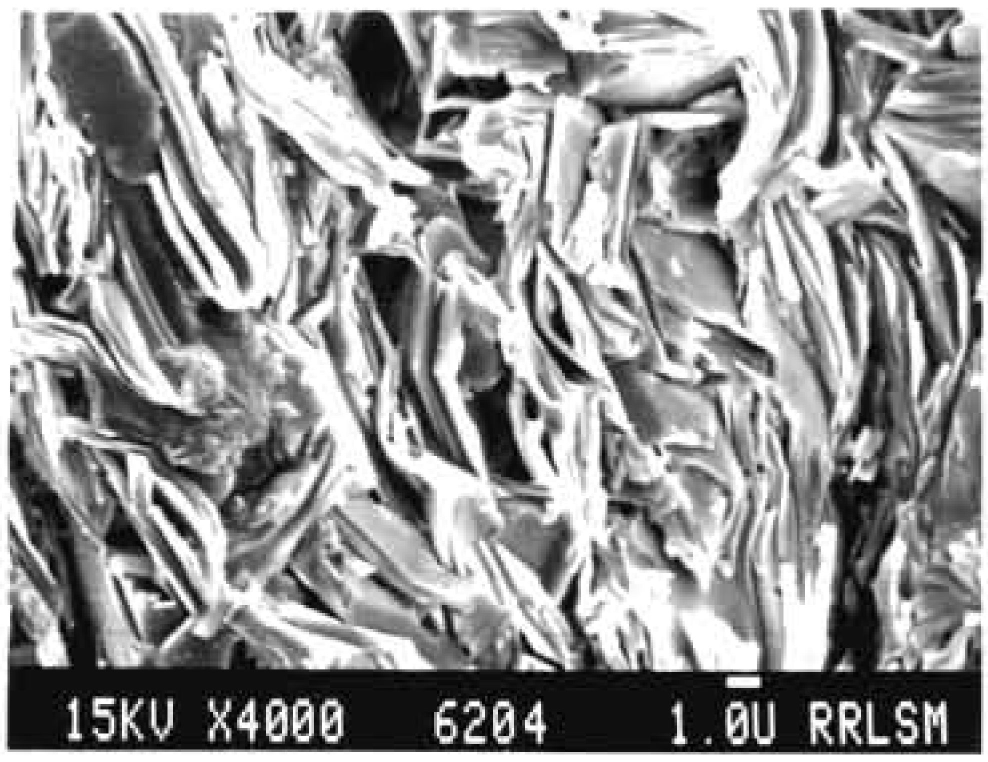
Fig. 5.15 Fractographs of filter pressed green bodies



powder pressed



water medium



isopropanol medium

Fig. 5.16 Fractographs of sintered filter pressed compacts

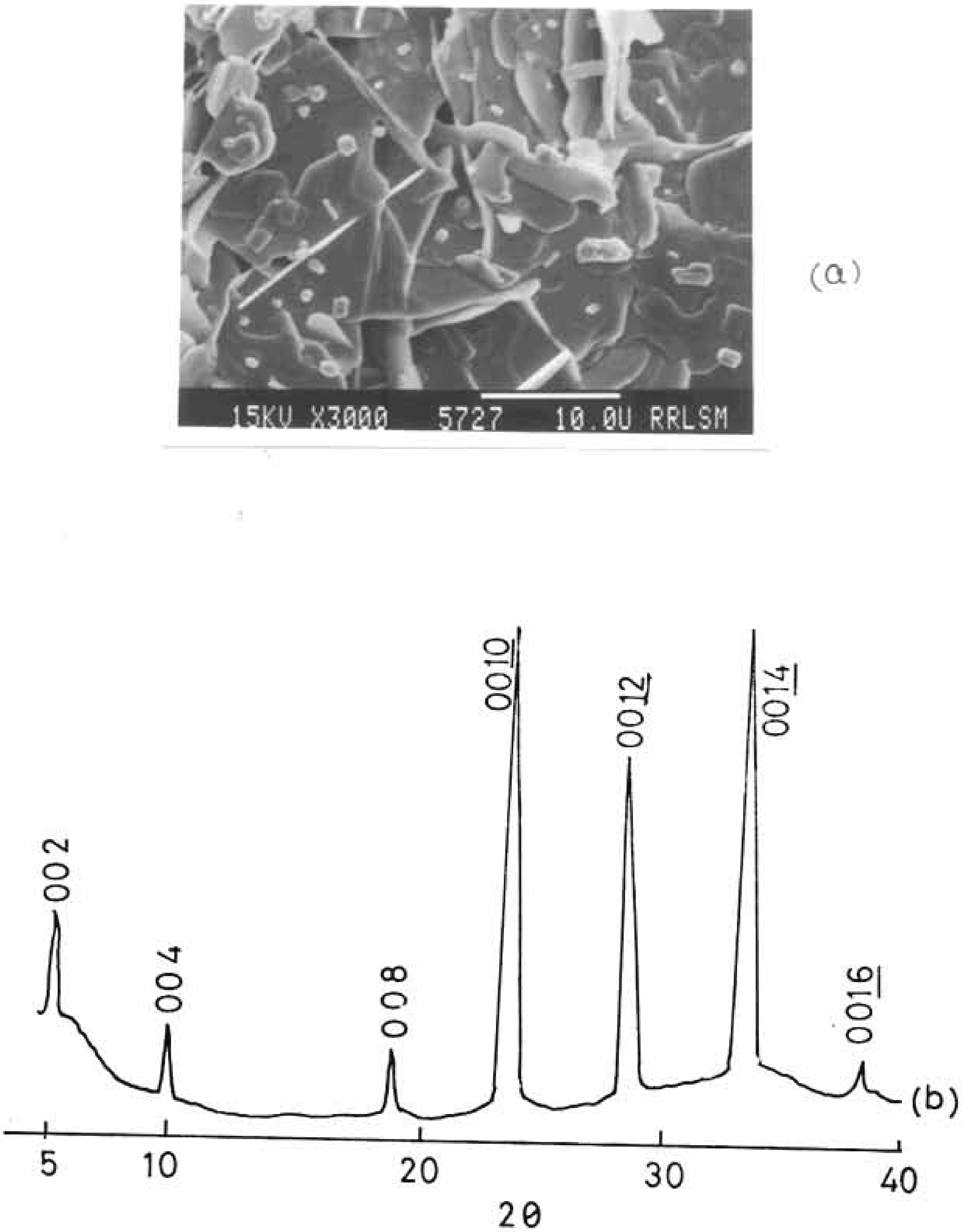


Fig. 5.17 Micrograph of surface - normal to the pressure application and XRD from the same face

been true in water and isopropanol derived samples with flaky grains larger than 50 micrometers. The sintered compact obtained from uniaxial dry pressing has randomly oriented grains of 10-15 micron size. Surface morphology of filter pressed samples from isopropanol in a direction perpenticular to the pressure application reveals flakes like large grains are stacked one over the other (Fig.5.17a). The XRD corresponding to this plane is given in Fig.5.17b, which shows that texturing has been attained along a-b plane. Samples from isopropanol have highest green and sintered densities (Table 5.3) while that of uniaxial powder pressed ones are the lowest.

Slurry pressing or viscous processing of BPSCCO superconductor powder could result in desirable compaction and sintered densities and microstructures. Orientation of flaky grains by application of low pressure under controlled rates on a suspension is now shown to be one of the methods for obtaining oriented microstructure in sintered bulk compact.

5.3.2 Zone Melting Refining (ZMR) of BPSCCO Compacts

(a) Experiments conducted:

110K phase rich superconductor powder prepared by sol-gel technique was ball milled for 12h in hexane using zirconia as grinding media in poly vinyl chloride containers. The slurry was filtered, dried and uniaxially compacted into 60 x 10 x 1 mm size strips under a pressure of 150 MPa and were sintered at

Table 5.3 Density-Microstructure variation in sintered samples

Mode of compaction	Green density (kg/m^3)	Sintered density (kg/m^3)	Microstructure
Powder pressing (Uniaxial, 150 MPa)	3100	5990	Random grains orientation
Colloidal forming (Uniaxial, 20 MPa)	4310	6200	Oriented grains

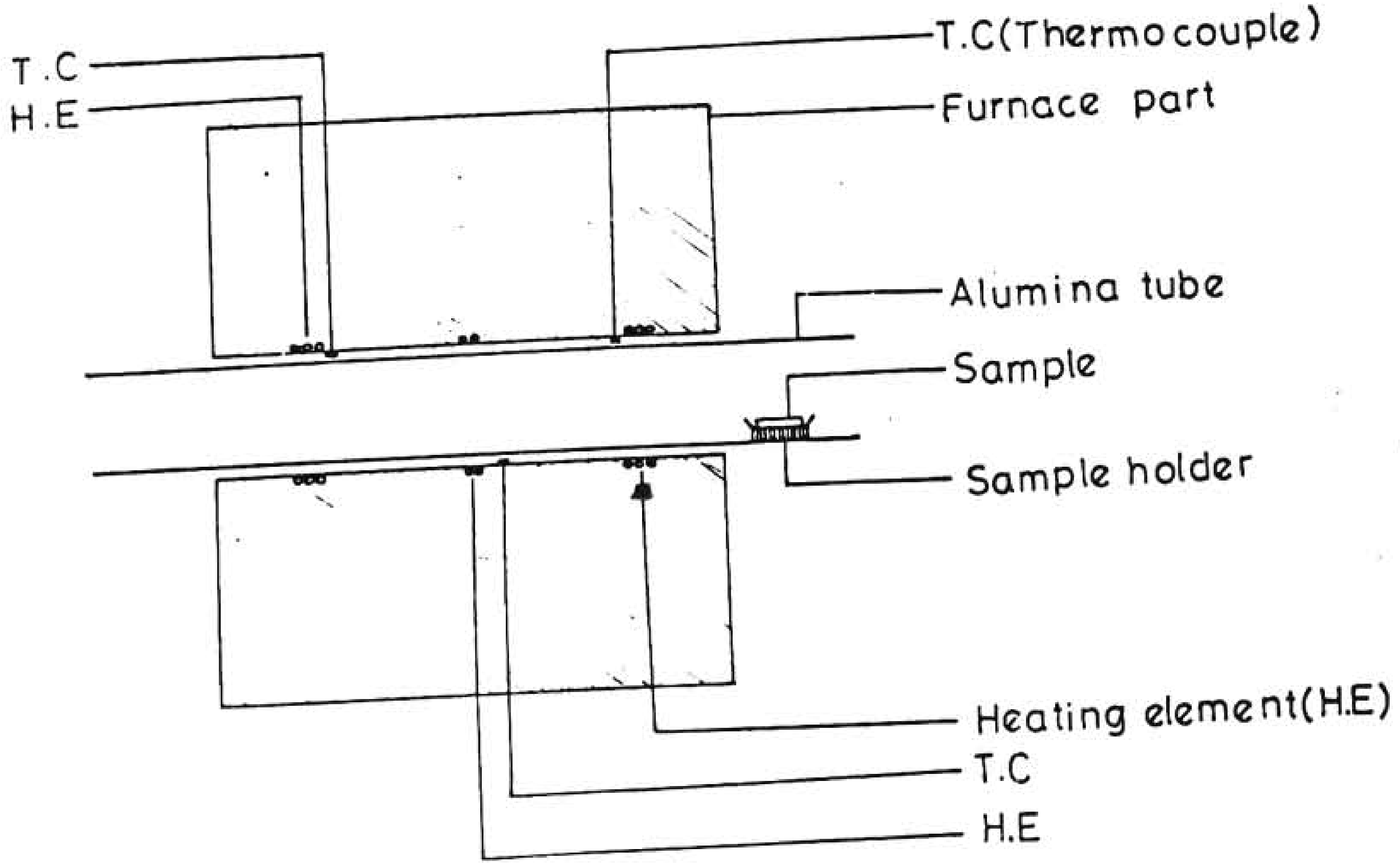


Fig.5.18 Zone melting furnace set up

845°C for 20h. The sintered strips were subjected to zone melting in a three zone furnace set up (Fig.5.18) with a furnace movement speed of 30 mm/h. The sample was kept on a platinum plate inside a static alumina tube of 250 mm diameter.

The three zones of the furnace are independently controlled to result in premelting 750°C, melting 845-860°C and cooling 750°C zones. Table 5.4 describes the different conditions adopted for zone melting. Strips were repeatedly zone melted upto five times at the optimum temperature conditions. The microstructure features of as sintered and zone melted samples were observed under SEM (JEOL 35C,Japan). Identification of the phases and orientation were noted by XRD (Rigaku, Japan).

(b) Results and discussion:

The three heating zones of the zone melting (ZM) furnace are independently controlled. The width of the melting zone is 0.5 cm and other zones are kept two centimeters apart from the central zone. The temperature distribution inside the alumina tube has a profile as given in Fig.5.19 which can be varied as required. A temperature difference of 100°C was maintained between zones in order to minimize convection heating and to keep distinct gradient between the melting and adjascent zones. BPSCCO superconductor is sensitive to melting near the sintering temperature and hence has only a narrow range of stability around 850°C beyond which it undergoes decomposition

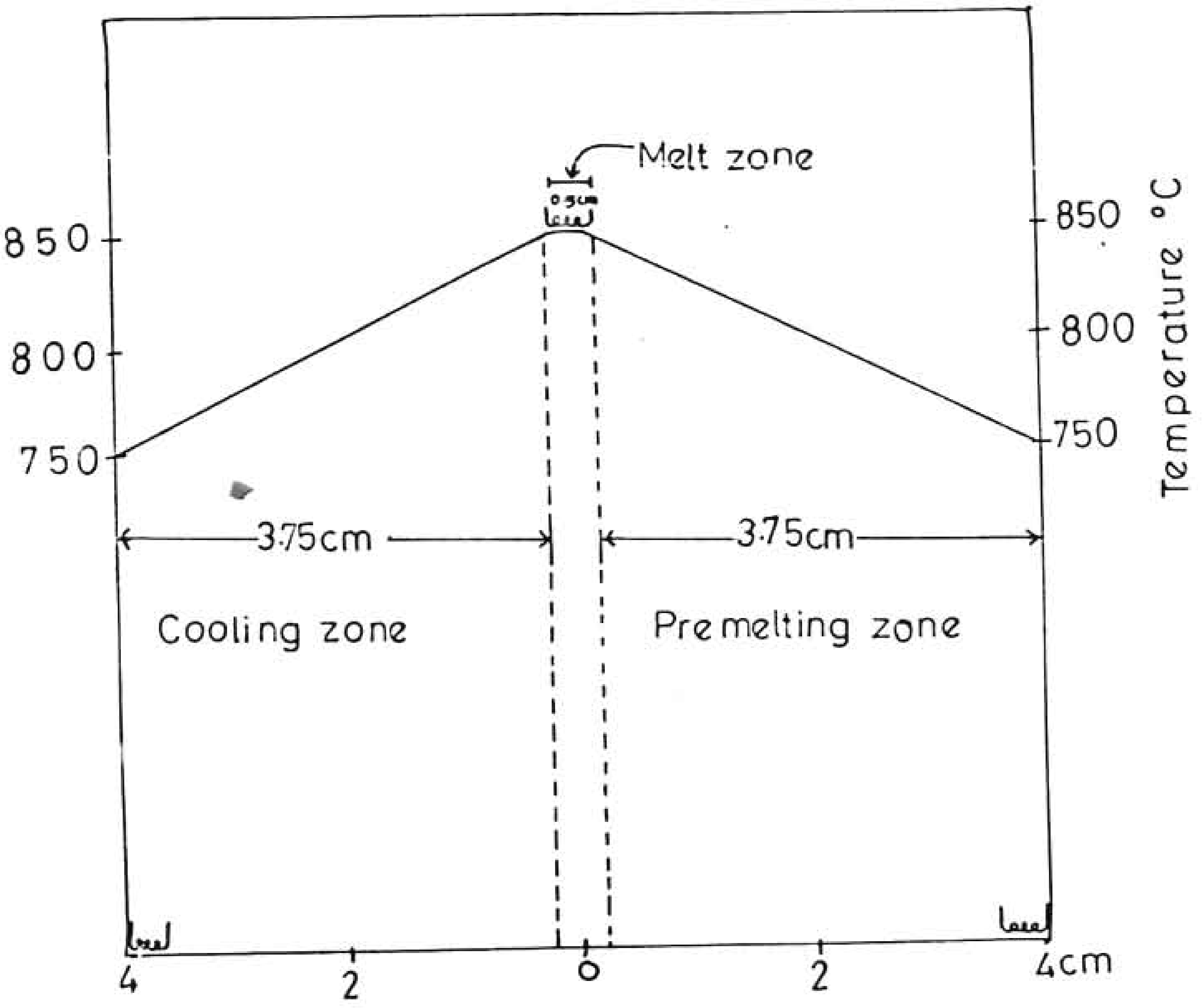


Fig. 5.19 Temperature profile of the furnace

to different binaries and individual oxides. Hence the sintering temperature is kept around 845° Particularly under zone melting experiments, it is still possible to subject to higher temperatures since the exposure time is very short. The sample portion remains at the melting temperature region only for 10 minutes. The optimum conditions for melting and other zones have been arrived at by following the microstructural and XRD data on the samples subjected to different zone melting conditions. The fractograph of sample heated to above 855°C showed additional phases apart from the high Tc BPSCCO flakes. Sample heated to above 860°C failed to exhibit even Meissner effect. On the contrary, heat treatment at 845°C did not show any visible microstructural variations from the sintered sample. Based on these observations, the melting zone temperature in the present investigation was fixed at 850°C with pre and post melting zones at 750°C (Table 5.4).

Figures 5.20a, b and c show microstructural evolution in samples during repeated zone melting for first, third and fifth time. One important thing to be stressed here is that the grain alignment is along the direction of zone movement which is demonstrated as in Fig.5.21. Though this phenomenon of grain alignment is difficult to explain liquid phase assisted sliding of the grains, dissolution and crystallisation in preferential direction at the melt-solid interface may be some possibilities. The zone melted BPSCCO after five repeated passes shows reflections only from (001) planes. Similar

Table 5.4 Standardisation of zone melting conditions

No.	Pre melting zone temp. (°C)	Melting zone temp. (°C)	Cooling zone temp. (°C)	SEM observation after 1st run
1	750	845	750	No change in the microstructure
2	750	850	750	Partial grain alignment
3	750	855	750	Partial grain alignment+partial decomposition
4	750	860	750	Distruction of platlets of BPSCCO superconducting grains

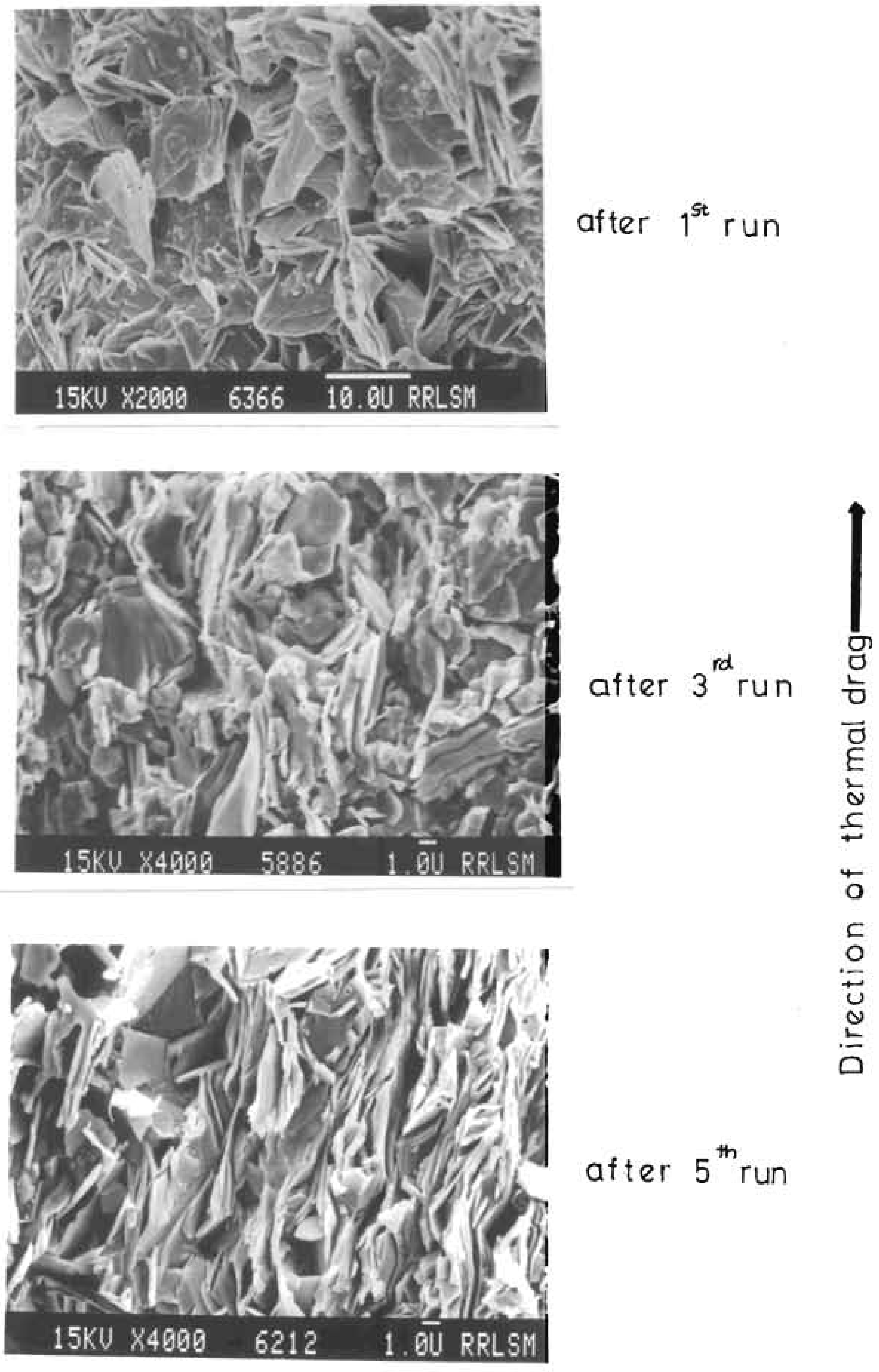


Fig. 5.20 Micrographs showing evolution of aligned grains during zone melting

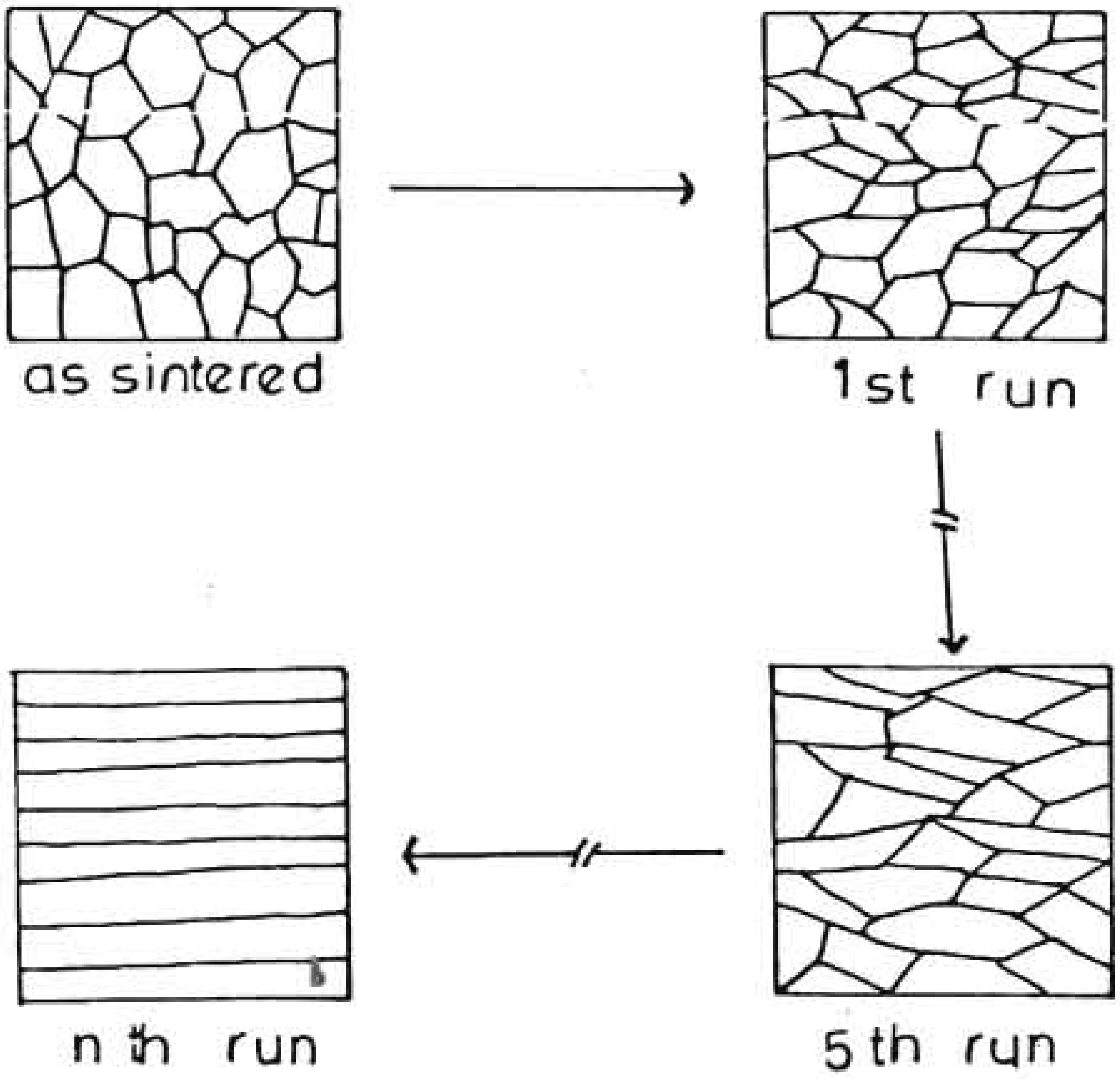


Fig. 5.21 Pictorious representation of grain alignment in BPSCCO strips.

oriented pattern was observed in samples polished down to half the thickness. The fractograph of zone melted samples show large flakes arranged one over the other, thus indicating that the effect of ZM is spread throughout the bulk of the sample. Further, zone melted BPSCCO sample gave XRD peaks corresponding only to (001) planes of 2223 phase though the starting material contains around 10% of 2212 phase also. Thus after fifth run, i.e. total 50 minutes exposure at melting zone yielded textured 2223 grains. Thus the total process may be termed as zone melting refining and the refining is based on the concept of differential rate of movement of the different phases under thermal drag conditions.

Thus a zone melting-refining technique using a three zone heat treatment system with horizontal sample loading pattern has been shown to be successful in achieving desirable textured grain structure in BPSCCO superconductors having an initial random grain microstructure. By adjusting the premelting, melting and cooling zones judiciously, it is further possible to seggregate the impurity phases and thus enrich the high Tc phase.

5.3.4 Integrated Pre- and Post- sintered Processing (IPSP) of BPSCCO Superconductor compacts for texture development

(a) Experiments conducted:

The BPSCCO superconductor powder prepared by sol-gel method rich in 2223 phase was ball milled in isopropanol for 12h

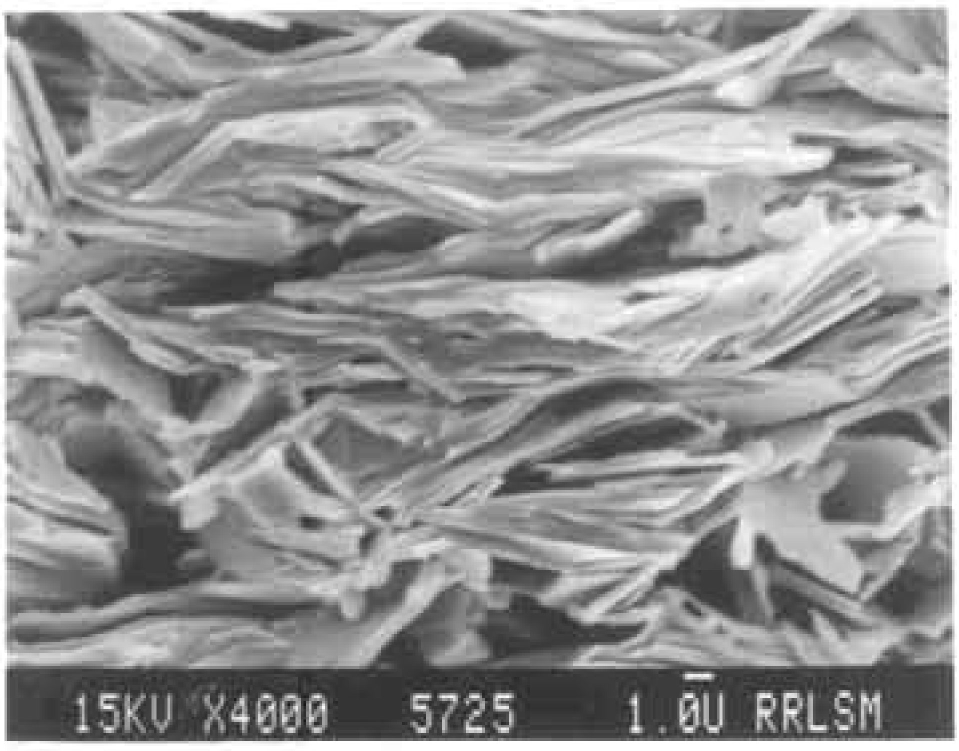


Fig. 5.22 SEM micrograph showing a-b plane oriented BPSCCO superconductor grains after integrated processing

and the slurry was filter pressed in a specially designed filter press as discussed in earlier section. The compact obtained was strip of size 60 x 10 x 1 mm which were dried at 80°C in an air circulting oven and sintered at 845°C for 10h. These strips were zone melted in the zone melting furnace as discussed in the earlier portion. Scanning Electron Microscopy was used to study the morphological features of these compacts during zone melting.

(b) Results and discussion:

The conditions of slurry preparation and zone melting are discussed in previous two sections. The SEM result of the zone melted compact shows beautiful arrangement of BPSCCO grains one over the other. The grains have grown along a-b plane. The aspect ratio of the grains are about 50 (Fig.5.22).

Thus, by a combination of controlled pre and post sintering process, it has been possible to arrive at a-b plane oriented microstructures desirable for high Jc values in bulk BPSCCO superconductors, which is extremely difficult to obtain under normal processing conditions.

5.4 CONCLUSION

The total work on the BPSCCO superconductor were carried out to derive a right method for preparation of BPSCCO powder within very short time and to derive at right processing techniques for bulk compacts with aligned microstructure. The results obtained are concluded below:

(a) Powder preparation:

Above 95% 2223 phase was formed within a period of 35h at 845°C. This is an advantage over the conventional methods which required 150-200h of processing to attain 2223 rich composition. The exothermicity of decomposition of the gel at around 300°C produce a mixture of binaries and ternaries like Ca_2PbO_4 and $Bi_2Sr_2CuO_x$. The BPSCCO formed from the gel are all oriented along c-axis as indicated by XRD pattern. Peaks with maximum intensity are all from (001) plane. Activator induced microwave processing also resulted in a very high reactive precursor powder which formed 95% 2223 phase within 30 h of calcination at 845°C.

Effect of calcination in the 2223 phase formation was established by a systematic XRD analysis of powder heated at 845°C after various extent of calcination. Incorporation of microwave energy for the preparation of BPSCCO superconductor is yet another highlight of this study. Direct exposure of the mixture of nitrates of BPSCCO constituents does not undergo decomposition. But incorporation of an activator cum gelling agent could be effective to produce a precursor rich in binaries and ternaries like Ca_2PbO_4 and $Bi_2Sr_2CuO_x$ within a short interval of time of 10 minutes. The total time of processing for 2223 phase formation was reduced to 30h.

The Tc of BPSCCO powder produced by gel route is 107K.

(b) Processing of sol-gel BPSCCO superconductor:

Techniques like colloidal processing and zone melting and their combination are used to attain the objective.

A post sintering treatment (PST) like zone melting-aligning of the grains is the basic principle adopted in this case. Another approach is to process the powder before sintering (pre sintering processing, PSP) to align the grains and then sinter to high density compacts. Here the compaction of a slurry containing BPSCCO flakes are utilized to pack the flakes one over the other. During sintering these thickly packed grains attain good contact and the grains preferentially grow along c-axis. An aspect ratio of 30 is attained by this method.

Third and very important method is the combination of both PSP and PST to derive a compact with microstructural orientation. Grains of 50 μm and above are obtained by zone melting on already aligned compact. This helps to reduce the high angle grain boundaries in the compact. An aspect ratio of more than 60 is attained in this case.

Thus the application of novel techniques like zone melting, colloidal filtration and their combination could result in BPSCCO bulk compacts with a-b oriented grains with very large aspect ratio. In short, from the synthesis of BPSCCO powders till the post sintering procedures have been studied in detail and reported.

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CHAPTER VI

COMPARISON OF THE RESULTS OF THE STUDY ON ALUMINA, ALUMINIUM TITANATE AND BPSCCO POWDERS DERIVED BY SOL-GEL PROCESS

The three systems of different complexity were studied with respect to the synthesis methods and parameters. While alumina and aluminium titanate were prepared through nano dispersed sols, the BPSCCO was prepared by both organic polymer precursor and microwave techniques. The emphasis has been on the effect of formation conditions of the gel as the powder as well as sintered properties of the ceramic.

1. Alumina and aluminium titanate system

The salient results obtained in the case of alumina is presented in Table 6.1. Two important observations made in the results are,

(i) The thermal decomposition of the boehmite gel is extremely important in deciding the sintered properties of alumina. While the alpha alumina formed above 1100°C attains a sintered density of 3700 kg/m^3, the transition alumina phase obtained at about 1000°C attained a density as high as 3900 kg/m^3.

(ii) Pre-treatment of the boehmite gel by selected solvents

Table 6.1 Comparison of green and sintered densities of alumina powders calcined at various temperatures

Calc. temp. (°C)	Green density (kg/m^3)	Average (kg/m^3)	Sintered density (kg/m^3) 1600°c/2h	Average (kg/m^3)
200	1190 1300 1200	1230	3270 3290 3330	3296
400	1430 1310 1400	1380	3400 3470 3480	3450
600	1550 1360 1760	1400	3490 3550 3500	3513
800	1460 1380 1390	1410	3720 3695 3702	3700
1000	1580 1620 1420	1540	3903 3890 3907	3900
1200	1500 1720 1760	1660	3780 3703 3700	3720

disturb the structure and also influence the pore elimination during sintering (Table 6.2). A comparative study of specific surface area is provided in Fig.6.1 where the isopropanol treated powder shows higher specific surface area. While the sintered density as high as 3800 kg/m^3 is obtained for boehmite gel treated with isopropanol but the non treated gel attained only 2800 kg/m^3 at 1450°C over a soaking period of 4 h. Figure 6.2 shows the comparative study of sintered densities of alumina powders obtained from boehmite after various treatments. Spray drying of sol could produce particles with spherical morphology and with narrow size distribution.

Similarly, in the case of aluminium titanate, the phase formation is lowered only marginally both by washing with solvents as well as by preferentially subjecting to microwaves. However, the specific surface area is higher for the aluminium titanate powder derived from the microwave dehydroxylated gel. The inherent problem of aluminium titanate to undergo microcracking during cooling appears to have masked the effect of the solvent treatment and microwave drying. This is clear from the sintered densities provided in Table 6.3. In all the cases, the formation of aluminium titanate has been through solid state reaction between alpha alumina and rutile and this could be another reason for the absence of remarkable changes in the properties of aluminium

Table 6.2 Comparison of characteristics of alumina powders obtained from boehmite gel prepared under various conditions

Characteristics	Al_2O_3 powder from gels			
	Non-treated	Isopropanol treated	Acetone treated	Spray dried
Loss at 30-250°C	15%	5%	10%	7%
Loss at 250-300°C	40%	25%	30%	30%
Loss at 300-500°C	5%	Nil	5%	2%
α-Al_2O_3 formation temperature (°C)	1120	1090	1100	1120
Sp. surface area (1000°C)	54	65	46	38
Morphology (1000°C Cal.)	equiaxial non-spherical average 2um	equiaxial non-spherical average 1um	-	Spherical 1 um
Sinterability (1450°C)/4 h (kg/m^3)	2800	3800	3600	3500

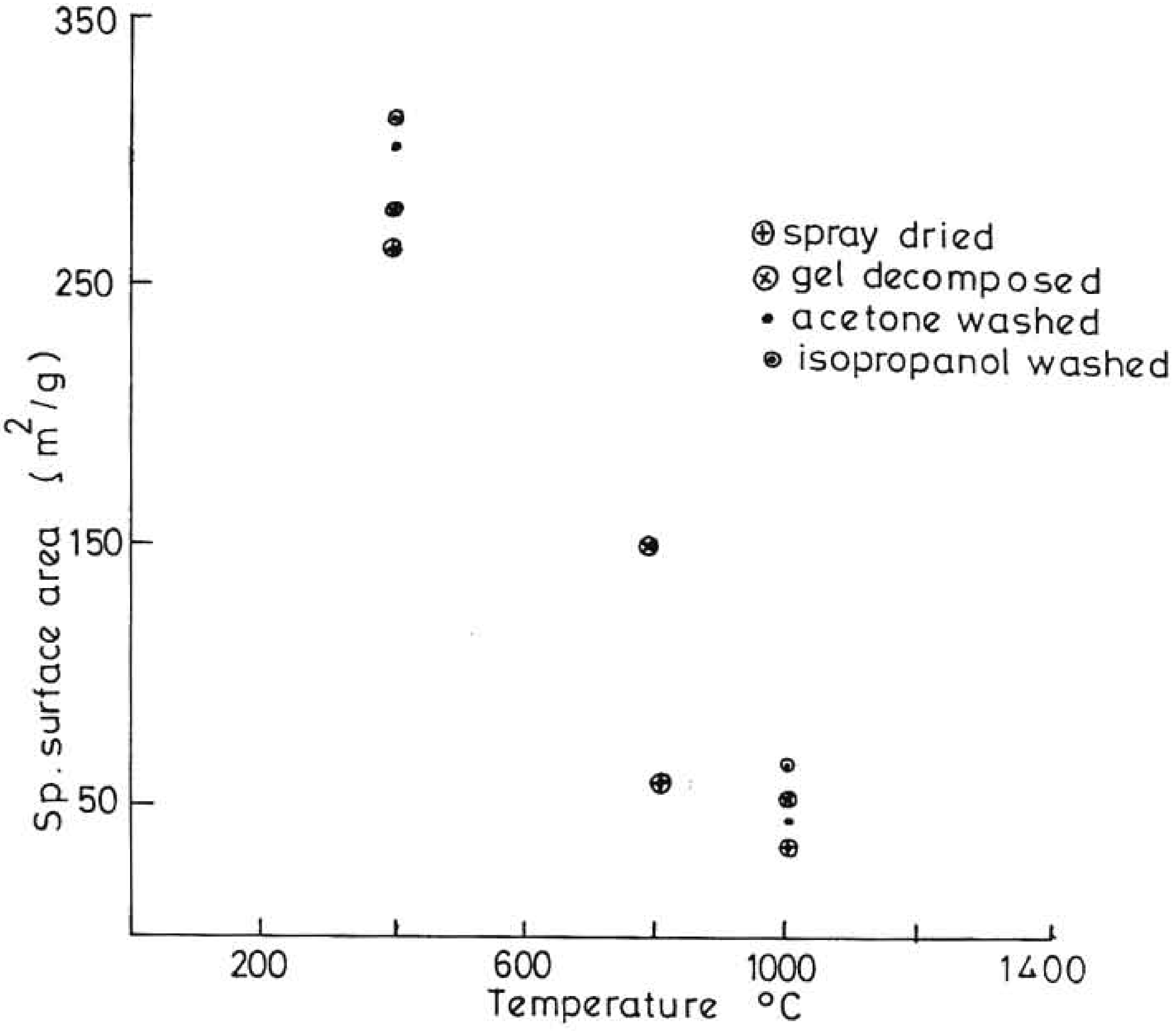

Fig. 6.1 Comparison of surface area values

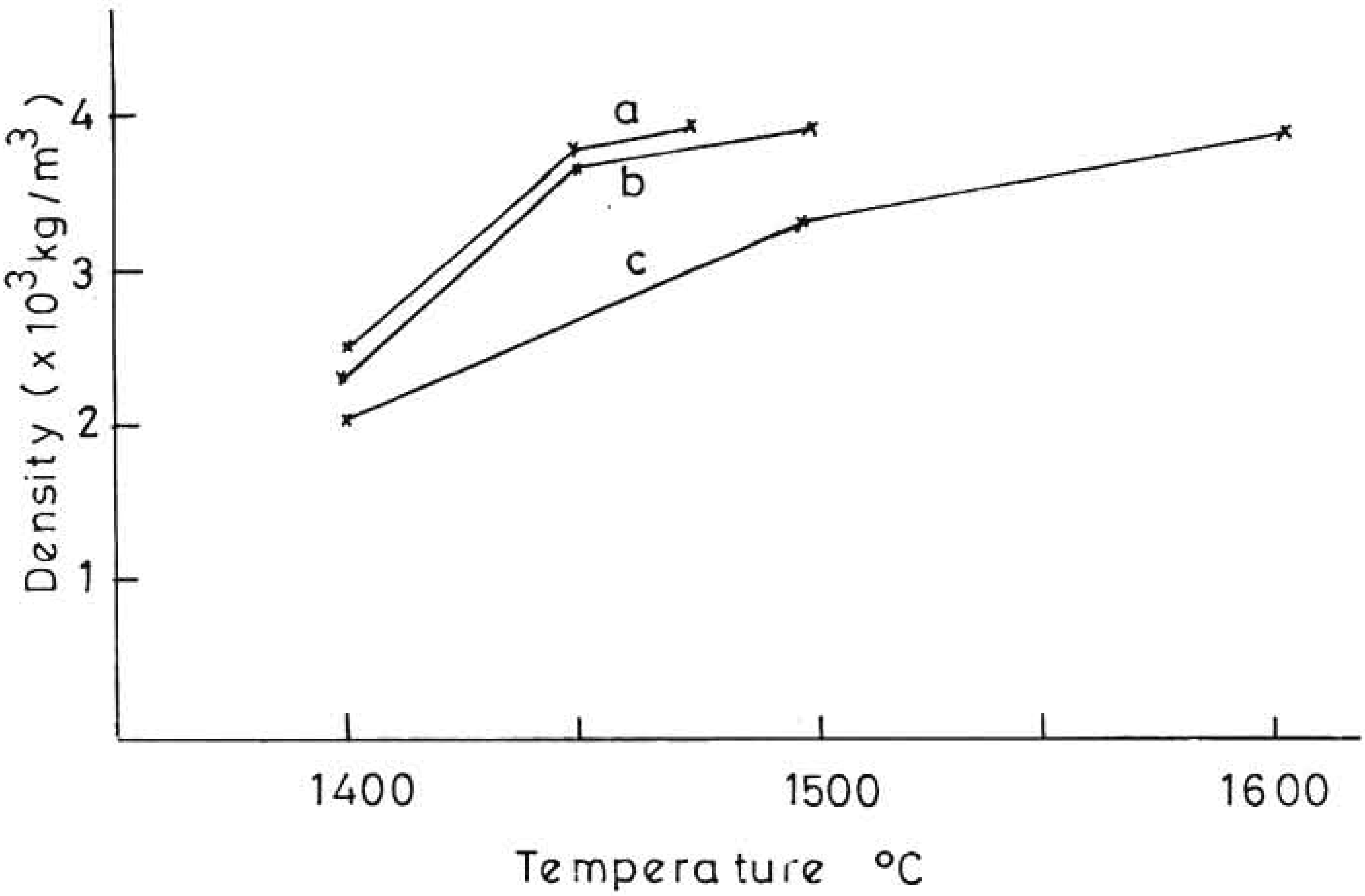

Fig. 6.2 Comparison of sintered densities of alumina samples from
(a) isopropanol and (b) acetone treated gel
(c) nontreated gel.

Table 6.3 Characteristics of aluminium titanate powders

Characteristics	Aluminium titanate powder from			
	Transparent gel	Isopropanol washed	Gel devoid of anions	Microwave dried
1. AT formation temp. (°C)	1375	1350	1347	1365
2. Sp. Surface area of AT powder (m^2/g)	0.5	0.8	0.6	1
3. Average particle size (μm)	2	1.8	2	2.3
4. Green density (kg/m^3)	2100	2030	2018	2020
5. Sintered density (kg/m^3)	3555	3410	3510	3420

titanate prepared through different treated gels. However, formation characteristics of aluminium titanate under different rate of heating and under various atmospheres have not been carried out in the present case and in such cases, the transition alumina phase could probably influence the formation and densification of aluminium titanate.

<u>Publications out of this study:</u>

1. Dependence of calcination conditions of boehmite on alumina particulate characteristics and sinterability. Materials Letters 19(5) 237-41 (1994).
2. Characteristics of alumina powders prepared by spray drying of boehmite sol. J. Am. Ceram. Soc., 77(6) 1597-1600 (1994).
3. Aluminium titanate powder synthesis via thermal decomposition of transparent gels. J. Am. Ceram. Soc., 74(10) 1807-10 (1991).
4. Gelation characteristics of aluminium titanate precursor sols in different solvent media. Ceramic International, 18, 69-72 (1992).

2. Bi-based superconductor

The acrylic acid method as well as microwave synthesis with the presence of an activator are basically gel precursor route. Essentially the change has been only in the nature of decomposition of the gel precursor. The comparative results presented in Table 6.4 show that there is different influence on the gel decomposition method on both the formation of the high-Tc phase as well as the densification characteristics. The particle size of the gel derived powders are smaller than that contain in oxide/carbonate derived powders. The use of microwave and the activator to produce BPSCCO powder are newly introduced in this study.

A slurry forming technique is used in the case of BPSCCO to prepare a-b plane oriented bulk compact. The slurry compact after zone melting resulted in well oriented grains with aspect ratio more than 50.

Publications out of the study:

1. Bi-Pb-Sr-Ca-Cu-O superconductor through decomposition of acrylate polymer precursor gels. Br. Ceram. Trans. J., 91(5) 120-23 (1992).
2. Pre-sintering processing of Bi-based bulk superconductor through viscous processing. Br. Ceram. Trans. J., 92(6) 246-50 (1993).
3. Texture development in Bi-Sr-Ca-Cu-O superconductor through integrated pre- and post- sintered processing

Table 6.4 Characteristics of BPSCCO powder

Characteristics	Acrylate	Microwave	Solid state
2223 formation time (h) (96% 2223 phase) at 845°C	35	30	120
Average particle size (um)	6-8	8	-
Morphology	Flaky	Flaky	Flaky
Green density	53%	50%	50%
Sintered density (845°C/12 h)	96%	94%	94%

(IPSP) (communicated to Am. Ceram. Soc. Bull.).

Thus the whole results of the total study show that while sol-gel route is in general acceptable for the preparation of ceramic oxide, adequate modifications are necessary depending on specific cases. While there is remarkable influence of the solvent treatment and calcination conditions of gel in boehmite system, similar routes are not appreciable in aluminium titanate. On the other hand, the gel decomposition approach is very significant in the case of BPSCCO.

SUMMARY

Ceramics used in high technology applications require fine grained microstructure with controlled compositional levels and these objectives are achieved from fine unagglomerated powders. Wet chemical methods based on sol-gel route are generally used to prepare the powders of required quality. The present study is based on the same for the preparation of fine ceramic powders coming under three systems such as a single component alumina, a binary aluminium titanate and a multicomponent Bi-based superconductor.

Boehmite (AlOOH) prepared by the hydrolysis of aluminium nitrate was converted to xerogel by drying sol. The evolution of oxide phase after calcination over a temperature range 400-1200°C was studied by X-ray diffraction. Gamma alumina is formed at around 400°C. A mixture of gamma, delta, theta and alpha alumina is formed at around 1000°C. This transition aluminas get converted to alpha alumina only above 1100°C in this case. The powder calcined at 400°C showed very high specific surface area of 274 m^2/g which decreases to 10 m^2/g as calcination temperature increased to 1200°C obviously due to aggregation and grain coarsening. Boehmite calcined at 1000°C showed maximum sintered density (3900 Kg/m^3) after a 2 h soaking at 1600°C compared to samples obtained after calcination at various other temperatures. Treatment of the gel with organic hydrophilic solvents to remove the solvated

water from the gel structure resulted in less agglomerated alumina powder which sintered to higher densities ($\approx$96%) at 1450°C.

Aluminium titanate precursor gel was formed from boehmite sol and acetic acid stabilized titanium isopropoxide. The conditions for attaining a transparent xerogel was optimized by controlling the concentrations of acid, water, solvent and alkoxide and drying conditions. Thermal analysis of the gel indicated aluminium titanate phase formation at around 1370°C. The gelation studies of aluminium titanate precursor sol was carried out using light scattering technique (Nephelometry) from different solvent systems. Water based sol took around 30 h to complete the gelation while the isopropanol based one gelled within 8 h. The variation of gel structure by different solvent treatment affected the formation temperature of aluminium titanate. The removal of anionic impurities from the gel by washing registered a lowest aluminium titanate formation temperature of 1347°C. The precursor gel was microwave dried and was found to result in low temperature aluminium titanate phase formation (1363°C) since the mechanism of removal of solvated water from the gel pores is different from that during usual oven drying conditions making the precursor more reactive.

Bi-based superconductor powder has been synthesised by involving acrylic acid as the gel former. The use of acrylic acid primarily prevents the precipitation of Bi-hydroxide in addition to aid the gel network formation. The calcination of the precursor gel at 845°C for 35 h produced a powder containing 95% 2223 phase and that for 50 h produces XRD pure 2223 powder. Decomposition of metal nitrates in presence of microwave active gel former such as starch was also done in a domestic microwave oven to prepare BPSCCO precursor powders. The precursor is formed within as short as 4 minutes which converted to 2223 phase within 30 h of calcination at 845°C. The 2223 grains thus obtained were flaky in morphology. It is observed that the gel initially got converted to spherical particles on calcination which later formed flaky grains. Although both the powders sinter to higher densities, the acrylate precursor derived one has resulted in slightly higher density value at similar conditions.

An attempt for processing BPSCCO bulk compacts for enhanced texture and grain alighment was done through techniques such as slurry processing as presintering processing (PSP) and zone melting refining as post sintered treatments (PST). Finely, integrated processing of PSP and PST resulted in highly a-b plane aligned grains of BPSCCO with very large aspect ratios.

The salient results of the total work can be summarised as follows:

1) Washing of boehmite gel with isopropanol can yield alumina powders which can sinter to high densities at 1450°C. The

calcination of boehmite gel at 1000°C resulting in a mixture of transition aluminas is found to be the right starting powder for densification.

2) Use of solvents influences the aluminium titanate precursor gels such that the formation temperature of aluminium titanate is decreased by 25°C in the case of isopropanol. Similarly, microwave drying of the precursor gels can result in low temperature aluminium titanate formation (1363°C).

3) Highly reactive precursors for BPSCCO is produced by acrylate gel decomposition and microwave decomposition of the starting nitrates. Higher sintered densities are obtained for acrylate gel derived powders over microwave derived ones. An integrated presintering processing and postsintered treatment of BPSCCO has been found to result in a well oriented BPSCCO high density bulk compacts.