Synthesis and sintering characteristics of Y-Ba-Cu-oxide superconductors


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Abstract

Y-Ba-Cu-Oxide (YBCO) powder were prepared by three different techniques and the isothermal sintering characteristics of the synthesized powder were systematically investigated using a thermo-mechanical analyzer (TMA). Expectedly the apparent densities of the sintered samples increased with the decrease of particle sizes of the synthesized powder due to high specific surface energy. The nano-sized powder generated by a chemical pyrophoric reaction exhibited excellent sinterability than the powder synthesized by either the conventional ceramic process (CCP) or the co-precipitation process (CP). The variation of apparent activation energies for sintering \(Q\) and sintering kinetic parameter \(n\) with the change of particle sizes of the green compacts indicated differing nature of mass transport phenomena operating in the system during sintering. The apparent activation energies for sintering were estimated from the respective Arrhenius plots.

Keywords: YBCO, Superconductor, Synthesis, Sintering, Activation energy

1. Introduction

Extensive research activities are being carried out on high temperature superconducting \(YBa_2Cu_3O_7\) (123) for its high critical transition temperature \(T_c = 92\) K and high critical magnetic field \(H_{c2} = 120\) T. Like any other ceramic material, high temperature superconductors also require phase pure powder as the starting raw materials to yield good specimens. For this, various synthetic strategies have been employed to prepare single-phase Y-Ba-Cu-Oxide (YBCO) powder with Y:Ba:Cu = 1:2:3 stoichiometry. Several important techniques that have been used extensively for this purpose are solid-state synthesis [1,2], co-precipitation [3-5], sol-gel process [6,7], alkal flux process [8], combustion synthesis [9], spray drying [10], freeze drying [11], aerosol [12], and pyrophoric process [13]. Synthesized powder are normally sintered by pressureless solid-state sintering technique [14-16], liquid phase sintering technique [17], and hot isostatic pressing (HIP) technique [18] to yield superconducting specimens. However, all these sintering techniques suffer due to various reasons. For example, the existence of high vapor pressure of Ba and Cu above 1173 K [19,20] results in composition fluctuation in the samples during pressureless sintering. Decomposition of YBCO (123) to Ba-cuprate, CuO, and 211-phases takes place during liquid phase sintering and at high pressure and high temperature sintering using HIP. Composition, fluctuations, and decomposition lead to poor transport properties of the sintered pellets. Though voluminous research works are being carried out on various aspects of these superconductors, very little is known about the sintering kinetics of these materials particularly on the role of synthetic conditions.

In our earlier communication, a comparative study on the synthesis of YBCO powder by different techniques were reported [21]. However, the sintering kinetics was not being studied. In this paper, the synthesis and sintering characteristics of YBCO powder prepared by three different processing routes are carried out to investigate the role of synthetic condition on the sintering characteristics of YBCO superconductors. Here, the pressureless sintering process is studied because of its simplicity and to avoid the complex sintering kinetics of the other techniques. Single step of milling and calcination is used to minimize the processing parameters.
2. Experimental

2.1. Powder preparation

YBCO powder with nominal composition of YBa$_2$Cu$_3$O$_x$ was prepared by three different techniques namely, conventional ceramic process (CCP), co-precipitation process (CP), and pyrophoric process (PP). Starting materials of Y$_2$O$_3$ (99.99%) (Indian Rare Earth Ltd.), Ba(NO$_3$)$_2$ (99%) (Merck India) and Cu(NO$_3$)$_2$·3H$_2$O (99.5%) (Merck India) were used in the present investigation. The processes are discussed below.

2.1.1. CCP

In this process, appropriate amounts of the chemical constituents were taken in a polypropylene bottle and dry milled for 24 h (without balls) and precursor mixture is prepared. Thermal analysis (TG and DTA) of the mixed constituents was carried out at 10K/min in air by a thermal analyzer (Stanton, UK). The milled mixture is subsequently calcined at 1173 K for various periods in a platinum crucible to yield the YBCO powder and the calcined powder was characterized.

2.1.2. CP

In this technique, a simultaneous coprecipitation of Y, Ba, and Cu oxalates by precipitating in ethanol:water (70:30) medium and using triethylammonium-oxalates (TEO) as the precipitating agent under controlled pH conditions was adopted. Dissolving the oxides in nitric acid and evaporating the solutions to dryness yttrium nitrate was prepared. Stock solutions of Ba(NO$_3$)$_2$ [0.25 M], Cu(NO$_3$)$_2$ [0.5 M], and Y(NO$_3$)$_3$ [0.5 M] were prepared by dissolving the corresponding metal nitrates in distilled water. The precipitating agent, TEO ([C$_2$H$_5$N]$_3$C$_2$O$_4$ [0.25 M]) was prepared by dissolving triethylamine (TEA) and oxalic acid (2:1 mol ratio) in ethanol. After mixing the metal nitrate solutions (Y:Ba:Cu = 1:2:3) in a beaker, the pH of the

Fig. 1. Flow diagram for the preparation of YBCO powder by co-precipitation process.
solution was adjusted to 4.0 by 5% solution of TEA in 70:30 ethanol:water mixtures. Appropriate amount of TEO was added to the mixed nitrate solutions so that a ratio of $Y:Ba:Cu:TEO = 1:2:3:6$ was achieved. Bluish colored precipitate appeared. The solution was stirred for 30 min and then filtered. The crystalline precipitate was dried in an oven at 393 K. Thermal analyses, TG/DTA of the dried precipitate was carried out at 10 K/min by thermal analyzer (Stanton, UK). The dried precipitate is then calcined at 1173 K in air for various periods to yield the YBCO powder. The detail of the process is given in Fig. 1.

2.1.3. PP
A pyrophoric chemical reaction is utilized to yield ultrafine powder of multicomponent ceramic materials. In this process [13], aqueous solutions of metal nitrates were mixed in the mole ratio of $Y^{3+}:Ba^{2+}:Cu^{2+} = 1:2:3$. Calculated amount of citric acid, was added to the above solution and the resultant solution was neutralized to pH 7 by adding ammonia. The solution in the beaker was dried by concurrent heating from the top by an infrared lamp and by a pit furnace preheated at 523 K at the bottom. Whence the solution was dried, a blue colored mass was obtained, which on continued heating suddenly foamed up and caught fire leaving a black finely dispersed powder in the form of low density sponge. The as-prepared powder was then calcined at 1173 K for various periods to yield YBCO powder and the calcined powder was characterized. The detailed process is given in a flow sheet (Fig. 2). A thermal analyzer (Stanton, REDCROFT, UK) is used to investigate the decomposition behavior of the dried blue colored mass.

2.2. Powder characterization
Particle sizes of the calcined powder were estimated microscopically using either optical or transmission electron
microscope (TEM) (Philips CM 12). The histograms were created from the micrographs using line intercept method. X-ray diffraction (XRD) analysis of the calcined powder were studied for the phase analysis. Phillips PW 1840 X-ray diffractometer with Ni filtered Cu Ka radiation was for XRD studies.

The compressibility of the powder was investigated by pressing equal amount (5 g) of the powder into the form of 2.54 cm diameter pellets by applying various loads. Double acting press was used in the present investigation. The variation of green densities with the amount powder is also investigated at constant load. Green densities of the pellets were estimated from the volume and mass of the pellets. The apparent densities of the pellets sintered at 1173K for 1 h were measured using Archimedes principle of liquid immersion technique. The accuracy of the density measurement was estimated to be ±2% in the present investigation. The effect of the amount of mass pressed was also studied by palletizing under constant load of 12.4 MPa.

2.3. Sintering studies

Before the sintering studies, the calcined powder obtained from the CCP, CP, and PP routes were compressed by applying a load of 3 MPa to increase their compressibility and then crushed to yield the powder. The pellets were then fabricated by pressing 6 g of the crushed powder under a constant load of 12.4 MPa. The pellets were then cut into rectangular shapes (~5 mm x 4 mm x 4 mm) to study the sintering characteristics. The green densities of the rectangular pieces were also measured by the Archimedes principle. Similarly the sintering specimens were also fabricated using the powder prepared by CCP and CP routes.

The sintering studies were carried out in argon atmosphere, as better densification of YBCO superconductors has been reported in low partial pressure of oxygen [22,23]. SHIMADZU DT-30 thermal analyzer system with quartz dilatometer (TMA/30) was used to study the sintering characteristics of the green compacts. Details of the experimental setup are schematically shown in Fig. 3. The change in length could be measured with an accuracy of ±5 (im and the temperature of the furnace could be controlled within ± 1K. Since the furnace had a larger volume compared to the YBCO samples, it was expected that uniform temperatures would be maintained throughout the samples. A thermocouple was also placed below the sample holder, which showed the temperature variation of ±1K. Platinum plates (0.05 mm thick) were used as barrier between the sample and quartz sensor rod on top and sample holder at the bottom to avoid interaction between the quartz and YBCO. Isothermal sintering studies at different temperatures were carried out for all the samples by soaking for 1 h while the heating rate was maintained at 10K/min. The cylindrical test samples had a smaller dimension of height as compared to the base dimensions. The push rod having a mass of 20 g was rested gently on the sample. The weight of the rod is accounted for a load of 138 Pa. This load is so low that it discounts the possibility of any creep deformation during sintering.

Apparent densities of the sintered pellets were measured using Archimedes principle of liquid immersion technique with an accuracy of ±2%. Ethylene glycol, which is having high viscosity, was used for the density measurements. X-ray diffraction, scanning electron microscopy (SEM), and optical microscopy of the samples at various stages of sintering were performed. Gold-coated fractured surface of the samples were analyzed using SEM-CAM SCAN (UK). Superconducting properties of the samples sintered at 1233 K for 1 h in flowing argon atmosphere were also measured after oxygenation at 773 K for 20 h.

3. Results and discussion

3.1. Powder preparation and characterization

3.1.1. CCP

Thermal analysis (TG and DTA) of the mixed powder obtained after milling of the respective constituents in the CCP process indicated the melting of Ba(NO3)2 with a strong endothermic peak at 783 K (Fig. 4), which subsequently decomposed at 863 K. The observation of a small endothermic peak below 673 K was due to loss of chemically bonded water or dissociation of hydroxides. From the TGDTA plots it was also evident that the formation of YBCO started at 1123K. The detailed X-ray diffraction analyses of the powder calcined at 1173K showed the increase of 123-phase formation with the calcination periods and a maximum amount of 123-phase formation was observed after single step calcination of 12 h. The powder calcined at 1173 K for 12 h was found to be tetragonal and small amount of unreacted phases of 211 could be detected in the sample (Fig. 5). It is well known that the formation
of single-phase powder by the CCP requires several times of calcinations and grinding at 1173 K. As discussed earlier, in this investigation, only single step of processing, which include mixing, calcination and grinding was used to yield the YBCO powder for the sintering study. We deliberately used the single step calcined and ground powder for sintering study with the assumption that the presence of unreacted Ba-Cu-oxide phases will facilitate the liquid phase sintering and the phase formation will take place during sintering. From the optical microscopy study, the powder generated by CCP route were found micrometer in size (Fig. 6). Though these particles appeared to be spherical during optical microscopy studies, whereas, the high magnification studies using SEM and TEM revealed the irregular shapes. From the histogram (Fig. 7a), average particle size of the powder is estimated to be 1.07 μm. The particle sizes could not be reduced below the micron size due to inherent problem associated with the CCP process i.e. the size of the reactant used in the process.

3.1.2. CP

The thermal analysis, TG/DTA of the dried precipitate obtained in the CP process shows that the decomposition was over at ~673 K with a mass loss of 50%. From the TG/DTA, the formation of 123-phase was observed to take place at 1023 K (Fig. 8). During decomposition, the following reactions could take place if we consider the co-precipitated powder is a mixture of Y, Ba, and Cu oxalates.

$$2Y_2(C_2O_4)_3 \cdot 9H_2O + 3O_2 \rightarrow 2YO_2 + 12CO_2 + 18H_2O$$  \hspace{1cm} (1)

$$2CuC_2O_4 + 2H_2O + O_2 \rightarrow 2CuO + 4CO_2 + 4H_2O$$  \hspace{1cm} (2)

$$2BaC_2O_4 + 2H_2O + O_2 \rightarrow 2BaO + 4CO_2 + 2H_2O$$  \hspace{1cm} (3)

The reactions (3) and (4) are known to occur at ~573 K, whereas, the reaction (5) occurs at ~673 K. From the thermogram (TG/DTA plot), the decomposition of the dried precipitate, i.e. oxalates of Y, Ba, and Cu was observed to be a two-step process with two DTA peaks at ~573 and ~673 K. The first DTA peak at ~573 K confirms the decomposition of Y(C_2O_4)_3-9H_2O and CuC_2O_4-2H_2O yielding the respective oxides, whereas, the decomposition of 2BaC_2O_4-2H_2O to BaO and CO_2 at 673 K is confirmed to take place in the second step. If we consider the mass loss from the stoichiometric mixture of the oxalates in appropriate ratio, the reaction (3) and (4) accounts for 51% mass loss and the reaction
(5) accounts for 4% mass loss during decomposition and a total 55% losses of mass during the entire thermal decomposition process. From the TG plots, the total losses of mass during TG experiments were found to be 59%, which was more than the calculated mass loss. This excess loss of mass is due to evaporation of free water in the precipitates. The 4% loss of mass in the TG thermogram after the completion of first DTA peak is consistent with the proposed reaction scheme, which suggests that the oxalate precipitates are in the form of mixtures. Typical micrograph of the powder generated by the CP showed that the powder are submicrometer in size (Fig. 9). The XRD analyses of the YBCO powder calcined at 1173 K for various periods showed the formation of single 123-phase after 3 h calcination. A representative XRD pattern of the single-phase 123-powder is shown in Fig. 10. The average particle sizes were estimated to be 166 nm from the histogram (Fig. 7b) that was derived from the TEM images of the powder. The particle sizes obtained in this process could not be reduced further by single step of calcination and grinding. Further reduction is possible by super fine grinding using attrition or high-energy ball milling. However, that is not in the scope of present investigation.

3.1.3. PP

The thermal analysis (TG/DTA) of the dried blue mass obtained in PP showed a strong exothermic reaction 498 K with a concurrent weight loss of 6.4 mg (s<sup>80%</sup>) (Fig. 11). The heat liberated during the exothermic decomposition of NH<sub>4</sub>N<sub>3</sub>O<sub>3</sub> was sufficient for the complete calcination of the respective metal compounds. The flash pyrolysis of NH<sub>4</sub>N<sub>3</sub>O<sub>3</sub> yielded nitrogen, H<sub>2</sub>O, and nascent oxygen [24], which also excluded the formation of NO<sub>x</sub> and HCN species in the process. During drying of the blue mass, the citric acid melted at a temperature of 426 K to form itaconic acid (mp 439 K), which upon continued heating, polymerized and swelled up with the de-carboxylation process releasing...
CO2. The decomposed mixture after the completion of exothermic reaction was found to be a foamy mass and 6 g of the powder occupied a volume of 0.25 l (Fig. 12).

The X-ray diffraction analyses of the as-prepared powder showed that the as-generated powder were mixtures of Y2O3, CuO, and BaCO3, which required to be calcined at elevated temperatures for phase formation. The formation of BaCO3 was due to the back reaction of Ba and CO2 that evolved during pyrophoric reaction. The detailed XRD analyses of the powder obtained after calcination at various temperatures and times indicated that a minimum temperature of 1023 K and soaking period of 12 h was required for the complete formation of 12 3-phase. The lowering of phase formation temperature is attributed to the ultra fineness of the precursor and intimate mixture of the constituents. The complete phase formation was not only dependant upon the calcining temperatures but also depended on the calcination times. For instance, a minimum soaking period of 10 min at 1173 K was sufficient for the completion of phase formation. A typical XRD pattern of the YBCO powder calcined at 1173 K for 1 h is shown in Fig. 13. The TEM studies indicated that the pyrophorically generated powder was very fine and nanometer in size. A
Fig. 14. TEM image of the pyrophorically generated YBCO powder after calcination for 1 h at 1173 K.

Fig. 15. XRD pattern of the pyrophorically generated YBCO powder after calcination for 1 h at 1173 K.

3.2. Compressibility of YBCO powder

The variation of the green density of the powder compacts with the applied load (Fig. 15A) expectedly showed low compressibility of finer particles in comparison to the powder fabricated by CCP. This variation of green densities with the reduction of particle sizes was due to frictional forces acting on the powder during compaction. It is well known that two types of frictional forces namely inter-particle friction and die-wall friction operate during compaction of ceramic powder. It is also expected that if the mass (i.e. volume) of the powder is increased, the die-wall friction area will increase and this will lead to further increment of die-wall frictional force and decrease the compact densities. The plot of green densities of the pellets with the mass of powder used for pressing showed no variation (Fig. 15B). This suggests that the die-wall friction does not play any significant role on particle size dependent variation of green densities and the lowering of compressibility of the finer powder is predominantly due to inter-particle friction. The apparent densities of the sintered pellets were found to depend upon the green densities of the compacts (Fig. 15C). This increase of sintered densities for the samples having high green densities is due to easier mass transport in better densified bodies compared to the loose specimens. The sintered densities are also noticed to depend upon the initial particle sizes of green compacts. This increase of sintered densities with the reduction of particle sizes is due to high specific surface area of the fine powder (Fig. 15C). It has also been observed that a maximum green density of \( \approx 3.8 \text{ g cm}^{-3} \) at 12.4 MPa can be achieved with the YBCO powder after grinding followed by pelletisation of the compressed powder. The improvement of green densities for the powder is due to increase of particulate sizes during pre-grinding compression that decreases the inter-particle friction.

3.3. Sintering behavior

The densification of any sample is related to the dimensional shrinkage occurring in the samples during sintering and the linear shrinkage parameter, \( \delta L/L_0 \) is also known as densification parameter, \( \alpha \). Because of the systematic decrease of porosity of the compacts with the sintering time and temperature, the parameter \( \alpha \), is time and temperature dependent. Experimentally it is also convenient to measure
the parameter $\delta L/L_0$ continuously with time using dilatometry. The densification parameter, $\alpha$ can be expressed as a function of sintering variables [25,26] as:

$$\alpha = \left( \frac{m}{t} \right)^{n} e^{Q/RT}$$

(4)

where, $Q$ is the activation energy for the rate governing step in sintering, $n$ is sintering kinetic parameter, $R$ is gas constant, $t$ is time, $T$ is temperature in K and $K'$ is a constant.

From Eq. (4) we can have,

$$\ln(\alpha) = n\ln k' - n\ln T - \frac{Q}{RT} - n\ln(t)$$

(5)

The values of $n$, calculated from the slopes of straight lines obtained by plotting $\ln(\alpha)$ versus $\ln(t)$ at various temperatures could be subsequently used for the calculation of activation energy ($Q$) from the Eq. (5).

It is observed that the samples have shown no changes other than the thermal expansion and contraction during heating or cooling cycles before and after sintering. It has also been noticed that, at temperatures above the onset of sintering temperatures, shrinkage has started even before the final temperature could be reached. The shrinkage prior to isothermal sintering changes the initial sintering condition and an iterative method is adopted to make the sintering conditions identical by adding the time required for the pre-isothermal shrinkage. Details of the process are reported elsewhere [26].

Fig. 16 showed the variation of sintering parameter ($\alpha$) with sintering times for the compacts made from powder prepared by (a) CCP, (b) CP, and (c) PP, which was isothermally sintered at various temperatures. The variation of linear shrinkages with sintering time and at various isothermal temperatures showed a continuous increase of shrinkage with sintering temperatures and time. From the figure (Fig. 16), it is evident that the CCP powder undergoes only $\approx 6\%$ linear shrinkage at 1273 K and CP powder experienced a maximum linear shrinkage of $\approx 6\%$ at 1233 K, whereas, the PP powder shrunk linearly to $\approx 19\%$ at 1218K. The more linear shrinkage for the pyrophorically synthesized powder indicates the higher densification of the PP powder compared to CCP and PP powder. The corresponding logarithmic time
dependence of the isothermal shrinkage ($\alpha$) has been plotted in Fig. 17 and the slopes of these curves yield the values of $n$ at different temperatures and it has been observed that the kinetic parameter, $n$, is dependent on sintering temperatures and sintering time. The decrease of kinetic parameter, $n$ for any isothermal temperature is due to the change of sintering mechanism that resulted from the continuous decrease of driving force with the sintering time during sintering [27]. The variation of sintering kinetic parameter, $n$ with the isothermal holding temperatures and for the first 20 min is shown in Fig. 18. From the figure, it was noticed that at high temperatures the values of $n$ decreased drastically from 0.41 at 1223 K to 0.11 at 1238 K for the PP powder compacts.

This decrease of $n$ was due to change of sintering stage from intermediate to final stage of sintering, where the pores became isolated and rounded. From the figure, it appeared that the $n$ values decreased linearly from 0.38 at 1187 K to 0.34 at 1233 K for the CP powder compacts and $n$ values almost remain constant at 0.12 for the CCP powder compacts. From the variation of sintering kinetic parameter, it is apparent that distinctly two different sintering mechanisms, one at low temperature and one at high temperature are operating for the PP powder, whereas, only single mechanism is operative during sintering of CCP and CP powder compacts. As discussed earlier, the decrease of $n$ for the PP powder at high temperature is due to change of sintering mechanism with the densification from the intermediate stage of sintering to final stage of sintering [28]. It is well known that at the final stage of sintering the driving force for the sintering, which predominantly governed to minimize the surface free energy of the system will not be available. This will lead to change of sintering mechanism. Since there are fluctua-
tions in the values of $n$ with sintering times and temperatures only the regime having small variations of $n$ is considered for the estimation of activation energies for sintering. The small variation of $n$ also suggests that same sintering mechanism is operative for any particular batch of sample in that specific temperature and time regime. This can be true for the PP powder compacts in the low temperature regime in the present investigation. The average values of $n$ are calculated to be 0.12 for CCP, 0.36 for CP, and 0.48 for PP. The values of the sintering kinetic parameter, $n$ is also noticed to decrease from 0.48 for PP powder compacts to 0.12 for the CCP powder compacts and this is due to the change of mass transport from the volume diffusion to surface diffusion as the particle sizes are increased. From the literature on sintering mechanism, it can be suggested that the volume diffusion processes are operating in the PP and CP samples [29]. The low value of the $n$ in the final stage of sintering of PP powder compacts is due to sintering by surface diffusion and evaporation condensation mechanism.

The logarithmic rate of change of length for the powder compacts prepared by different routes has been plotted as a function of the inverse of absolute temperature in Fig. 19.
As discussed earlier, the average values of \( n \) are used to calculate the apparent activation energies for sintering from the slope of this Arrhenius plot. The activation energies are estimated to be 3600 ± 119 kJ/mol for the CCP powder, 1452 ± 40 kJ/mol for CP powder and 1218 ± 12 kJ/mol for the PP powder. It may be noted that these apparent activation energies for sintering are obtained for the initial period (>20 min) of the isotherms. In the case of CCP powder, the high activation energies also suggest that the sintering is through evaporation condensation mechanism, since the activation energies for the surface diffusion mechanism is low. The estimated activation energies for all the samples are much higher than the normal activation energies for diffusion. Therefore, the possibility of other mechanism for the sintering, such as chemical reaction and creep mechanism cannot be ruled out in this system.

The variation of the apparent density for the samples sintered at different temperatures for a fixed soaking period of 1 h showed more densification for the powder compacts made from the pyrophoric process compared to the other two processes (Fig. 20). The highest densification of about 88% was achieved for the powder compact made from PP process, whereas, the CP powder underwent about 80% densification after 1 h sintering at 1233 K and the CCP powder attained R = 60% densification after 1 h sintering at 1273 K. The better densification for the powder prepared by the pyrophoric process than the powder of CP and CCP techniques is mainly due to the fine size, which enhanced the mass transfer rates. The reduced particles also decreased the activation energies for sintering and changed the sintering mechanism.

During sintering degradation or dissociation of YBCO-123 phase was not observed from the XRD patterns, which only showed the presence of single YBCO-123 phase in all the samples (Fig. 21). Extensive platelet type of grain growth with very little porosity was observed in the SEM micrographs for sintered pellets prepared from pyrophoric powder (Fig. 22c), whereas less grain growth and more porosity was observed for the sintered pellet prepared by CP and CCP (Fig. 22a and b). From the superconducting measurements it was observed that the pellet prepared from the powder generated by the pyrophoric process exhibited sharp \( T_c(0) \) at 92 K, whereas CP and CCP compacts showed a \( T_c(0) \) at 85 and 80 K, respectively. The decrease of transition temperature was due to the presence of porosity within the sintered samples made from CCP and CP powder. The pores hindered the transport of supercurrents and limited the transport properties, which was evident from the increase of resistivity with the porosity of the samples. As expected, the critical current density values of these sintered samples were found to be very low of the order of \( 10^2 \) A cm\(^{-2} \) at 77 K and, therefore, not emphasized here. Further studies were required to improve the transport properties.

4. Conclusions

The sinterability of the powder compacts made from the powder synthesized by the three different techniques was studied, which showed that the nano-sized particles synthesized by the pyrophoric process required the minimum sintering time and temperature. The highest densification
of α98% was achieved for the powder compact made from PP process, whereas, the CP powder underwent α90% densification after 1h sintering at 1233 K and the CCP powder exhibited α60% densification after 1h sintering at 1273 K. The apparent activation energy of sintering and the sintering kinetic parameter were observed to be particle size dependent, which suggested differing sintering mechanisms with the initial particle size. Extensive platelet type of grain growth with very little porosity was observed in the SEM micrographs of sintered pellets prepared from pyrophoric powder, whereas less grain growth and more porosity was observed for the sintered pellet prepared by CP and CCP.

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