The discovery of 'superconductivity above liquid nitrogen temperature' has generated an enormous amount of activities in the field of superconductivity. The immediate application of high temperature superconductors is likely to be in the form of thick and thin films. Thick films are complex, non equilibrium systems having physical properties that are intimately related to their microstructure which in turn is determined by the combination of material properties and processing conditions. Thick films of high temperature superconductors have wide range of applications in microwave integrated circuits, transmission lines and other high frequency electronic devices. Extensive work has been attempted by a large number of investigators to obtain superconducting $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ [YBCO] thick films on various substrates using the thick film techniques such as screen printing, spray pyrolysis, paint on, spin coating and plasma spray. Films developed on commercially available substrates such as MgO, SrTiO$_3$, ZrO$_2$, Al$_2$O$_3$, Si etc. produced films with inferior superconducting properties and the maximum critical transition temperature [$T_{c(0)}$] reported on these substrates was less than 85K with poor critical current densities [$J_c$]. A detailed literature survey of the work done on superconducting YBCO thick films revealed us that the poor superconducting properties of the film was mainly due to the chemical reactivity of the substrate with the film. Thus one of the most important criteria for the selection of any material as substrate for high $T_c$
superconducting film is their chemical compatibility with the film. In addition, for microwave application of the film the substrate should have low dielectric constant \( \varepsilon' < 20 \) and loss factor \( \tan \delta \sim 10^4 \). Therefore it was realised that for the fabrication of high temperature superconducting films with \( T_c(90) = 92\,\text{K} \), new substrate materials have to be developed. Hence in the present work, our first aim was to develop new chemically non-reacting substrates suitable for the preparation of YBCO thick films.

Our work on the effect of hafnium oxide addition in the superconducting properties of YBCO has led us to develop a new class of rare earth based materials, Rare Earth Barium Hafnates \( \text{REBa}_2\text{HfO}_{5,5} \) where \( \text{RE} = \text{Y}, \text{Gd}, \text{Sm} \) which are found to be ideally suitable for their use as substrates for YBCO thick films. YBCO thick films prepared on these substrates showed excellent superconducting properties with zero restivity superconducting transition at 92K.

The present thesis entitled "Development and Characterisation of \( \text{YBa}_2\text{Cu}_3\text{O}_{7,8} \) Thick Films \( T_c(90) = 92\,\text{K} \) on Rare Earth Barium Hafnates: A new class of Perovskite Ceramic Substrates" contains nine chapters. In chapter I we have presented a general introduction of superconductivity with special reference to YBCO superconductors. A review on superconducting YBCO thick films on various conventional substrates is also given in this chapter. The different types of experimental techniques employed for the preparation and characterisation of different materials used in the present work is discussed in Chapter II.
A detailed study on the effect of hafnium oxide \([\text{HfO}_2]\) addition in \(\text{YBa}_2\text{Cu}_3\text{O}_{7.5}\) superconductor is presented in chapter III. These studies have a special significance in our present work since the development of \(\text{REBa}_2\text{HfO}_{5.5}\) substrates for \(\text{YBa}_2\text{Cu}_3\text{O}_{7.5}\) films in fact originated from these studies. The x-ray diffraction studies and temperature-resistivity measurements revealed that \(\text{HfO}_2\) addition up to 5 wt% does not have any detrimental effect on the superconducting properties of YBCO. It was also found that the widely accepted procedure of slow cooling or prolonged heating at 600°C for oxygenation of the sample is not essential to obtain superconductivity in an \(\text{HfO}_2\) added YBCO system. A superconducting transition of 92K was obtained by directly quenching the \(\text{HfO}_2\) added YBCO samples in air from a sintering temperature of 950°C. A tetragonal to orthorhombic transformation has taken place within seconds indicating that the rate of oxygen absorption has increased tremendously by \(\text{HfO}_2\) addition. Addition of \(\text{HfO}_2\) in YBCO has resulted in the formation of a second phase during high temperature annealing. This second phase was identified as \(\text{YBa}_2\text{HfO}_{5.5}\), a new compound having perovskite cubic structure.

In chapter IV, a detailed study on the synthesis and characterisation of \(\text{YBa}_2\text{HfO}_{5.5}\), a new perovskite ceramic compound identified in the YBCO-HfO\(_2\) system is presented. \(\text{YBa}_2\text{HfO}_{5.5}\) was synthesised for the first time as a single phase material by solid state reaction. The new compound was found to have a complex perovskite cubic structure \(A_2(BB')_O_6\). It has also been found that the superconducting YBCO does not react with
YBa₂HfO₅½ even after heating a 1:1 molar mixture at 950°C. The dielectric constant and loss factor of this material measured in the frequency range 30 Hz to 13 MHz were found to be in a range suitable for its possible use as substrate for YBCO films. Other isostructural new compounds such as GdBa₂HfO₅½ and SmBa₂HfO₅½ could be obtained by replacing yttrium by gadolinium and samarium respectively. Detailed studies on the synthesis and characterisation of these new materials are also included in this chapter.

In order to study the suitability of the newly developed compounds, REBa₂HfO₅½ [RE = Y, Gd and Sm] as substrates, a detailed study on the electrical transport and superconducting behaviour in YBCO superconductor - REBa₂HfO₅½ [RE = Y, Gd, Sm] insulator composites were carried out and the results are presented in chapter V. Percolation behaviour of the normal state resistivity and superconductivity of YBa₂Cu₃O₇-δ - REBa₂HfO₅½ composites has been studied by x-ray diffraction and temperature-resistivity measurements. No detectable chemical reactivity was observed between YBa₂Cu₃O₇-δ and ceramic insulators REBa₂HfO₅½ even when the materials were mixed thoroughly and sintered at about 1020°C. The percolation studies on these superconductor-ceramic insulator composites showed that the superconductor and insulators remain as two separate phases in the composites with their own characteristics even under severe heat treatments. Normal state and percolation threshold values are found to be ~22 vol% of YBa₂Cu₃O₇-δ in these composites. The values obtained for the critical exponents describing the normal state transport behaviour of the system matched with theoretically
expected values for an ideal conductor - insulator percolation system.

Highly polished REBa$_2$HfO$_{5.5}$ substrates developed by us were used for the preparation of YBCO thick films using screen printing technique. The film properties were studied using XRD, $T_c$ measurements, $J_c$ measurements and scanning electron microscopy [SEM]. Details of the processing conditions and characterisation of the films are given in chapter VI. The partial melting technique could be adopted successfully for the preparation of high quality YBCO thick films because of the non-reactivity of REBa$_2$HfO$_{5.5}$ substrates with YBCO even at an elevated temperature of 1000°C. The films prepared by partial melting showed excellent (001) orientation with zero resistivity transition temperature of 92 K and $J_c$ values of the order of $\sim 10^4$ A cm$^{-2}$. The excellent adhesion of the films with the substrates was confirmed by peel-off test using adhesive tape.

The YBCO thick films were also prepared by dip-coating method. Dip-coating is found to be a relatively simple and reliable method for the fabrication of superconducting YBCO thick film of thickness <5 μm. Partial melting method was used for the processing of superconducting films dip-coated on REBa$_2$HfO$_{5.5}$. These films having thickness $\sim 3$μm also showed excellent superconducting properties with $T_c(0)$ at 92K and enhanced $J_c$ values. The preparation and characterisation of dip-coated YBCO thick films are presented in chapter VII.

In chapter VIII, we discuss the preparation and characterisation of YBCO-Ag composite thick films on REBa$_2$HfO$_{5.5}$ substrates. It has been
observed that addition of Ag in YBCO for the preparation of YBCO-Ag composite thick films have no detrimental effect on their superconducting properties and the composite films showed better superconducting properties with enhanced critical current densities. Another important advantage of silver addition in YBCO was that the partial melting temperature was lowered making it possible to process the film at relatively lower temperature. The details regarding the processing conditions of YBCO-Ag composite thick films are also included in this chapter.

The summary of the results, conclusions and the scope of future work are given in chapter IX.

The papers published during the course of the research work are listed in this thesis.