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SYNTHESIS AND SINTERING CHARACTERISTICS OF $SrTiO_3$ POWDER PREPARED BY COPRECIPITATION PROCESS

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ABSTRACT

A detailed study on the synthesis and characterisation of submicrometre sized single phase $SrTiO_3$ powder by an oxalate precipitation technique has been carried out. Sintering studies have shown that the generated fine powders can be densified to near theoretical density by heating at 1350°C for 1h. The variation of shrinkages of STO powder compacts shows the onset of sintering at 1100°C and accelerated densification and grain growth after 1250°C. The apparent activation energy for sintering is estimated to be 240 ± 2.4 kJ/mole. The sintered pellets can also be used for depositing polycrystalline superconducting YBCO films.

KEY WORDS: SrTiO3, PEROVSKITE, POWDER, SINTERING AND SUBSTRATE

1. INTRODUCTION:

The tremendous growth of electronic industries during last few decades has directed the extensive research activities on the ferroelectric perovskite materials for their various applications in multilayer capacitors, piezoelectric components and microwave appliances. The research activity on $SrTiO_3$ (STO) is increased only during last several years for application as substrate and microwave sensor. It is well known that fine powder with less than 1 μm particle sizes is required for the fabrication of good ceramic bodies and several processes are available for the synthesis of these fine powders. Amongst them, precipitation [1, 2] and sol-gel processes [3, 4] are noteworthy. The economically viable oxalate-precipitation route has been widely investigated [5] but the optimisation of the process to avoid the leaching out of the cations is a great problem. Though extensive literature is available on various aspects of these materials, studies on sintering behaviour of these materials are a few [6,7].

Here, in this paper, synthesis of submicrometre sized STO powder by oxalate precipitation technique and the sintering characteristics these fine powders have been discussed.

2. EXPERIMENTAL:

Powder Preparation:

STO powder was prepared by Sr-Ti-O-Oxalate precipitation method from the starting materials of $SrCl_2$ [99%], $TiCl_4$ [99%] and oxalic acid [99%]. In this process, $TiCl_4$ was added slowly to the distilled water at 0°C. Temperature of the solution was maintained by adding liquid nitrogen that also helped in preparing a clear solution of $TiOCl_2$. It had been observed that inert nitrogen atmosphere created by the boiling of liquid nitrogen prevents the formation of $Ti(OH)_4$. The Ti content of the solution was estimated by the weight chemical analysis. Appropriate amount of $SrCl_2$ solution was added to the clear solution of Ti-chloride so that Sr:Ti ratio was 1:1. The mixture of Sr and Ti chloride was added drop by drop to the oxalic acid solution in doubly distilled water. The oxalic acid ratio was taken in excess so as to avoid the leaching out of the metal oxalates. During addition of the oxalic acid solution become turbid and a whitish precipitate

was obtained after more addition of chloride solution. The acid solution was stirred by a magnetic stirrer during chloride addition and stirrer was continued for 30 minutes after the completion of solution addition. The precipitate was washed by water and alcohol and then filtered by using a buchner funnel. The filtrate was analysed for the leaching out of Sr and Ti from the solution. The absence of metal ions in the filtrate indicated the complete precipitation. The precipitate was oven dried at 150°C and calcined at 900°C for 1h. The detail of the powder preparation technique is schematically shown in figure 1.

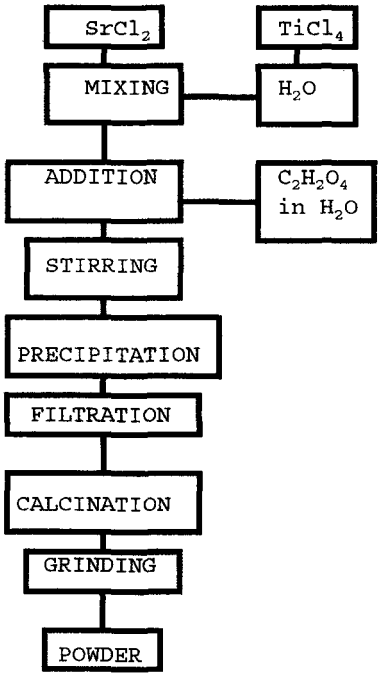


Fig. 1. Schematic of the powder preparation process.

The calcined powder was characterised by using X-ray diffractometer (Phillips PW 1540), transmission electron microscope (TEM -Phillips CM 12) and particle size analyzer (Joyce Loebl). X-ray diffraction (XRD) was used for the phase analysis of the powders by using Ni filtered CuKα radiation (λ = 0.15406 nm). TEM was used for the investigation of ultrasonically dispersed particulate supported on 100A thick carbon coated copper grids.

Sintering Studies :

The calcined powder was pelletized in the form of 2.5 cm diameter pellets by a pressure of 12.4 MPa. The green densities of the pellets were measured from the weight and dimensions of the samples and observed to be 3.0 $g.cm^{-3}$. The green pellets were sintered for 1h at various temperatures ranging from 1100°C to 1350°C. The apparent densities of the sintered samples were measured by Archimedes principle with an accuracy of ± 2%. The true densities of the samples were also measured by liquid penetration technique where liquid was allowed to penetrate into the open pores. The dimensional shrinkages of the samples were also studied after sintering. Gold coated fractured or polish etched surfaces of the sintered pellets were investigated by a scanning electron microscope (SEM). Aqueous solution of nitric acid (0.1%) was used as the etchant.

Y-Ba-Cu-Oxide (YBCO) superconducting films were deposited by an rf magnetron sputtering system on polished STO substrates (sintered at 1350°C) and post annealed in flowing oxygen at 900°C for 1h. The films were deposited at a pressure of 1.8^{-1} torr and at a rf power of 40 watt. The superconducting properties of the annealed films were characterised by using a close cycle He cryo-refrigerator (APD-Cryogenics USA). Resistivities of the samples were measured by Vender Pow method.

3. RESULTS AND DISCUSSION:

Powder Charactersation:

From the detailed X-ray diffraction analyses, the white precipitate is observed to be Sr-Ti-O-C_2O_4, which decomposes to yield single phase $SrTiO_3$ powder after calcination at 900°C. A typical XRD pattern of the STO powder calcined at 900°C for 1h is shown in figure 2. The XRD analyses indicate the absence of impurity phases of TiO_2 and Sr related compounds in the powder. This suggests that the impurity phases even if present in the powder their volume percentages are less than 5%. TEM images of the powders indicate the particle sizes are less than 1 μm [Fig. 3]. The average particle size obtained from the particle size distribution [Fig. 4] is observed to be 0.8μm, which also tallies with the TEM observations indicating the particles are weakly agglomerated.

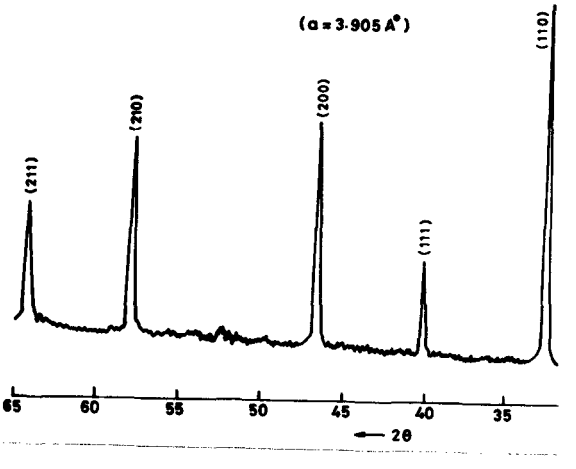


Fig. 2. XRD pattern of the $SrTiO_3$ powder calcined at 900°C for 1h.

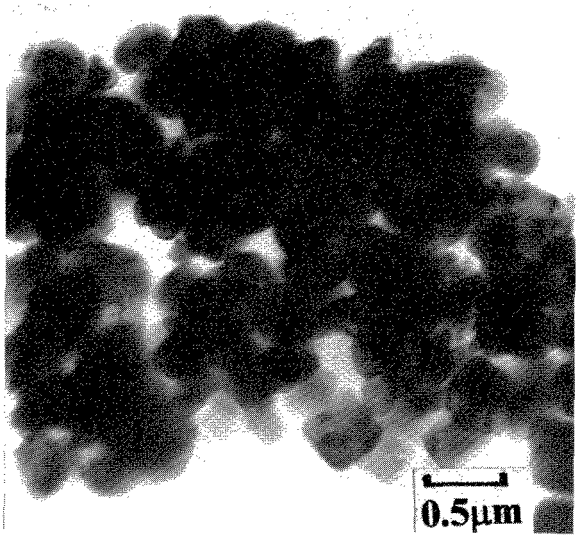


Fig. 3. Transmission electron micrograph of the $SrTiO_3$ powder.

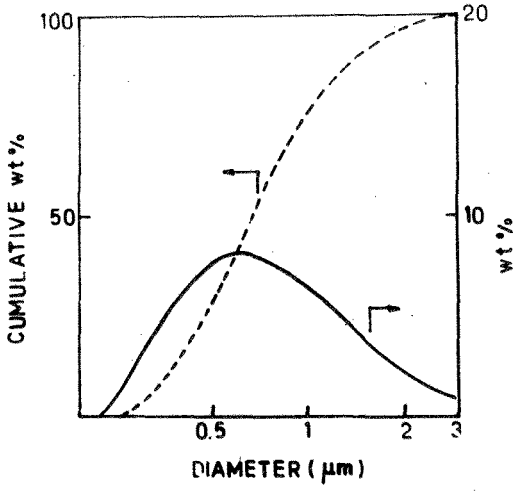


Fig. 4. Particle size distribution of the calcined $SrTiO_3$ powder.

Sintering Characteristics :

The sintering or densification of compacts is always associated with some amount of dimensional shrinkages during the course of heating at elevated temperatures. Thus study of shrinkage characteristics of the compacts is a useful method for understanding the sintering as well as the sintering mechanism operating in the system. From the shrinkage behaviour of STO powder compacts, it has been observed that the shrinkage starts at 1100°C and accelerates after 1250°C [Fig. 5a].

In ceramics, three types of densities: apparent density, true density and theoretical density are known and all these densities have useful significance to understand the densification behaviour. Both the open pores and close pore volumes are included with the materials volume to calculate the apparent density of the specimens, whereas, only the close pore volume is included with the material volume to obtain the true density. The theoretical density is calculated from the molecular mass and the unit cell volume obtained from the X-ray diffraction analyses.

The densification behaviour of the powder compacts shows that the apparent densities of the samples increase with the temperatures and reach a maximum density of 5.05 $g.cm^{-3}$ at 1350°C [Fig. 5b] whereas true densities initially increase with the opening up of the pores and then decrease due to pore closure and finally increase during elimination of closed pores at the final stage of sintering [Fig. 5c].

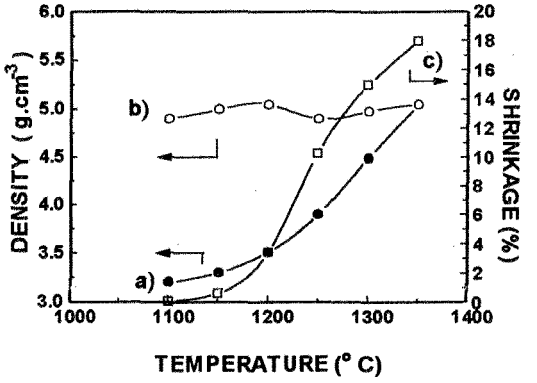
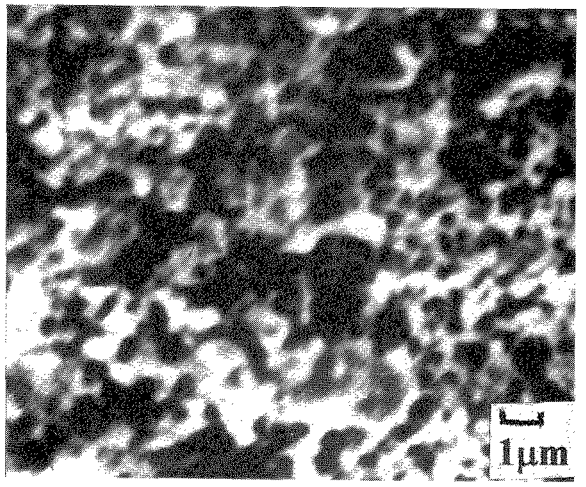
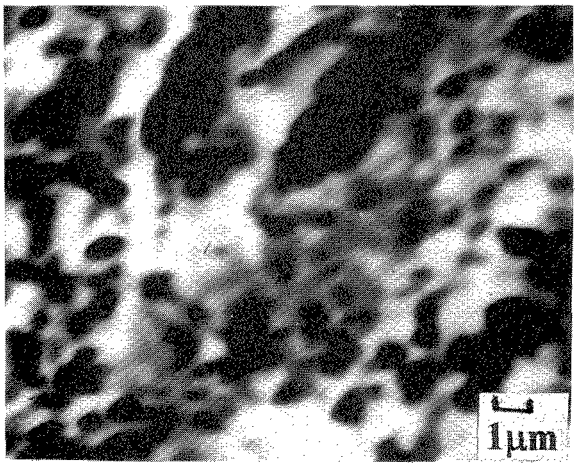


Fig. 5. Variation of linear shrinkage (a), apparent density (b) and true density (c) of the $SrTiO_3$ powder compacts with sintering temperature.

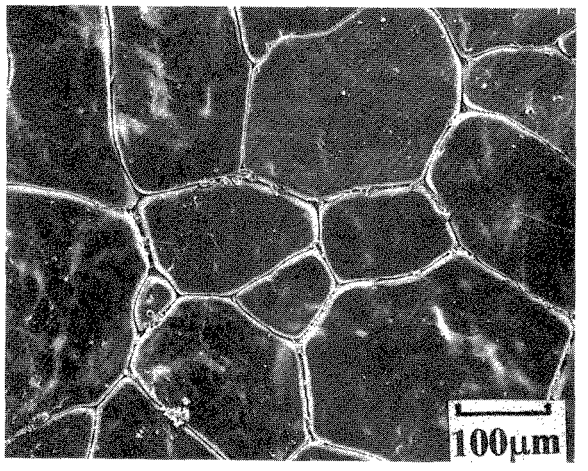
The SEM images of the gold coated fractured or polished etched surface is given in figure 6 (a, b, c). SEM image of the pellet sintered at 1150°C (Fig. 6a) shows the presence of submicrometre sized grains and formation of pore channels. The pore channels helps in more liquid penetration that decreases the close pore volume and as a result increases the true density of the samples. The formation of round pores is observed at 1250°C (Fig. 6b) and the rounding of pores increases close pore volume that decreases the true density as has been shown in figure 5b. From the SEM studies, the grain growth has also been observed to be prominent after 1250°C. Complete elimination of pores and formation of close packed structure is observed in the sample sintered at 1350°C (Fig. 6c). The elimination of pores also indicates the maximum densification of the compacts.



(a)



(b)



(c)

Fig. 6. SEM images of the $SrTiO_3$ pellets sintered for 1h at: a) 1100°C, b) 1250°C and c) 1350°C.

The densification behaviour can be expressed by using a simplified sintering theory [8] as,

$$dg/dt = (k/T)\, D_o e^{-Q/KT}$$

where, dg/dt is the rate of densification, k is the rate constant, T is the temperature, D_o be the diffusion constant, Q is the activation energy for sintering and K is the Boltzman constant.

By plotting ln(T x dg/dt) with the inverse of temperature the activation energy has been calculated to be 240±2.4 kJ/mole [Fig. 7]. The estimated activation energy has been observed to be in agreement with that of Chang et al. [6], where they have studied the sintering of (Sr-Ba)TiO_3 powder. It has been reported that the segregation of Ti^{+4} clusters retarded the formation of necking process that is essential for sintering of STO powder compacts [7]. Here we have not found such segregation of TiO_2 at the grain boundaries possibly due to better homogeneity in chemically synthesised powders.

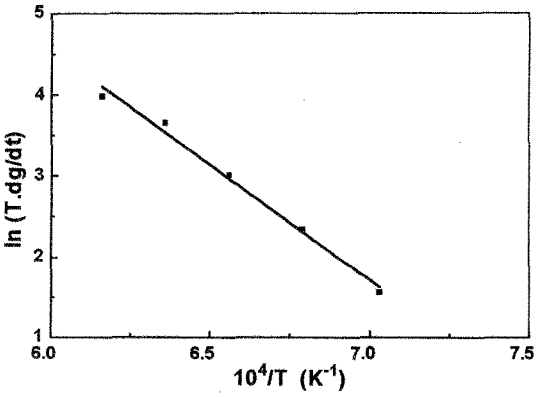


Fig. 7. Arrhenius plot for the estimation of activation energy for sintering of $SrTiO_3$ powder compacts.

Post annealed oxygenated YBCO films on the STO pellets are also observed to be polycrystalline in nature. A typical YBCO film deposited on STO substrate and post- deposition annealed at 900oC for 1h in flowing oxygen atmosphere is shown in figure 8. The films are observed to be metallic and exhibit a broad superconducting transition with a T_c onset at 92 K. The broad transition is due to the presence of a large number of weak links in the ploycrystalline films and diffusion of Ba into the STO substrates which resulted in the formation of Ba deficient YBCO films.

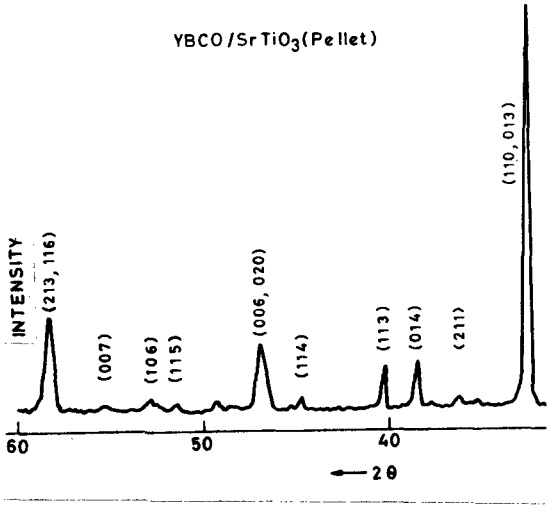


Fig. 8. XRD patterns of YBCO films deposited on STO substrate and post-annealed at 900°C for 1h in air atmosphere

CONCLUSIONS:

Submicrometre sized single phase $SrTiO_3$ powder is prepared by oxalate precipitation technique. The powders can be densified to near theoretical density at 1350°C and the apparent activation energy for sintering is estimated to be 240±2.4 kJ/mole. The shrinkage behaviours of STO powder compacts indicate that the onset of sintering at 1100°C and accelerated densification after 1250°C. The sintered pellets can also be used for depositing superconducting YBCO films. More studies are required to improve the superconducting properties.

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